

## MEASUREMENT OF VISCOSITY OF CLAY AND ORGANO-CLAY DISPERSIONS UNDER HIGH PRESSURE

**Key Words**—Drilling mud, High pressure, Organo-clay dispersions, Rheology, Viscosity.

### INTRODUCTION

Rheological properties of clays and organo-clay dispersions are affected by pressure, but the extent of these effects on their dynamic flow properties is not well known. Rheological measurements on clay suspensions and drilling fluids using a rotational viscometer were made by Hiller in 1963. From the flow properties and static gel strengths of homoionic montmorillonite suspensions measured at temperatures up to 177°C and at 10,000 psi, he concluded that the properties of clay suspensions and drilling muds differ considerably under bottom-hole conditions from those measured under surface conditions and that the magnitude of these differences is not generally predictable. Hiller's work and that of Amerson *et al.* (1963) were directed toward the role of smectite clays in the formulation of water- and oil-based muds used in the rotary drilling of oil and gas wells.

Organo-clays, consisting of quaternary ammonium smectite complexes, have been used for many years as thickeners and viscosity builders in numerous organic fluids. They are used in oil-based drilling muds and as additives to oil to form non-soap greases for the lubrication of bearings. In recent years, as the drilling for oil and gas has gone to greater and greater depths, higher pressures have been encountered by commonly used oil- and oil-water emulsion-type fluids. Similar high pressures also have been measured in the immediate vicinity of clay-lubricated bearing surfaces. In applications such as these, the organo-clays are dispersed in organic fluids such as hydrocarbons and oils. The effect of high pressures on the viscosity of hydrocarbons has been studied by Griest *et al.* (1955) who used a rolling ball viscometer to measure the viscosity of seven pure hydrocarbons having 25 or 26 carbon atoms up to pressures of 3450 bars and to temperatures of 135°C. They found a pronounced increase of viscosity with pressure. Lowitz *et al.* (1959), also using a rolling ball viscometer, measured the viscosity of 14 high molecular weight hydrocarbon liquids up to 3400 bar pressure and 135°C and concluded that the pressure-viscosity effects were strongly related to the size and shape of the hydrocarbon. They found that the viscosity of higher molecular weight and aromatic hydrocarbons were more strongly affected by an increase in pressure than were the lower molecular weight, straight chain substances. Reamer *et al.* (1959), using a rotating cylinder (Couette) viscometer capable of operating at pressures up to 25,000 psi and 260°C, found moderate increases in viscosity with pressure.

Because a falling or rolling-ball type viscometer is much simpler to construct and to operate at high pressures than a rotating cylinder viscometer, the former was chosen to be developed as an instrument for the study of clays and organo-clay dispersions at high pressures. A falling ball viscometer was designed, using as a model the high pressure equipment described by Claesson *et al.* (1970). Two advantages of this type of equipment are that it can be pressurized in such a manner that the pressure is locked in and that it is lightweight and portable.

The purpose of this paper is to describe a technique for the study of rheological properties of clay and organo-clay dispersions under high pressure. A few examples of the results that have been obtained will be presented.

### THEORY OF THE FALLING-BALL VISCOMETER

The development of formulae for rotameters with spherical floats treats the flow of fluid past the float as if the ball were

falling at terminal velocity (Gilmont and Maurer, 1961). The same theory may be applied to a falling-ball viscometer because the ball is assumed to be falling at terminal velocity.

Gilmont and Maurer give the following equation for volumetric flow in terms of a rotameter coefficient:

$$q = 59.8C_R R(R/100 + 2)D_f \sqrt{W_f(\rho_f - \rho)/\rho_f} \quad (1)$$

where  $q$  = flow in ml/min,  $C_R$  = rotameter coefficient,  $D_f$  = diameter of float,  $R$  = [diameter of tube (inches) - diameter of float (inches)]  $\times$  100/diameter of float,  $W_f$  = weight of float,  $\rho_f$  = density of float (g/cm<sup>3</sup>), and  $\rho$  = density of fluid (g/cm<sup>3</sup>).  $C_R$  is a generalized function of the Stokes-modified Reynolds number which Gilmont and Maurer (1961) defined as

$$S - R_n = 1.042W_f(\rho_f - \rho)R^3/\eta^2\rho_f \quad (2)$$

where  $\eta$  is the viscosity in centipoise. Gilmont (1964) noted that  $C_R$  reduces to the simple function

$$C_R = k(S - R_n)^{1/2} \quad (3)$$

when the Stokes-modified Reynolds number is less than 5. The constant  $k$  is different for each instrument. For measurements of viscosity, where the  $S - R_n$  values are less than five, one can combine these equations to give

$$q = 61.05k[D_f W_f(\rho_f - \rho)R^{5/2}/\rho_f]^{1/2}(2 + R/100) \quad (4)$$

For viscometry work,  $k$  must be determined by calibration because of the need for a high degree of precision (Gilmont, 1964).

As the ball falls through the viscometer tube at terminal velocity, a given volume of fluid flows through the space between the ball and the wall of the tube. If  $t$  is the time required for the ball to fall through a distance,  $L$ , the volume of fluid that flows past the ball is

$$q = (2.54)^2(L\pi D_f^2/4t) \quad (5)$$

If  $L$  is measured in centimeters, the constant 2.54 is needed to convert the diameter of the float,  $D_f$ , from inches to centimeters.

The right-hand sides of Eqs. (4) and (5) can be equated, and the resulting equation can be solved for viscosity as follows:

$$\eta = 61.05[D_f W_f(\rho_f - \rho)R^{5/2}/\rho_f L \pi D_f^2]^{1/2}[2 + R/100]4t \quad (6)$$

Because  $W_f$  = weight of the float, the value  $\rho_f V_f$  can be substituted into the equation and the resulting equation can be rearranged to give

$$\eta = [244.2k D_f \rho_f V_f / 2.54^2 \rho_f L \pi D_f^2]^{1/2} R^{5/2} / (2 + R/100)(\rho_f - \rho)t \quad (7)$$

The volume of a sphere is  $4/3\pi r^3$ , and  $r$ , in terms of  $D_f$ , is  $D_f/2$ ; therefore,

$$V_f = (4/3)\pi(D_f/2)^3 \quad (8)$$

Substitution of Eq. (8) into Eq. (7) gives

$$\eta = [244.2k D_f (4/3)(D_f/2)^3 R^{5/2} / 2.54^2 L D_f^2]^{1/2} / (2 + R/100)(\rho_f - \rho)t \quad (9)$$

which reduces to

$$\eta = 6.31k(D_f^2/L)R^{5/2}(2 + R/100)(\rho_f - \rho)t \quad (10)$$

The value  $6.3k(D_f^2/L)R^{5/2}(2 + R/100)$  is a constant for a par-

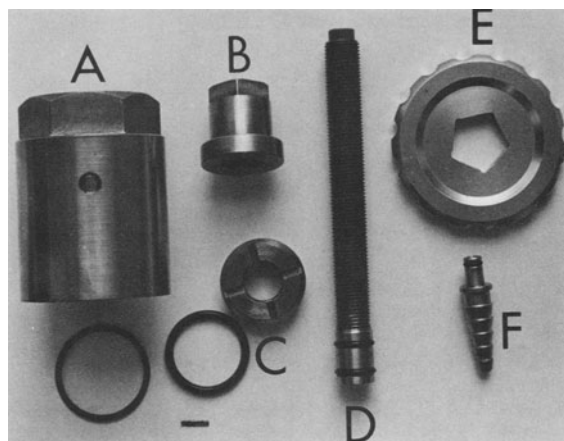


Figure 1. Photograph of the disassembled top cap and piston of high pressure viscometer. A = Top cap, B = Locking nut, C = Piston housing, D = Piston, E = Lock-nut wrench, F = Vacuum line connector. Bar represents 1 cm.

ticular viscometer. If this value is defined to be  $K_1$ , Eq. (1) reduces to the familiar

$$\eta = K_1(\rho_t - \rho)t, \quad (11)$$

which is the equation that is used to calculate the viscosity of the fluid under investigation.

#### VISCOMETER DESIGN

The high pressure falling-ball viscometer is basically a heavy-wall steel cylinder with the end plugs designed in such a manner as to allow pressurization during the time needed for the measurements. Figure 1 shows disassembled top cap and piston; Figure 2 shows the bottom cap and end-plug. Figure 3 is a cross section diagram of the bottom cap and end-plug. All pressure seals are obtained by using standard o-rings (1) on the piston that is used to apply the pressure, (2) on the end-plug that is used to stop the timer, and (3) in the top cap. The purposes of these seals is discussed below.

#### Timing device

A standard Gralab Universal Timer is connected to a relay circuit which has two electrical leads. When the bottom plug is in place and the bottom cap is attached to the viscometer

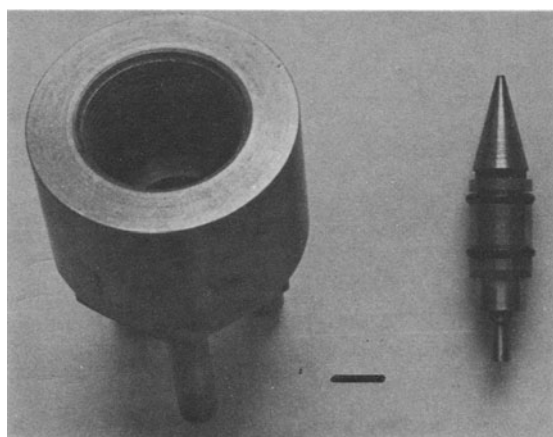


Figure 2. Photograph of the bottom cap and end-plug of high pressure viscometer. Bar represents 1 cm.

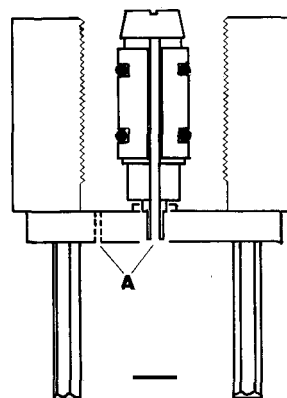


Figure 3. Cross section diagram of bottom cap and end-plug. A = Connections for electrical leads from timer. Bar represents 1 cm.

tube, the two leads are inserted into two small holes (A, in Figure 3). One hole is in the bottom plug and one is in the bottom cap. The bottom plug is insulated from the cap by a piece of Nylon mounted in the bottom of the cap, ensuring an open circuit between the plug and the cap until the falling ball (rolling along the inner wall of the cylinder) makes contact with the plug. When contact is made, the circuit is closed and the timer stops. Contact is also detected by a neon bulb in the sensor circuit.

#### Pressure-locking system

The major components of the pressure-locking system are illustrated in Figure 1: A cap (A) has a small opening which allows entrapped air to be removed from the dispersion; a locking nut (B) ensures that the desired pressure is maintained on the system; the piston housing (C) ensures the proper positioning of the piston; a piston (D) is used to apply the pressure to the system; a lock-nut wrench (E) is used to move the locking nut up and down on the piston and a vacuum line connector (F).

Figure 4 is a schematic of the assembled top cap. The locking nut is threaded in such a manner as to allow it to be screwed onto the piston. As pressure is applied to the piston by means of an hydraulic jack, the liquid is compressed and is pushed down into the viscometer. Simultaneously, the locking nut, which is in position on the piston, is pushed down into the cap. When the desired pressure, as determined by means of a pressure gauge on the jack, has been applied to the system, the lock-nut wrench is turned counterclockwise until the locking nut is again flush with the top of the inside of the cap. At this point, the back pressure asserted by the system cannot push the piston out of the tube. The release valve on the jack is then opened and viscosity measurements can be made.

The piston has two o-ring seals on the end that come in contact with the liquid. The number of o-rings on the piston determines the maximum pressure that can be applied. Each o-ring seal can withstand a pressure of  $2.7 \times 10^8$  Pa before the liquid leaks past the o-ring. Therefore, with the piston that is currently being used, a maximum pressure of  $5.4 \times 10^8$  Pa can be applied. If higher pressures are desired, a piston can be used with enough o-ring seals to withstand the pressure.

#### SAMPLE PREPARATION

The organo-smectites used were dimethyldioctadecyl ammonium montmorillonite and dimethyldioctadecyl ammonium hectorite. The organo-clay complexes were prepared by dispersing Na-exchanged, centrifuged Wyoming montmorillonite and California hectorite, obtained from Baroid Division, NL

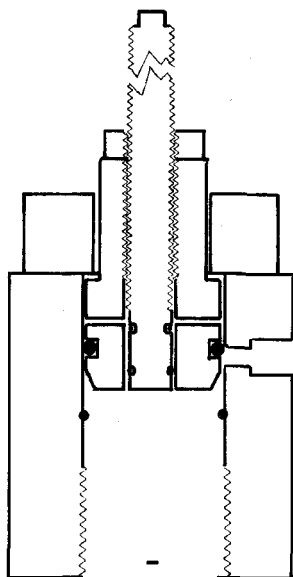


Figure 4. Cross section diagram of the assembled top cap. Bar represents 1 cm.

Industries, in water and slowly adding dimethyldioctadecyl ammonium chloride salt while stirring at high speed in a Waring Blendor. A mixture of 100 meq of the organic cation and 100 g of clay was allowed to sit overnight to obtain equilibrium. The organo-clay was then filtered, washed, and dried. The dried organo-clays were ground to  $-200$  mesh in a mortar and pestle and dispersed in the appropriate organic fluids by slowly adding them to the fluid while stirring for 30 min in a high speed Waring Blendor. In many samples, such as the Texaco SAE 30 HD oil, methanol at 10% by weight of the clay was added to disperse the organo-clay in the organic fluid. For the oil samples, after stirring, the mixture was transferred to a beaker and further dispersed using a probe-type ultrasonic dispersing apparatus for an additional 30 min.

#### EXPERIMENTAL PROCEDURE

At the beginning of a run, the bottom plug was inserted into the bottom of the viscometer tube and the bottom cap screwed into position. The viscometer was then brought to a vertical position and clamped onto a lab rack so that it could be filled with a sample. The falling steel ball was dropped into the tube, and the tube was then filled with the sample to within one or two millimeters of the top. The assembled top cap was then screwed into place. With the locking nut, piston, and the piston housing flush against the top of the inside cap, a vacuum pump was connected via the small opening in the side of the cap. This connection was made using an o-ring sealed adapter (F, in Figure 1) which is part of the vacuum line. The viscometer was evacuated for 2–3 min to remove the trapped air. After the first evacuation period, the top cap was removed to check for volume loss. After refilling the tube, if necessary, the system was again evacuated for another 2–3 min. With the vacuum line attached to the viscometer, the piston was pushed down so that the piston housing was in contact with the top of the viscometer tube. When the piston housing made contact with the top of the tube, the housing, also o-ring sealed, was pushed past the vacuum opening to ensure that air did not reenter the viscometer when the vacuum line was removed. The viscometer was now ready for measurement at atmospheric pressure, or it could have been pressurized to a desired pressure.

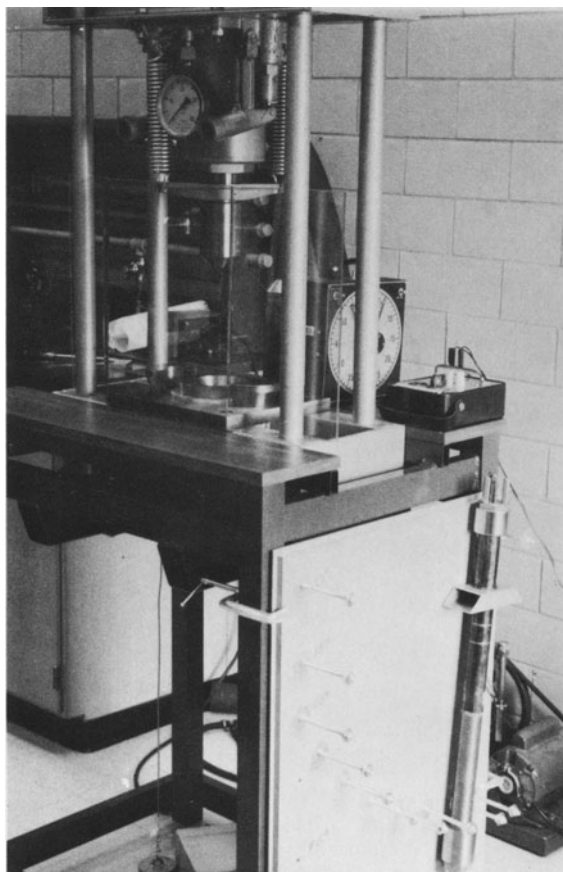


Figure 5. Photograph of high pressure viscometer in position for viscosity determination.

Viscosity measurements were made by first inverting the apparatus and allowing the ball to move to the top of the tube, (starting position). Adequate time was allowed for the ball to reach the starting position before the tube was inverted to the desired angle. The timer was set so that the second hand would be started about 5 sec before time zero. As soon as the second hand reached zero, the tube was brought quickly to the desired angle. Figure 5 illustrates the viscometer tube in position for viscosity determination.

#### RESULTS AND DISCUSSION

The viscosity curves in Figures 6 and 7 are representative of the high pressure viscosity studies that have been made in this laboratory. Viscosity curves of pure Texaco SAE 30 HD motor oil and of organo-smectite dispersions in this oil at various pressures are illustrated in Figure 6. It should be noted that all of the viscosity curves increase exponentially with an increase in pressure. Viscosity is represented in terms of the time in seconds that the ball took to travel from one end of the viscometer to the other. It should be noted that the viscosity of the organo-montmorillonite dispersion increases at a faster rate than that of the blank Texaco SAE 30 oil and that the viscosity of the organo-hectorite increases at a still faster rate.

Figure 7 is a plot of viscosity (time in seconds) of various concentrations of organo-montmorillonite dispersed in the Texaco SAE 30 HD oil at four different pressures. As the pressure increased from atmospheric to  $3.67 \times 10^7$  Pa, the slope

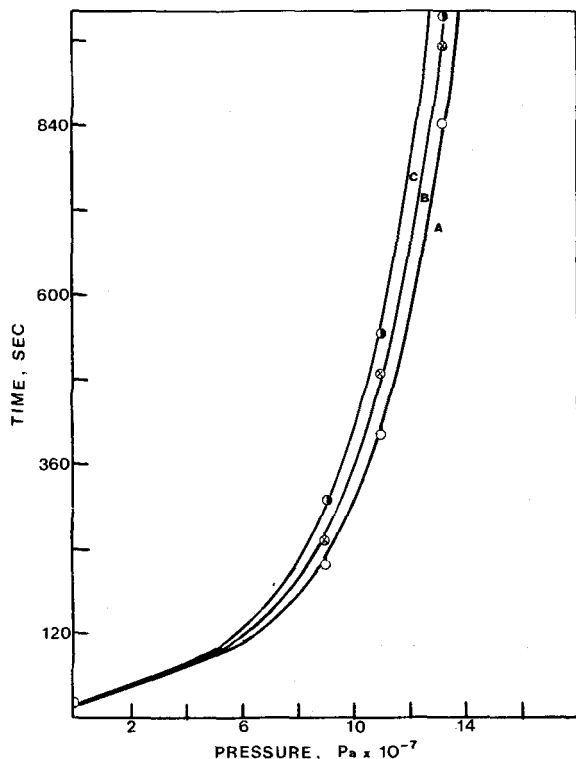


Figure 6. Viscosity of 3% organo-clay in Texaco SAE 30 HD oil with increasing pressure. A = Base oil, B = Organo-smectite, C = Organo-hectorite.

of the viscosity vs. percent organo-clay curve increased from 2.35 to 68.9.

Apparently with a complex mixture such as that found in the Texaco oil, molecules associated to contribute to a rapid increase in viscosity as the pressure was increased. The addition of organo-clays to the oil allowed even greater association or interaction of molecules to take place because the observed rate of increase in viscosity with increasing pressure was even greater. Not only Texaco oil, but several crude and solvent-refined oils were also investigated. In all experiments, the oil and organo-clay dispersions showed an exponential rise in viscosity as the pressure increased.

When the viscosity of small molecules such as toluene and straight chain hydrocarbons up to C-18 were measured with increasing pressure, no increase in viscosity was found. Likewise, when organo-clays were added to toluene and these hydrocarbons, no measurable viscosity changes were observed. Apparently these molecules did not orient or associate in a manner that led to an increase in viscosity with increasing pressure. Further speculation regarding the relationships between pressure, viscosity, and molecular size and shape cannot be made until further experiments are completed using a wider variety of hydrocarbons and organo-clays.

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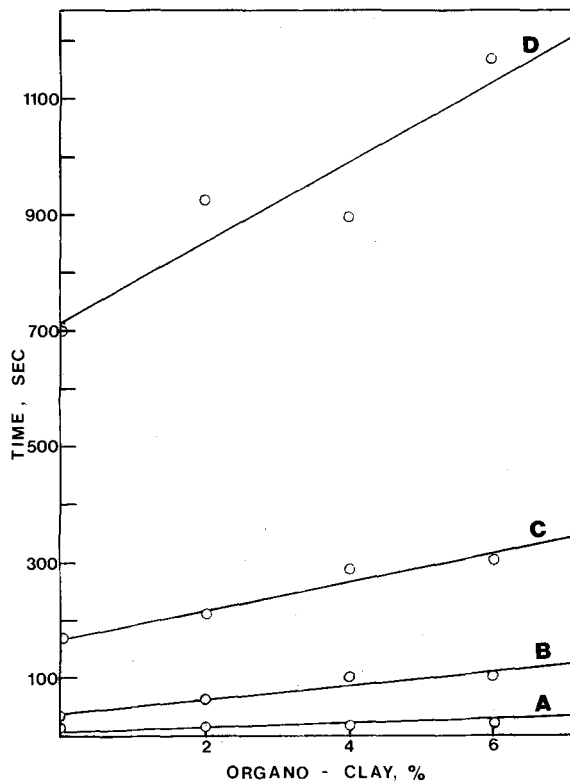


Figure 7. Viscosity of increasing concentrations of organo-montmorillonite in Texaco SAE 30 HD oil. A = Atmospheric pressure, B =  $1.73 \times 10^7$  Pa, C =  $2.45 \times 10^7$  Pa, D =  $3.67 \times 10^7$  Pa.

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