

FIG. 13. First-cycle and reversible-cycle flow curves for 5 temperatures.

curves, both straight lines passing through the origin, coincide; the up and down curves are the flow curves which are obtained while the shear rate is uniformly increased or decreased, respectively. The slope of the straight line in Fig. 12(b) gives the viscosity as  $\eta = 6.38$  P at 26°C: this value agrees with the literature value of 6.29.

Figure 12(c) shows a first-cycle rheopectic flow curve which was obtained on attapulgite suspension in water immediately following the "calibration." Successive 60-sec cycles produced the family of curves shown in Fig. 12(d). Complete reversibility was obtained with cycles 10–12, Fig. 12(e), indicating a complete build up of structure. Figure 12(f) shows the results of final recheck of the viscometer, again using the glycerol standard. It confirms proper machine operation during the recording of flow curves shown in Fig. 12(c) to 12(e).

Figure 13 shows the first and reversible-cycle flow curves for attapulgite, at 5 temperatures. In each case the reversible cycles were achieved by successive cycling as in Fig. 12.

### 3. Fluidity

The entire experimental data<sup>22,23</sup> together with those shown in Figs. 12 and 13 are qualitatively explained on the basis of fluidity being a function of the "free" water available to lubricate particles in suspension. Fluidity depends on (a) time since  $\dot{\gamma}$  became zero, (b) shear rate, and (c) amount of surface. At high rates of shear, the majority of the particles are in parallel orientation and water is available to lubricate the slippage of one particle over another; however, this parallel orientation of particles is a state of low entropy. Randomization occurs when the material is held at low shear rates or when there is no shearing action. The nonparallel particles immobilize water, trapping it in the interstices between the cross-linked particles. As the

<sup>22</sup> A. F. Gabrysh, T. Ree, H. Eyring, Nola McKee, and I. Cutler, *Trans. Soc. Rheology* **5**, 67 (1961).

<sup>23</sup> A. F. Gabrysh, H. Eyring, and I. Cutler, *J. Am. Ceram. Soc.* (to be published).

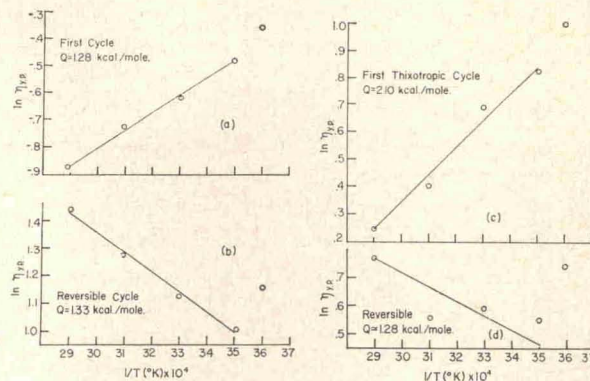


FIG. 14. Temperature dependence of yield-point viscosity for (a) first rheopectic cycle, (b) first reversible cycle, (c) first thixotropic cycle following a 12-h rest period after first reversible cycles were obtained, and (d) second reversible cycle.

rate of shear is increased, a yield point is observed when the cross linkage breaks up. With a further increase of shear rate more complete orientation is obtained, water is freed and absorbed on individual particle surfaces. Better lubrication between particles is the result.

### 4. Activation Energy

The stability of the cross-linked structures obtained with the attapulgite suspension at rest may be observed by plotting the logarithm of the viscosity at the yield point as a function of reciprocal temperature, Fig. 14. The viscosity yield points, Fig. 14(a), are rather low for the first cycles but, where particles are tightly bound in bundles, they follow an exponential relationship as a function of temperature. Yield point viscosities are highest at low temperature where the cross-linked structure is most stable. At high temperatures the thermal activity is sufficient to keep the structure loose and the yield-point viscosity ( $\eta_{yp}$ ) is low. The slope of this linear relationship [ $\ln \eta_{yp} = f(1/T)$ ] is a measure of the energy ( $\sim 1.2$  kcal/mole) of stability of the cross-linked-type structure. The same explanation holds for the thixotropic condition recorded for the suspension after a twelve hour rest period which followed the first reversible cycle. In this case, however, viscosities at the yield point are much larger because many more individual particles are available following the bundle break up. The energy of stability is about 2.0 kcal/mole, Fig. 14(c).

The speed with which the cross-linked structures form may be deduced from the viscosities at the yield point of the suspensions during the reversible cycling, Fig. 14(b) and 14(d). In these cases, the network structure is only partially formed. Thermal energy will allow the random structure to form more rapidly (or to a greater extent if the time interval is fixed) at high temperatures than at low temperatures. With limited time of formation available, the viscosities at the yield point become a measure of the

rate of formation of the cross linkage. In this case a plot of the logarithm of the viscosities at the yield point versus the reciprocal of temperature has a negative slope. Activation energies for this process are comparatively low,  $-1.3$  kcal/mole. Both the stability and the activation energy are of the same order of magnitude and it appears that mobility of the water is the controlling factor in both cases.

In the considerations for activation energy only the 70, 54, 26, and  $12^{\circ}\text{C}$  points were used. The viscosity at  $1^{\circ}\text{C}$  ( $1/T=0.0039$ ) varied appreciably from the straight line in all four plots of Fig. 14. The variation is perhaps caused by internal frictional heat bringing about the peak density change of water which occurs at  $4^{\circ}\text{C}$ .

## II. APPARATUS FOR THE STUDY OF THE EFFECT OF HIGH PRESSURE ON THE FLOW NATURE AND THE NON-NEWTONIAN CHARACTER OF GREASES

### INTRODUCTION

Investigations<sup>24</sup> of pressures between gear teeth and bearings have shown that lubricants in those areas are subjected to pressures of thousands of pounds per square inch and that the viscosity of the lubricants in the contact areas undergoes a marked change. To study the changes in viscosity a number of methods have been used.

In P. W. Bridgman's Laboratory, at Harvard University, Flowers<sup>25</sup> invented a rolling-ball viscometer with which Hersey<sup>26,27</sup> later investigated fats and mineral oils. Hersey and Shore<sup>28</sup> working in the 1000- to 4000-atm range found that, under constant temperatures, certain oils undergo apparent solidification. Sage and Lacey<sup>29,30</sup> used an inclined-plane "rolling-ball" apparatus where saturated solutions, under saturation pressure and temperature, showed a decrease in viscosity. Dow<sup>31-33</sup> studied the effects of pressure on oils with a rolling ball apparatus designed for pressures of 41 000 atm.

In 1941, Norton<sup>34</sup> departed from the study of Newtonian viscosity, with which the preceding investigators were concerned, and using a capillary undertook to determine the non-Newtonian character of the flow curves of oils under pressure. In general, it was found that critical rates of increase of the pressure produced either soft solids or much stiffer consistencies which behaved like plastic

greases. More recently Hahn,<sup>35</sup> also using a test capillary, reported on some non-Newtonian behavior of lubricating oils under pressure.

The capillary-type apparatus reported here is similar to that used by Norton and Hahn but makes use of a five-cylinder, axial-piston pump which is supercharged by a gear pump for the high pressure stage and an oil "reservoir" to completely eliminate the antagonistic pressure ripples caused by the action of a pump. The ripples were experienced in the designs of apparatus used by the previous workers. The reproducibility of the experimental results is within 2%.

## CONSTRUCTION

### 1. General

The essential features of the apparatus are shown in Figs. 15-17. Pressure is produced in the system by a "Vanguard" Y26-A hydraulic pumping unit obtained from the Owatonna Tool Company, Owatonna, Minnesota, Fig. 16 A. The unit is specially equipped with (1) a 4-way, lever-operated, "shear-seal, open-center" type control valve, (2) a pressure gauge calibrated in psi, (3) a pressure regulating valve which bypasses oil when a predetermined pressure has been reached and which adjusts from 1000 to 10 000 psi, and (4) a 5-gallon oil reservoir. It was found that on continuous operation the oil in the reservoir became hot. The reservoir was subsequently equipped with coils through which water is circulated to cool the hydraulic fluid.

The pumping unit is connected, by a high-pressure hose, through a "T," to two parallel sets of three "oil-reservoir" tanks in series Fig. 16 C. These old oxygen and nitrogen tanks were obtained as war surplus property. The tanks are connected by high-pressure stainless steel tubing through another "T" and an oil filter (Fig. 16 B) to an OTC single acting 20-ton hydraulic ram, Fig. 16 D, whose specifications are as follows: maximum working pressure, 10 000 psi; length closed,  $11 \frac{5}{16}$  in.; length open,  $16 \frac{5}{16}$  in.; diameter of moving shaft,  $2 \frac{1}{4}$  in.; oil capacity, 26 cu in.; effective ram area, 5.16 in.<sup>2</sup>

### 2. Pressure Intensification

A pressure chamber, Fig. 16 E, consists of a piston  $0.750 \pm 0.001$  in. in diameter. With the effective ram area of 5.16 in.<sup>2</sup>, the pressure in the chamber is intensified about 12 times that of pump pressure. The war-surplus tanks have been tested and safely operated at a hydrostatic pressure of 5000 psi, therefore the safe operating pressure is approximately 60 000 psi. Two O-rings on the piston and one in the cylinder, Fig. 17, serve effectively as seals to

<sup>24</sup> C. W. Georgi, *Motor Oils and Engine Lubrication* (Reinhold Publishing Corporation, New York, 1950), p. 57.

<sup>25</sup> A. E. Flowers, *Proc. ASTM*, **14**, Part 2, 565 (1914); *Trans. ASME* **43**, 1269 (1921).

<sup>26</sup> M. D. Hersey, *J. Washington Acad. Sci.* **6**, 525 (1916).

<sup>27</sup> M. D. Hersey and G. S. Snyder, *J. Rheology* **3**, 298 (1932).

<sup>28</sup> M. D. Hersey and H. Shore, *Mech. Eng.* **50**, 231 (1928).

<sup>29</sup> B. H. Sage, *Ind. Eng. Chem.* **15**, 261 (1933).

<sup>30</sup> B. H. Sage and W. N. Lacey, *Ind. Eng. Chem.* **32**, 587 (1940).

<sup>31</sup> R. B. Dow, *J. Appl. Phys.* **8**, 367 (1937).

<sup>32</sup> R. B. Dow, M. R. Fenske, and H. E. Morgan, *Ind. Eng. Chem.* **29**, 1078 (1937).

<sup>33</sup> R. B. Dow, *J. Colloid Sci.* **2**, 81 (1947).

<sup>34</sup> A. E. Norton, M. J. Knott, and J. R. Muenger, *Trans. ASME* **63**, 631 (1941).

<sup>35</sup> S. J. Hahn, H. Eyring, I. Higuchi, and T. Ree, *NLGI Spokesman* **22**, 121 (1958).