

## 潤滑油의 粘性學의 研究\*

Shao-mu Ma\*\* · 李 泰 圭

韓國科學院 · 理論 物理 및 化學센터

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## Rheological Studies of Greases\*

Shao-ma Ma\*\* and Taikyue Ree

*Korea Advanced Institute of Science, Center for  
Theoretical Physics & Chemistry, Seoul, Korea*

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**要 約.** 鋼製毛細管粘度計를 제작하여 윤활유의 流動性質을 연구하였다. 使用한 윤활유는 bentone 윤활유(thickener의 무게 농도 2.0, 4.0, 6.0, 8.0 및 10.0 %)와 Lime-soap윤활유(thickener의 무게농도 2.4, 7.0, 9.3, 12.1 및 15.2%)이었다. Lime-soap 윤활유의 流動性質에 대하여 resident-time (毛細管內에 윤활유가 殘留하는 時間) 效果를 研究하기 위하여 半徑( $R$ )과 기리( $L$ )를 달리하는 各種毛細管을 使用하였다. 그러나 bentone 윤활유의 流動性質의 仔細한 研究를 위하여서는 單一種의 毛細管을 使用하였다. 實驗結果(流出量對 shear 速度)에 대하여 Ree-Eyring 式에 나타나는  $X_1\beta_1/\alpha_1$  (Newton 單位에 對한 量),  $X_2/\alpha_2$  및  $\beta_2$  (非 Newton 單位에 對한 量) 등의 係數가 thickener 농도와 溫度에 對하여 어떻게 變化하는가를 보았다. 이 研究의 分析結果에 依하면  $\Delta H_1^*$  와  $\Delta H_2^*$  (각각 流動單位 type 1 과 type 2 의 流動活性化엔탈피)가 溶媒(base oil)의 流動活性化엔탈피( $\Delta H_b^*$ )에 近似的으로 一致한다. 이 事實로부터 thickener의 流動單位 (type 1, type 2 共히)는 溶媒分子의 移動으로 因하여 장단된 小孔에 꿰어드러감으로써 全體系의 流動이 이루어짐을 알 수 있다. Bentone 윤활유에 對하여  $\beta_2$ 는 어느 주어진 溫度에 있어서 thickener 농도에 無關함을 알아냈으니 이것은 既往文獻에 發表된 事實과 一致한다.

殘留時間效果를 lime-soap 윤활유에 對하여 보려고 試圖하였으나 그 結果는 分明치 않았다. 그 理由는 lime-soap 윤활유 自身의 性質에도 依存하지만 著者들의 使用한 毛細管의  $L/R$  值(殘留時間에 比例하는 常數)가 너무 적었음에 原因이 있다고 생각된다.

**ABSTRACT.** A steel capillary viscometer was built for the study of rheological properties of greases. Bentone greases with thickener concentration of 2.0, 4.0, 6.0, 8.0, and 10.0 weight percent and lime-soap greases with soap concentrations of 2.4, 7.0, 9.3, 12.1 and 15.2 weight percent were studied. Capillaries with various radii  $R$  and lengths  $L$  were used to study the *resident-time* effect on the flow properties of lime soap greases. Detailed studies on bentone greases were con-

\*The main parts of this research were conducted at the Department of Chemistry, University of Utah, U. S. A. while the authors were working in that institute.

\*\*Present address: Department of Materials Science and Engineering, University of Utah, Salt Lake City, Utah, U. S. A.

ducted using a capillary with a fixed size. The results were analyzed by using Ree-Eyring flow equation. The factors appearing in the latter, ( $X_1\beta_1/\alpha_1$  for Newtonian units,  $X_2/\alpha_2$  and  $\beta_2$  both for non-Newtonian units), were studied in order to investigate how they change with thickener concentrations and temperatures. Through this analysis, we have found that  $\Delta H_1^*$  and  $\Delta H_2^*$ , the activation enthalpies for flow of type-1 unit and of type-2 unit, respectively, are approximately equal to that of the base oil, the solvent. From this fact, it is concluded that these type units flow into the holes which were produced by the movement of solvent molecules. For bentone greases, the  $\beta_2$  is about constant independent of concentration at a given temperature as found in the literature.

The resident-time effect has not been clearly demonstrated in this research; this is due partly to the nature of the greases used in our research and partly to the small values of  $L/R$  of our capillaries, the resident time being proportional to the value  $L/R$ .

## 1. INTRODUCTION

Rheological studies of grease made by using a rotational viscometer show that the flow is thixotropic,<sup>1~4</sup> i.e., structural breakdown occurs in the flow. Hahn, Ree and Eyring<sup>2,3</sup> attributed the thixotropy to the disentanglement of entangled molecules of the thickeners, and explained successfully the hysteresis loops obtained by cyclic deformation of the grease with the use of the rotational viscometer.

Thixotropy of grease occurs also in capillary flow.<sup>5</sup> The so-called Ostward's curve, which is obtained with capillary viscometers, is also due to the thixotropy of liquids.<sup>3</sup>

We started this work in the hope of studying the thixotropy of grease by using a capillary viscometer and to compare the results with those obtained with a rotational viscometer.<sup>1~4</sup> Unfortunately, we have found that a notable thixotropy effect of grease occurs only at very high shear rates and shear stresses which are not available with our present apparatus. We have also found that for the study of thixotropy of grease it is very important to know the rheological behavior of greases at lower shear rates where the thixotropy of grease does not occur. Thus, in this paper, we studied bentone grease and lime-soap grease by using a capillary visco-

meter over the range of shear rates from zero to  $1.2 \times 10^4 \text{ sec}^{-1}$  and of shear stress from zero to  $2 \times 10^5 \text{ dyne/cm}^2$ , where the thixotropy did not occur. The flow curves (shear rate versus shear stress) were analyzed by applying the Ree-Eyring flow equation,<sup>6</sup> and the properties of the rheological parameters involved in the latter were studied. Here we report the results and consider the conditions where the thixotropy occurs.

## 2. EXPERIMENT

**Samples.** The greases used in this study were (1) bentone greases 72934, 72934 A, B, C, D and E furnished by Socony Oil Company and (2) lime-soap greases A, D and E of the five sample furnished by Esso Research and Engineering Company. The compositions of the bentone greases and lime-soap greases are summarized in *Table 1* and *Table 2*, respectively.

**Apparatus and Procedures.** The capillary viscometer, which was constructed in this laboratory and was used in the experiments, is shown in *Fig. 1* where GC is a grease chamber made of stainless steel, the volume of which is about 250 cc. A stainless capillary tube was tightly fitted to the grease chamber by a teflon "O" ring and an adaptor. The grease in the chamber was pressed out through the capillary

Table 1. Bentone greases.

Batch No.	72939	72934A	72934B	72934C	72934D	72934E
Bentone 34	10.0%	8.0%	6.0%	4.0%	2.0%	0.0%
Propylene carbonate	1.0	0.8	0.6	0.4	0.2	0.0
Antioxidant <sup>a</sup>	0.5	0.5	0.5	0.5	0.5	0.5
Mineral oil <sup>b</sup>	88.5	90.7	92.9	95.1	97.3	99.5
ASTM worked Penetration (at 77 °F)	273	318	365	460	580	—

<sup>a</sup> Mixture of octylated diphenyl amines.<sup>b</sup> Specific Gravity: 0.9001

Saybolt viscosity:

100 °F: 2385 secs. 472 centipoises

210 °F: 153 secs. 29.2 centipoises

Kinematic viscosity:

100 °F: 514.3 cs.

210 °E: 32.3 cs.

Table 2. Hydrated calcium soap greases.

	A	B	C	D	E
Soap <sup>a</sup>	2.4%	7.0%	9.3%	12.1%	15.2%
Stringiness agent	0.4	0.4	0.4	0.4	0.4
Water	0.2	0.7	0.9	1.6	2.0
Mineral oil <sup>b</sup>	97.0	91.9	89.4	85.9	82.4
ASTM worked penetration	—	370	325	280	235

<sup>a</sup> Calcium soap of animal fat<sup>b</sup> Viscosity at 210 °F: 70 S. U. S.

Pour point: 0 °F.

by using a commercial nitrogen tank. Between the pressure source and the grease chamber, a steel cylinder C (volume about 250 cc), which was lined with 1/4" thick teflon and furnished with a 1" thick teflon piston, was inserted. The reason for using C was to introduce the grease into the grease chamber smoothly, as well as to avoid its direct contact with the gas, which otherwise made bubbles in the grease because of the high pressure-head used.

Only one capillary of 8 cm length and  $3.4234 \times 10^{-2}$  cm radius was used for bentone greases. For lime-soap greases, three or more capillaries were used. The lengths  $L$  and radii  $R$  are listed

Table 3. Capillary sizes\* at 25 °C.

Capillary Code	$L(\text{cm})$	$R \times 10^2(\text{cm})$	$L/R$
S	4.859	3.4057	142.67
M	8	3.4234	233.68
L	12.13	3.5019	346.48
EL	22.657	3.3492	676.49

\* All the capillaries were calibrated by using the standard oil of the National Bureau of Standards, Washington, D. C.

in Table 3. The quantity,  $L/R$ , is proportional to the "resident time" which is defined as the time during which a molecule stays in the capillary and it is a very important factor for

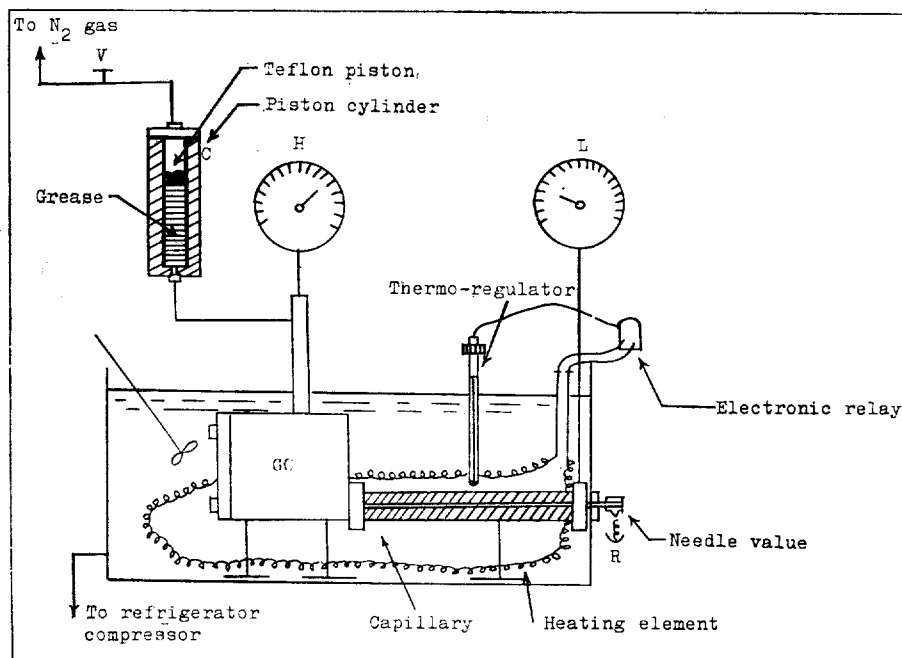


Fig. 1. Apparatus (GC: grease chamber; R: receiver; H: high pressure gauge; L: low pressure gauge).

thixotropy.

The pressure-head was obtained from the difference of the readings at the high pressure gauge H and the low pressure gauge L which was attached to the nearest side of the outlet of the capillary. The grease was pressed out through a needle valve into a receiver R as shown in Fig. 1. By weighing the grease which flowed during a given time, the flow rate,  $Q$  (cc/sec), was readily obtained; the density of the grease required for this purpose was determined pycnometrically. Various flow rates were obtained by varying the pressure-head.

Because of the extremely low thermal conductivity of grease, the grease chamber and the capillary had to be immersed in a bath for at least 8 hours to reach temperature equilibrium. For concentrated greases at low temperatures, the time required was even longer. The bath temperature was controlled within  $\pm 0.003^\circ\text{C}$  by using a thermoregulator and an electronic

relay. At temperatures lower than  $0^\circ\text{C}$ , however, the temperature fluctuation was controlled within  $\pm 0.2^\circ\text{C}$  by incorporating a refrigerator.

### 3. RESULTS and ANALYSES

#### Experimental Results

Fig. 2 through Fig. 5 represent the flow curves (shear rate  $\dot{S}$  versus shear stress  $f$ ) of bentone greases. The quantity  $\dot{S}$  is obtained from the flow rate  $Q$  by using the Rabinowitsch equation,<sup>7</sup>

$$\dot{S} = \frac{1}{\pi R^3} \left( 3Q + P \frac{dQ}{dP} \right)$$

and  $f$  is calculated from the formula,  $f = RP/2L$ ,  $P$  being the pressure head.

For all the greases 72934, 72934A, B, C and D, the flow curves have been obtained, but the curves for greases A and D are not shown here. All the flow curves are non-Newtonian and become increasingly fluid as the temperature rises. This fact can be noticed more clearly in

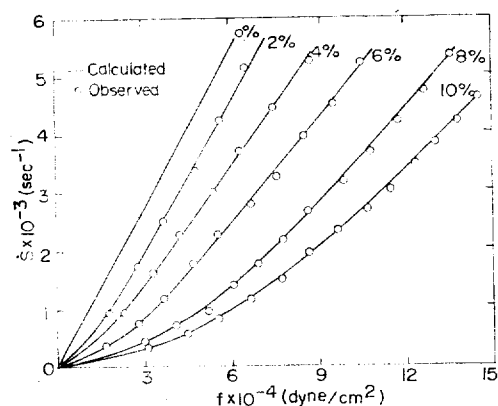


Fig. 2. Flow curves of bentone greases at various concentrations and at 25 °C.

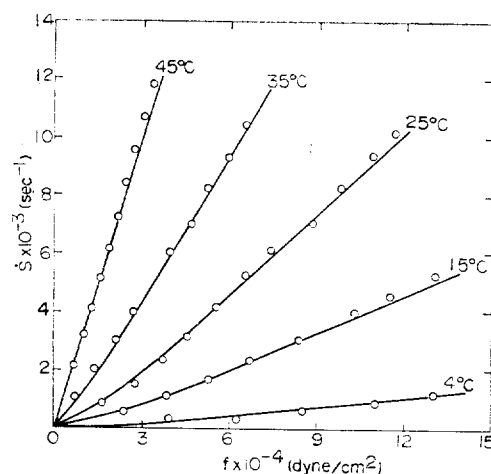


Fig. 5. Flow curves of bentone grease 72934D (2%) at various temperatures.

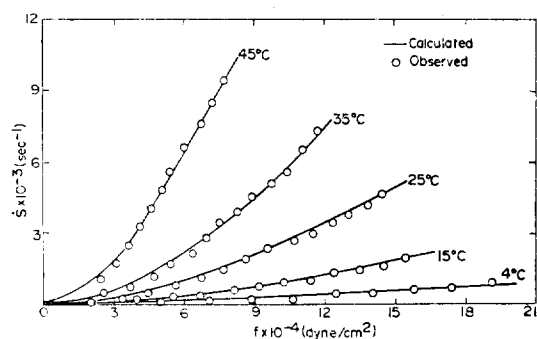


Fig. 3. Flow curves of bentone grease 72934 (10%) at various temperatures.

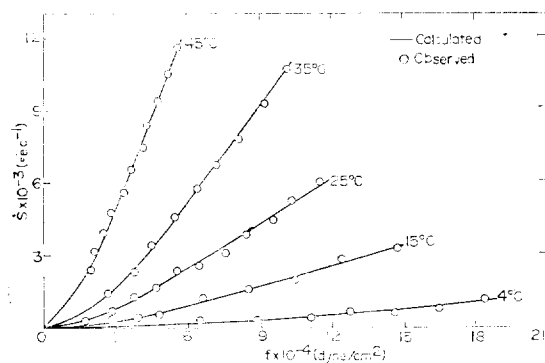


Fig. 4. Flow curves of bentone grease 72934B (6%) at various temperatures.

Fig. 5 where the flow curve at 45 °C is almost a straight line, i.e., Newtonian. In Fig. 2, the thickener concentration effect is shown, one

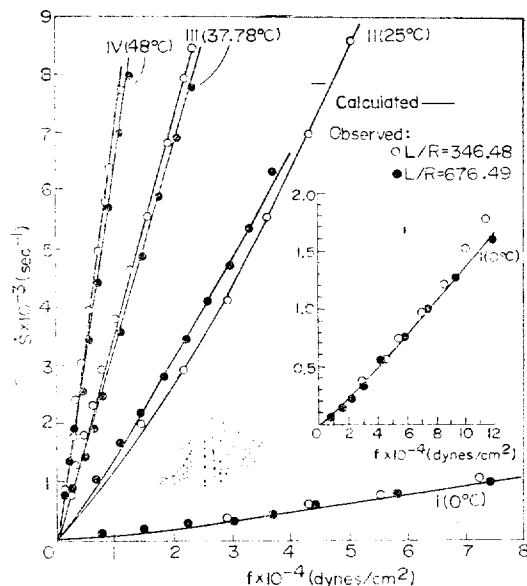


Fig. 6. Flow curves of lime soap grease A at various temperatures. In the inset, is shown the lower portion of curve I (0°C) in enlarged scales.

notes that the non-Newtonian character increases with increasing concentration.

In Figs. 6 and 7, the results obtained by using lime-soap greases are shown. The brand of the greases and the capillaries used in the experiments are shown in the figures. For the composition of the various brands and the di-

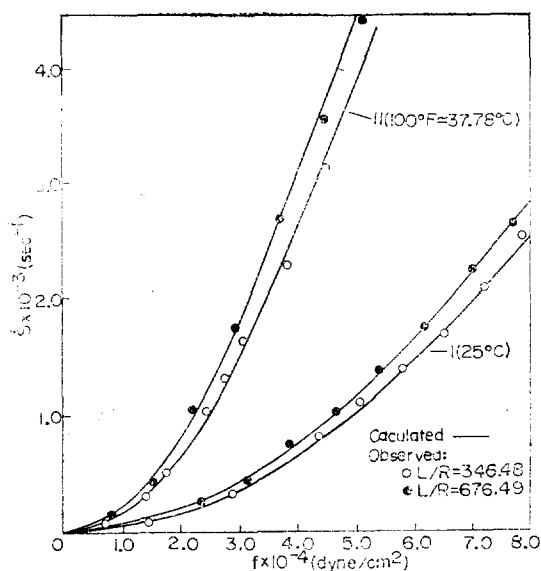


Fig. 7. Flow curves of lime soap grease D at various temperatures.

mensions of the capillaries, refer to Tables 2 and 3, respectively.

In the experiments with the lime-soap greases, we studied the effect of the resident time on the flow properties. If the breakdown of flow units (thickener molecules) occurs in the capillary, the flow curve for a capillary with a small value of  $L/R$  will lie below the curve for the tube of large  $L/R$ , because in the latter case the thickener molecules have a better chance to be broken down, and consequently the grease will become more fluid. A weak resident-time effect may be found in Figs. 6 and 7, for grease A and D, respectively.

We have also tested grease lime-soap E (15.2%) by using capillaries S, M, and L (cf. Table 3) at temperatures 15, 25, 37.78 and 48°C. The figure showing the results is not shown here. The order of flow curves using these capillaries was not S, M and L (from lower to higher  $\dot{S}$ ), i.e., there was no regularity because of the intercrossing of the S, M and L curves. If our proposition from the resident

time is right, the order must be S, M and L. We regard that the irregularity is due to the high concentration of the thickener as well as to the poor reproducibility of the flow curves which is inherent to the grease.

### Analyses of Experimental Results

#### (1) Flow Equation

The generalized equation of flow proposed by Ree and Eyring<sup>6</sup>

$$f = \sum_i^n \frac{X_i}{\alpha_i} \sinh^{-1} \beta_i \dot{S} \quad (1)$$

reduces to the following form in the simplest non-Newtonian case:

$$f = \frac{X_1 \beta_1}{\alpha_1} \dot{S} + \frac{X_2}{\alpha_2} \sinh^{-1} \beta_2 \dot{S} \quad (2)$$

Here, subscripts 1 and 2 indicate a Newtonian-type and a non-Newtonian-type unit, respectively;  $X_i$  represents the fraction of the area occupied on a shear surface by a group of type  $i$  ( $i=1$  or  $2$ );  $\beta_1$  and  $\alpha_1$  are given by the following equations:

$$\beta_1 = \left( 2 \frac{\lambda}{\lambda_1} k' \right)_i^{-1} \quad (3)$$

$$\alpha_i = \frac{(\lambda \lambda_2 \lambda_3)_i}{2 k T} \quad (4)$$

where  $k'$  is the jumping frequency of the flow unit when there is no stress, and  $\lambda$ ,  $\lambda_1$ ,  $\lambda_2$  and  $\lambda_3$  are the familiar molecular dimensions in Eyring's theory of viscosity.<sup>8</sup> The quantity  $\beta_i$  is a quantity proportional to the relaxation time of unit  $i$ , and  $1/\alpha_i$  is proportional to the shear modulus,<sup>9</sup>  $\beta_i/\alpha_i$  being the viscosity. Equation 2 is similar to that proposed by Powell and Eyring<sup>10</sup> except for explicitly writing the factors including  $X_i$ .

It is advisable to consider here the nature of the flow units in more detail. As Ree and Eyring<sup>6</sup> postulated, a Newtonian flow unit is a molecule or a cluster of molecules isolated from other units, while a non-Newtonian unit is a Newtonian unit bonded (or entangled) with

another Newtonian unit or units. Thus, for flow of non-Newtonian units, this bond (or entanglement) must be broken (or disentangled), i. e., for the jumping of non-Newtonian units, a larger activation free energy is required than for the Newtonian unit.

In bentone grease, the thickener has a platelet form ( $0.5 \times 0.5 \times 0.1 \mu^3$ ), and the thickener in lime-soap grease is a fiber form ( $\pi 0.1 \times 0.1 \times 1 \mu^3$ ).<sup>11</sup> The isolated platelets and fibers are

Table 4. Parametric values for the flow curves of bentone greases.

Temperature °C	$\beta_2 \times 10^2$ (sec)	$(X_2/\alpha_2) \times 10^{-3}$ (dyne/cm <sup>2</sup> )	$X_1\beta_1/\alpha_1$ (poises)
Grease 72934 (10% bentone 34)			
4	3.02	26.2	116
15	1.55	20.3	38.4
25	0.908	15.4	16.7
35	0.397	13.9	7.4
45	0.277	10.2	3.86
Grease 72934A (8% bentone 34)			
4	3.02	23.0	107
15	1.55	17.7	33.8
25	0.908	12.0	15.1
35	0.397	11.0	6.82
45	0.277	5.51	3.74
Grease 72934B (6% bentone 34)			
4	3.02	18.2	99.2
15	1.55	8.35	33.5
25	0.908	6.64	14.4
35	0.397	7.02	6.51
45	0.277	4.00	3.41
Grease 72934C (4% bentone 34)			
4	3.02	13.2	88.1
15	1.55	9.14	25.1
25	0.908	3.43	13.3
35	0.397	4.48	5.95
45	0.277	1.40	3.29
Grease 72934D (2% bentone 34)			
4	3.02	8.35	84.0
15	1.55	3.61	22.0
25	0.908	2.73	10.5
35	0.397	2.04	5.49
45	0.277	2.59	2.86

Newtonian units, the contacted platelets and entangled fibers being non-Newtonian units.

## (2) Determination of the Rheological Parameters

Equation 2 is applied to the flow curves mentioned above, and the parameters,  $X_1\beta_1/\alpha_1$ ,  $X_2/\alpha_2$  and  $\beta_2$  are determined. The results are shown in Table 4 and 5.

By using the tabulated parametric values, the full curves in Figs. 2 through 7 are calculated from Eq. (2). One sees that the agreement between calculated and observed values is quite good.

## (3) Factors Governing $\beta_2$

From Table 4 for bentone greases, one may note that the  $\beta_2$  value is independent of the concentration of the thickener. This fact is similar to that found by Ree and Eyring<sup>6</sup> for dilute high polymeric solutions.

For lime-soap greases (Table 5), however, the  $\beta_2$  value depends on the concentration of the thickener. The larger the concentration, the greater the  $\beta_2$  value.

The weight percentages of lime-soap in the A

Table 5. Parametric values for the flow curves of lime-soap greases.

Temperature (°C)	$\beta_2 \times 10^2$ (sec)	$(X_2/\alpha_2) 10^{-3}$ (dyne/cm <sup>2</sup> )	$X_1\beta_1/\alpha_1$ (poises)	L/R
Grease A				
0	0.531	13.0	43.4	346.48
25	0.469	8.69	4.18	
37.78	—	—	2.87	
48	—	—	1.50	
0	1.05	4.31	60.9	676.49
25	0.150	1.60	5.39	
37.78	—	—	3.00	
48	—	—	1.55	
Grease D				
25	3.36	7.75	16.2	346.48
37.78	1.50	5.41	6.3	
25	1.34	10.0	13.5	676.49
37.78	2.18	4.05	6.8	

and D greases are 2.4 and 12.1%, respectively, whereas the weight percentage of thickener in the bentone greases ranges from 2 to 10.0%. Thus, the different rheological behavior concerned with  $\beta_2$  in the bentone and lime-soap greaser is not due to the coccentration differences of the thickeners, but due to the different structures of lime-soap and bentone. As mentioned previously, lime-soap has a fiber structure while bentone has a platelet structure. Thus the former makes a network more easily than the latter. Consequently, for lime-soap grease, the dependency of  $\beta_2$  on the thickener concentration appears even for fairly dilute concentrations, whereas the  $\beta_2$  for bentone grease is constant.

For both the bentone and lime-soap greases,  $\beta_2$  decreases with increasing temperature. In Fig. 8,  $\ln \beta_2$  for bentone grease is plotted against  $1/T$ . From the slope, we can obtain the activation enthalpy  $\Delta H_2^*$  for the jumping process [cf. Eq. (3)]. The following data are obtained from Fig. 8:  $\Delta H_2^* = 11.1$  kcal and  $\Delta S_2^* = -13.2$  e. u., where the assumption  $\lambda = \lambda_1$  has been made.

#### (4) Dependence of $X_2/\alpha_2$ and $X_1\beta_1/\alpha_1$ on Temperature and Concentration

The  $X_2/\alpha_2$  values obtained for bentone greases are plotted against concentration in Fig. 9. One sees that at a given temperature  $X_2/\alpha_2$  increases with increasing concentration, and that at a fixed concentration  $X_2/\alpha_2$  decreases with increasing temperature. This kind of concentration dependence may be expected from the fact that  $X_2$  increases with concentration while  $\alpha_2$ , a characteristic property for flow unit 2, is independent of concentration. For the quantity  $\alpha$ , it has been known that  $\alpha$  is independent of temperature.<sup>9</sup> Thus, the decrease of  $X_2/\alpha_2$  with increasing temperature is due to  $X_2$ ; the reason for this will be considered below.

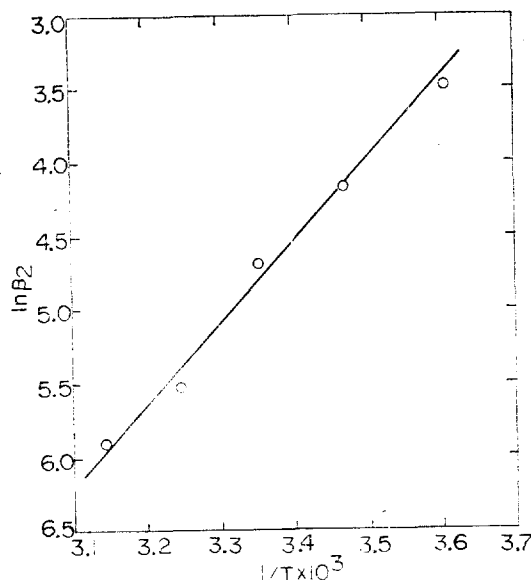


Fig. 8. plot of  $\ln \beta_2$  vs.  $1/T$  for bentone greases. From the slope of the straight line, the value of  $\Delta H_2^* = 11.1$  kcal is obtained.

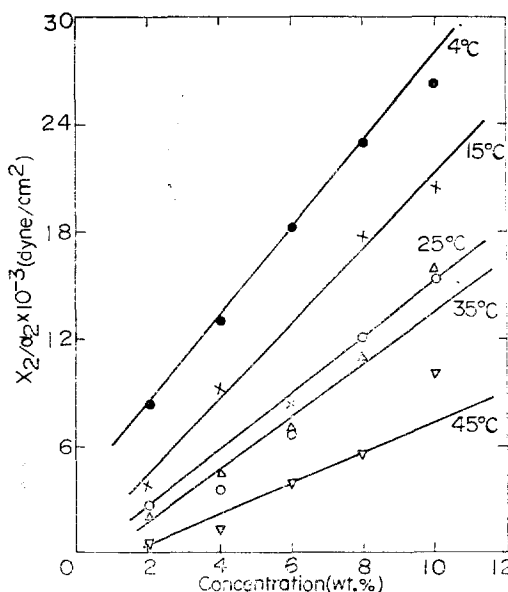
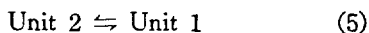


Fig. 9. Plot of  $X_2/\alpha_2$  vs. concentration of bentone greases at various temperatures.

As previously mentioned, unit 2 is a Newtonian unit bonded with other neighboring units. Thus,  $X_2$  will decrease with increasing temperature because of the equilibrium:





where higher temperatures favor the forward reaction. The equilibrium constant  $K$  is given by the following equation:

$$K = \frac{[\text{Unit 1}]}{[\text{Unit 2}]} = e^{-\frac{\Delta G^\circ}{RT}} \approx \frac{X_1}{X_2} \quad (6)$$

where the last approximate equality is derived from the relations  $[\text{Unit 1}] \propto X_1$  and  $[\text{Unit 2}] \propto X_2$ . We may assume that  $X_1 \approx \text{const}$  whereas  $X_2$  changes with temperature since the relation,  $X_1 \gg X_2$ , holds. By plotting  $\ln(X_2/\alpha_2)$  against  $1/T$  using the data given *Table 4*, we obtained  $\Delta H \approx 5$  kcal which may be regarded as the enthalpy change of reaction (5). This suggests that the activation energy of the forward reaction (5) must be 5 kcal or more, which, in turn, means that unit 2 is readily broken down by stress.

The factors,  $X_1\beta_1/\alpha_1$ , are shown in *Table 4*. It is not possible to obtain the values of  $X_1/\alpha_1$  because  $\beta_1$  cannot be measured independently. In *Fig. 10*, the factors  $X_1\beta_1/\alpha_1$  obtained at various temperatures are plotted against concentration. One may notice that  $X_1\beta_1/\alpha_1$  increases with increasing concentration at a given temperature and that it increases with decreasing temperature at a fixed concentration. The first experimental fact seems to be natural because  $X_1$  should increase with increasing concentration, and since  $\beta_1/\alpha_1$  is the viscosity of the unit 1 liquid which may be considered as constant over the range of concentration in the experiments. The second experimental fact, i.e., the temperature dependence of  $X_1\beta_1/\alpha_1$ , is explained as follows: Although  $X_1$  increases with temperature because of the equilibrium with  $X_2$ , the increase in  $X_1$  is overshadowed by the decrease in the viscosity  $\beta_1/\alpha_1$  with temperature, consequently  $X_1\beta_1/\alpha_1$  decreases with increasing temperature and vice versa.

In *Fig. 11*,  $\ln X_1\beta_1/\alpha_1$  is plotted against  $1/T$ .

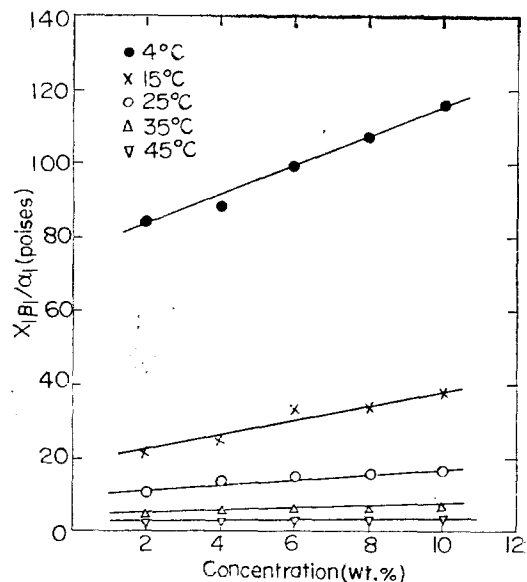


Fig. 10. Plot of  $X_1\beta_1/\alpha_1$  vs. concentration of bentone greases at various temperatures.

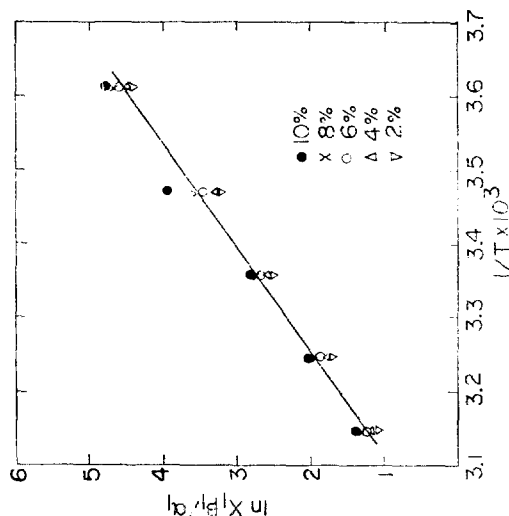


Fig. 11. plot of  $\ln X_1\beta_1/\alpha_1$  vs.  $1/T$  for bentone greases. From the slope of the straight line, the value of  $\Delta H_1^\ddagger = 14.22$  kcal is obtained.

From the slope of the straight line, a value of  $H_1^\ddagger = 14.2$  kcal is obtained. This value is not exactly the activation enthalpy for the viscous flow of unit 1, since as mentioned above,  $X_1\beta_1/\alpha_1$  is a composite factor including  $X_1$  and  $\beta_1/\alpha_1$ .

$\alpha_1$ , both being temperature dependent. But, as we mentioned previously,  $X_1$  may be assumed as about constant over the temperature range. Thus,  $\Delta H_1^* = 14.2$  kcal is understood as the activation enthalpy of unit 1.

We measured the viscosity of the base oil (grease 72934E, cf. Table 1) by using our capillary viscometer, and obtained the following values (in poise): 0.727 (4°C), 0.250 (14°C), 0.108 (25°C), 0.0510 (35°C), and 0.0269 (45°C). From these values, the activation enthalpy  $\Delta H_b^*$  for the viscous flow has been found to be  $\Delta H_b^* = 14.1$  kcal. One may notice that  $\Delta H_1^*$  (14.2 kcal),  $\Delta H_2^*$  (11.1 kcal) and  $\Delta H_b^*$  (14.1 kcal) are about equal with each other within experimental errors. This fact suggests that units of types 1 and 2 move into the holes which had been formed by the movement of base oil molecules in the viscous flow of the latter.

The factor  $X_1\beta_1/\alpha_1$  is explicitly written down as follows:

$$\frac{X_1\beta_1}{\alpha_1} = X_1 \frac{h}{V/N} \exp\left(\frac{\Delta H_1^*}{RT} - \frac{\Delta S_1^*}{R}\right)$$

where Eqs. (3), (4) and the equation expressing  $k'$  are substituted for  $\beta_1$ ,  $\alpha_1$  and  $k'$  respectively, and  $\lambda^2\lambda_2\lambda_3/\lambda_1 \approx V/N$  where  $V$  is the molar volume of bentone,  $N$  being the Avogadro number. If the values  $X_1 \approx 1$  and  $V \approx 100 \text{ cm}^3$  are assumed, from Fig. 11,  $\Delta S_1^*$  can be calculated by using  $\Delta H_1^* = 14.2$  kcal found in the above. The value ( $\Delta S_1^* = +25.2$  e. u.) is obtained. Except extremely small values of  $X_1$  and extremely large values of  $V$  (e. g.,  $X_1 < 10^{-3}$  and  $V > 10^4$ , which are highly unreasonable), the value of  $\Delta S_1^*$  is always positive.

In Eq. (2), the solvent (base oil) is not explicitly entered. The reason is as follows: if we take the solvent into account, the Newtonian term is expressed as  $X_0\beta_0/\alpha_0 + X_1\beta_1/\alpha_1$  where the subscript zero represents the solvent; the

first term is considered to be negligible compared to the second, thus the Newtonian term is nearly equal to  $X_1\beta_1/\alpha_1$ .

Previously, we obtained  $\Delta S_2^* = -13.2$  e. u. whereas  $\Delta S_1^* = +25.2$  e. u. The negative  $\Delta S_2^*$  indicates that the activated complex becomes more "tight", i. e., the volume becomes smaller than the initial state, and the positive  $\Delta S_1^*$  shows that a volume expansion occurs in the activated complex. This kind of structural change accompanying the activation process is explained from the nature of the non-Newtonian and Newtonian units.

#### 4. DISCUSSION

(1) Rotational and Capillary Viscometers in the Study of Thixotropy

In the following, we compare the conditions under which thixotropy occurs in rotational and capillary viscometers.

The volume of the capillary is  $\pi R^2 L$ . The required time  $t$  for a liquid to pass through the capillary is  $\pi R^2 L / Q$ . We define the resident time  $t_r$  as the average time  $t/2$ , i. e.,

$$t_r = \pi R^2 L / 2Q \quad (7)$$

During  $t_r$ , the grease shears against the wall, the surface area of which is  $2\pi RL$ . Therefore, the average shearing time per unit area,  $t_s$ , under given  $f$  and  $\dot{S}$  is approximately given by

$$t_s = t_r / 2\pi RL = R / 4Q \quad (8)$$

We calculated  $t_s$  according to Eq. (8) by using our experimental data, and obtained the following results:

For bentone grease 72934D:

$$R/4Q = 0.142 \text{ sec/cm}^2,$$

$$\text{when } \dot{S} = 3.14 \times 10^3 \text{ sec}^{-1},$$

$$R/4Q = 0.026 \text{ sec/cm}^2,$$

$$\text{when } \dot{S} = 11.93 \times 10^3 \text{ sec}^{-1}.$$

For bentone grease 72934B:

$$\begin{aligned}
 R/4Q &= 0.127 \text{ sec/cm}^2, \\
 \text{when } \dot{S} &= 2.45 \times 10^3 \text{ sec}^{-1}, \\
 R/4Q &= 0.0707 \text{ sec/cm}^2, \\
 \text{when } \dot{S} &= 11.57 \times 10^3 \text{ sec}^{-1}.
 \end{aligned}$$

Next, we consider the experiment with a rotational viscometer. In this case, the cyclic deformation takes one min.<sup>1</sup> During this time,  $\dot{S}$  is raised from zero to  $700 \text{ sec}^{-1}$ ; then it is lowered from this value to zero. The corresponding change in  $f$  is from zero to about  $2 \times 10^4 \text{ dyne/cm}^2$ , then from this value to  $f=0$ . Although, in this case, the range of  $\dot{S}$  and  $f$  is small compared to the experiments with our capillary viscometer, the exposure time to stress is far longer than in the capillary flow. Thus, the thixotropy effect is easily observed with a rotational viscometer whereas it is not observed (or hard to detect) with our capillary viscometer.

#### (2) Resident-Time Effect

From Eq. (7), the following is obtained:

$$t_r = \frac{\pi r^3}{2Q} \frac{L}{R} \quad (9)$$

i.e., resident time is proportional to  $L/R$ . As was previously mentioned, a prominent resident-time effect has not been observed in our experiment. This is due mainly to the small values of  $L/R$  of the capillaries used. Wilson and Smith<sup>5</sup> discovered the resident-time effect for barium- and aluminum-soap greases at  $25^\circ\text{C}$  by using capillaries with  $L/R$  values ranging from 14.1 to 2250. Comparing Wilson-Smith's capillaries with ours (cf. Table 3), one immediately notes that our  $L/R$  values are too small. Thus, it may be concluded that capillaries with larger values of  $L/R$  and higher pressure heads are required in order to study the thixotropy of grease.

#### (3) Differences between Rheological Properties of Bentone and Lime-soap Greases

We have already mentioned that  $\beta_2$  is independent of thickener concentration for bentone

greases whereas it increases with the concentration for lime-soap greases, and that this difference is attributed to the structural difference in the thickeners of the two greases.

We tested bentone greases by using capillaries L and EL (cf. Table 3) whose  $L/R$  values are larger than capillary M which was used to obtain the results previously mentioned. The resident-time effect for bentone greases has not been observed in these cases also. For lime-soap greases, a weak resident-time effect has been observed (cf. Figs. 6 and 7). The difference in the resident-time effect is also due to the structural difference of the thickeners. That is, because of its fiber-like structure, the lime-soap molecules readily make a network which breaks down in stress field whereas bentone, which has a platelet form, does not make a network under concentrations studied in this research, i.e., thixotropy does not occur in bentone greases.

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