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JONES, Lloyd Garner, 1933-
THIXOTROPIC BEHAVIOR OF A COLLOIDAL SUSPENSION.
The Ohio State University, Ph.D., 1968
Engineering, chemical

University Microfilms, Inc., Ann Arbor, Michigan
THIXOTROPIC BEHAVIOR OF A COLLOIDAL SUSPENSION

DISSERTATION

Presented in Partial Fulfillment of the Requirements for the Degree Doctor of Philosophy in the Graduate School of The Ohio State University

By


* * * * * * *

The Ohio State University
1968

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ACKNOWLEDGMENTS

The author wishes to acknowledge the superb financial, physical, and moral support supplied by Mobil Oil Corporation and its Field Research Laboratory. The personality, enthusiasm, and encouragement of Dr. Robert Brodkey as adviser and consultant have been both appreciated and enjoyed. Aside from those who have directly influenced this work, two personal acknowledgments must be made to Dr. Joseph H. Koffolt, without whose encouragement I would never have entered graduate school, and to my wife, Marilyn, without whose encouragement I would never have finished.
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# CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>i</td>
</tr>
<tr>
<td>VITA</td>
<td>iii</td>
</tr>
<tr>
<td>TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td><strong>I</strong></td>
<td><strong>II</strong></td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>LITERATURE SURVEY</td>
</tr>
<tr>
<td>Introduction</td>
<td>Thixotropy</td>
</tr>
<tr>
<td></td>
<td>Summary of literature on thixotropy</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
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<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Analysis of results of Denny and Kim</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## CONTENTS (Contd.)

### IV  EXPERIMENTAL PROCEDURES .................................................. 59

- Preparation of samples ............................................................. 59
- Description of the rheogoniometer ........................................... 62
- Experimental procedure ............................................................. 64
- Calculation procedures ............................................................
  - Plate and cone. ................................................................. 66
  - Mooney cup ........................................................................... 66
- Possible sources of error ......................................................... 67
- Normal force measurement developmental work .................... 74
- Determination of mechanical response .................................... 74

### V  RESULTS ................................................................. 76

- Results Associated with Equilibrium Conditions ...................... 76
  - Stepping up and down in shear rate from equilibrium ............. 76
- Results Obtained from Rate Studies ........................................ 82
  - Initial stress and viscosity values ....................................... 82
  - Viscosity decline at constant shear rates ............................ 82
  - Time from clutch engagement to peak shear stress ................ 93
  - Rates of viscosity rise upon stepping down to lower shear rates .. 94
  - Viscosity build-up at zero shear rate .................................. 94
  - Viscosity build-up while shearing ....................................... 98
  - Unexpected rate behavior .................................................. 98
  - Relation of rate behavior to structure curves ....................... 105
  - Analysis of the data using the Brodkey-Denny theory .............. 108

### VI  DISCUSSION OF RESULTS .............................................. 121

- Results Associated with Equilibrium Conditions ...................... 121
  - Step-up and step-down studies .......................................... 121
- Results Obtained from Rate Studies ........................................ 125
  - Initial stress studies ..................................................... 125
  - Viscosity decline at constant shear rates ............................ 125
  - Time from clutch engagement to peak shear stress ............... 126
  - Rate of viscosity rise upon stepping down to lower shear rates .. 126
## CONTENTS (Contd.)

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Viscosity build-up at zero shear rate</td>
<td>128</td>
</tr>
<tr>
<td>Viscosity build-up while shearing</td>
<td>131</td>
</tr>
<tr>
<td>Unexpected rate behavior</td>
<td>131</td>
</tr>
<tr>
<td>Relation of rate variations to structure curves</td>
<td>133</td>
</tr>
<tr>
<td>Analysis of the data using the Brodkey-Denny theory</td>
<td>133</td>
</tr>
<tr>
<td>VII GENERAL DISCUSSION</td>
<td>136</td>
</tr>
<tr>
<td>VIII CONCLUSIONS</td>
<td>152</td>
</tr>
<tr>
<td>IX RECOMMENDATIONS</td>
<td>155</td>
</tr>
<tr>
<td>APPENDIX A Normal Force Development Work</td>
<td>157</td>
</tr>
<tr>
<td>APPENDIX B Mechanical Equipment Response</td>
<td>207</td>
</tr>
<tr>
<td>LIST OF REFERENCES</td>
<td>212</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
</tr>
<tr>
<td>------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Characteristics of Kim's Polymer Solutions</td>
</tr>
<tr>
<td>2</td>
<td>Chemical Composition of &quot;Baymal&quot;</td>
</tr>
<tr>
<td>3</td>
<td>Step-up, Step-down and Equilibrium Shear Stresses</td>
</tr>
<tr>
<td>4</td>
<td>Step-up, Step-down and Equilibrium Viscosities</td>
</tr>
<tr>
<td>5</td>
<td>Initial Stress and Viscosity Values</td>
</tr>
<tr>
<td>6</td>
<td>Viscosity Decline at Constant Shear Rates</td>
</tr>
<tr>
<td>7</td>
<td>Comparison of Actual and Calculated Slopes</td>
</tr>
<tr>
<td>8</td>
<td>Time from Clutch Engagement to Peak Shear Stress</td>
</tr>
<tr>
<td>9</td>
<td>Rates of Viscosity Rise upon Stepping down to Lower Shear Rates</td>
</tr>
<tr>
<td>10</td>
<td>Viscosity Build-up at Zero Shear</td>
</tr>
<tr>
<td>11</td>
<td>Relation of Rate Variations to Non-Newtonian Behavior</td>
</tr>
<tr>
<td>12</td>
<td>Values Used in Determining p and K</td>
</tr>
<tr>
<td>13</td>
<td>Analysis of Rate Data Obtained by Stepping up to a Higher Shear Rate</td>
</tr>
<tr>
<td>14</td>
<td>Analysis of Rate Data Obtained by Stepping down to Lower Shear Rates</td>
</tr>
<tr>
<td>15</td>
<td>Analysis of Rate Data Obtained by Stepping down to Various Shear Rates</td>
</tr>
<tr>
<td>16</td>
<td>Compatibility between the Various Rate Theories and Properties of &quot;Baymal&quot;-Propylene Glycol Suspension</td>
</tr>
<tr>
<td>17</td>
<td>Normal Force and Tangential Stress Values</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------</td>
</tr>
<tr>
<td>1</td>
<td>Thixotropic Hysteresis Loop</td>
</tr>
<tr>
<td>2</td>
<td>Types of Fluid Equilibrium Viscosity Curves</td>
</tr>
<tr>
<td>3</td>
<td>General Concept of Plastic Fluids</td>
</tr>
<tr>
<td>4</td>
<td>Theoretical Flow Curves</td>
</tr>
<tr>
<td>5</td>
<td>Transducer Core Deflection versus Time - Movement Limited</td>
</tr>
<tr>
<td>6</td>
<td>Transducer Core Deflection versus Time - Movement Unlimited</td>
</tr>
<tr>
<td>7</td>
<td>Thixotropic Behavior of Kim's C-4 Solution</td>
</tr>
<tr>
<td>8</td>
<td>Thixotropic Behavior of Kim's C-5 Solution</td>
</tr>
<tr>
<td>9</td>
<td>Thixotropic Behavior of Kim's C-7 Solution</td>
</tr>
<tr>
<td>10</td>
<td>Weissenberg Rheogoniometer</td>
</tr>
<tr>
<td>11</td>
<td>Typical Step-down Sequence</td>
</tr>
<tr>
<td>12</td>
<td>Step-up, Step-down, Equilibrium and Initial Shear Stresses</td>
</tr>
<tr>
<td>13</td>
<td>Viscosity Decline at Constant Shear Rates</td>
</tr>
<tr>
<td>14</td>
<td>Viscosity Decline at Constant Shear Rates</td>
</tr>
<tr>
<td>15</td>
<td>Viscosity Decline at Constant Shear Rates</td>
</tr>
<tr>
<td>16</td>
<td>Viscosity Decline at Constant Shear Rates</td>
</tr>
<tr>
<td>17</td>
<td>Relationship of Viscosity Decline to Shear Rate</td>
</tr>
<tr>
<td>18</td>
<td>Stress Recovery while Shearing</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>19</td>
<td>Expected Viscosity Decline</td>
</tr>
<tr>
<td>20</td>
<td>Unexpected Viscosity Decline</td>
</tr>
<tr>
<td>21</td>
<td>Unexpected Viscosity Decline</td>
</tr>
<tr>
<td>22</td>
<td>Unexpected Rate Behavior</td>
</tr>
<tr>
<td>23</td>
<td>Estimation of Upper Newtonian Viscosity</td>
</tr>
<tr>
<td>24</td>
<td>Determination of p and K</td>
</tr>
<tr>
<td>25</td>
<td>Actual versus Calculated Equilibrium Curves</td>
</tr>
<tr>
<td>26</td>
<td>Correlation of Rate Data</td>
</tr>
<tr>
<td>27</td>
<td>Diagrammatic Layout of Normal Force System</td>
</tr>
<tr>
<td>28</td>
<td>Piezoelectric Load Cell</td>
</tr>
<tr>
<td>29</td>
<td>Load Cell Mounted for Tension or Compression</td>
</tr>
<tr>
<td>30</td>
<td>Charge Amplifier</td>
</tr>
<tr>
<td>31</td>
<td>Typical Measurement System</td>
</tr>
<tr>
<td>32</td>
<td>Modified Normal Force Apparatus</td>
</tr>
<tr>
<td>33</td>
<td>Glass Plate and Ball Bearing Arrangement</td>
</tr>
<tr>
<td>34</td>
<td>Normal Forces and Tangential Stresses</td>
</tr>
<tr>
<td>35</td>
<td>Normal Forces and Tangential Stresses</td>
</tr>
<tr>
<td>36</td>
<td>Normal Forces and Tangential Stresses</td>
</tr>
<tr>
<td>37</td>
<td>Load Cell Calibration</td>
</tr>
<tr>
<td>38</td>
<td>Placement of the Load Cell above the Plate and Cone</td>
</tr>
<tr>
<td>39</td>
<td>Essential Elements of the Measuring System</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>40</td>
<td>Forces Arising from a Ball and Cone Bearing.</td>
</tr>
<tr>
<td>41</td>
<td>Suggested Mountings of the Load Cell</td>
</tr>
<tr>
<td>42</td>
<td>Response with Cold Glycerine</td>
</tr>
</tbody>
</table>
I.

INTRODUCTION

Liquids have been classified according to viscometric behavior into two broad groups, those which have a constant viscosity as defined by Newton's law of viscosity and those that do not. Non-Newtonian behavior has been further subdivided into more specific classifications. Thixotropy refers to the variation of viscosity with time as a result of changes in the internal structure of the liquid. A viscoelastic liquid is one which exhibits a measurable elastic response in addition to viscous flow behavior. When shear rate is held constant the effects of thixotropy and viscoelasticity decrease with time until an equilibrium condition is reached, at which the apparent viscosity of the liquid remains constant indefinitely. An equilibrium curve is defined as the curve of viscosity or shear stress plotted versus shear rate determined by measurements taken after there are no longer changes with time.

An explanation of non-Newtonian behavior has long been sought. However, little real progress has been made in explaining the cause or providing a representation for thixotropic non-Newtonian behavior. Nevertheless, it is generally believed that thixotropy is the result of some structural change in the liquid that, in addition to being
a function of the shear level, is a function of time. The term structural level is used to denote a single viscosity at a given shear rate after a stated sequence of shear rates. The term structure is not precisely defined. Such terms usually refer to particle orientation, flocculation, or molecular order in the liquid. It is recognized that liquid structure is probably quite different from that in a solid and may in fact be unrecognizable as a structure at all.

Many directions of research have been pursued to provide some basis for theories to account for the rheological behavior of liquids. One type of theory which has been modestly successful is analogous to chemical kinetics. Although other types of theories have been developed, we will limit our discussion to this type. In a kinetic approach a change in viscosity is presumed due to a change in the internal structure of the liquid. The change in structure is considered analogous to a change in concentration during a chemical reaction. The assumption of different types of "reactions" taking place and different relationships between structure and viscosity account for most of the differences between the various rate theories of this type.

One of the more promising theories developed using the chemical kinetics approach is that of Denny and Brodkey (1). In the development of this theory it was assumed that the mechanism responsible for thixotropic behavior is also the sole cause of
all non-Newtonian behavior. The theory was tested using data on a polymer melt (2). The results were promising but inconclusive due to the short duration of the viscosity transient and the visco-elastic nature of such melts. The present study stems from a desire to test the theory under more controlled conditions where the viscosity transient is much longer and the elastic component in the liquid is much less important. As a result of these requirements, the decision was made to perform a series of experiments on a suspension of colloidal alumina in propylene glycol. These results and discussion of their implications make up the main body of this dissertation.

Before making our detailed study on a single liquid, some other work, aimed at extending the Brodkey-Denny theory to account for normal forces, was started. This work consisted of equipment development and was carried to a logical stopping point. These results are presented in Appendix A.

The equations resulting from chemical kinetic rate theories require that liquids exhibit certain specific types of rheological behavior if the equations are to apply. These requirements are discussed for a number of the theories. The colloidal suspension on which most of our data were taken was designed to allow the performing of experiments which would show whether the liquid's rheological behavior meets the requirements of the theories. With this liquid we were able to produce set structural levels and
obtain viscometric data in the absence of structural change. The "structure curves" obtained provide more basic information than common "down" curves because the structural level ordinarily varies when a downcurve is determined.

In addition to structure curves, the equilibrium curve, rates of change (fall-off) of viscosity at constant shear rates when the structure is completely built up, and rates of change of viscosity at various constant shear rates for numerous other structural levels were determined and are discussed.
The literature review is limited to a survey of pertinent literature concerning thixotropic behavior in liquids and a presentation of the rheological theories based on chemical kinetics (rate theories). A more general discussion of non-Newtonian behavior and the various theories to explain such behavior has been given by others (1,2,3,4,5) and the reader is referred to them for review. The literature section is divided into two parts, one for each of the topics chosen for examination. This is a natural division. Most of the literature concerning thixotropic behavior of liquids consists of reports of experimental results and discussion of the possible reasons for the occurrence of the observed behavior. Some equations are presented but for the most part these are empirical equations for which no theoretical justification is given. On the other hand, the rate theories have been used primarily for correlating equilibrium data. Only Denny and Brodkey (1,2) have attempted to evaluate the correctness of their theory by obtaining the constants in their equations independently from rate data and equilibrium data and comparing the results.
Thixotropy

Historically, thixotropic behavior in fluids was considered important only as a nuisance factor. For example, according to Green (6):

The subject of thixotropy is not a particularly important one in itself but it is highly necessary that the investigator should have a clear understanding of it because of the effect thixotropy has on his laboratory measurements.

Green developed the now well known procedure of taking an upcurve followed by a downcurve with the thickness of the resulting hysteresis loop being considered a measure of the amount of thixotropy. The upcurve is a plot of shear stress versus shear rate for which the data are obtained by shearing the fluid for a set time interval (perhaps ten seconds) at a given rate, observing the shear stress, and then changing the shear rate immediately to the next higher level, once again measuring the shear stress. This procedure is repeated until the top shear rate desired is reached, after which the downcurve is obtained by progressively lowering the shear rate in a stepwise manner and measuring the shear stress at each step until the bottom point on the downcurve is obtained.

Green's "rheological system" is based on two basic concepts. These are:

1. Plastic viscosity, i.e., the number of dynes per square centimeter of tangential shearing force in excess of the Bingham yield value that will induce a unit rate of shear (1 sec$^{-1}$).
2. The thixotropic hysteresis loop shown in Figure 1. Green suggested the concept of "thixotropic levels", which, in his systematic approach, meant that almost all downcurves are straight lines when plotted as shear rate versus shear stress, i.e., they exhibit Bingham plastic behavior. He also suggested that all down-curves for a single material would go through a common point.

Green explained yield and thixotropy in terms of flocculation, where flocculation is defined as particle aggregation with the particles being soft of "wooly". According to him:

Flocculation is necessary for the existence of thixotropy, but all flocculated systems are not necessarily thixotropic.

Concerning the relationship between yield values and thixotropy, Green said the following:

There are many statements in the literature that no difference exists between yield value and thixotropy. This situation has been in existence so long that it will probably never become clarified. Thixotropic materials break down in accordance with clear-cut laws - laws that are never associated with yield value. Thixotropy can produce yield value; but there is no evidence or known reason why yield value cannot exist without the presence of thixotropy.

Weltmann (7,8) was one of the earliest to study thixotropic behavior in a systematic way. Her equation for the relationship between the rate of decrease in plastic viscosity and time, after application of a constant shear rate, is

\[ B = \frac{d\mu}{dt} \]

where \( B \) is the coefficient of thixotropic breakdown with time, \( \mu \).
Figure 1. Thixotropic Hysteresis Loop.
is plastic viscosity, and \( t \) is time. Her experimental data were obtained in the following way. The viscometer was started at some top rpm. Time was measured from the occurrence of maximum shear stress. After the top rpm had been maintained for awhile, a downcurve was obtained. Then the viscometer was reset at the top rpm. Since viscosity rose during the determination of the downcurve, time was not measured or accumulated until the shear stress was once again down to the point at which the downcurve determination had begun. From that point the experiment was continued and time was accumulated until another downcurve was desired and obtained, after which the procedure was repeated until equilibrium was reached. A plot of \( \mu' \) versus \( \ln(t) \), where \( t \) was total accumulated time, was used to obtain \( B \) using the equation

\[
B = \frac{(\mu'_1 - \mu'_2)}{\ln(t_2/t_1)}
\]

where subscripts 1 and 2 refer to values at times 1 and 2 respectively.

In the fairly limited range of shear rates of her studies, she found that thixotropic behavior of many materials could be described with the equations given above and that \( B \) did not vary with shear rate.

In their book, Van Wazer et al (9) classify fluids according to Figure 2. In this figure, A is a Newtonian liquid; B, a pseudoplastic fluid; C, a dilatant fluid; D, a Bingham plastic; E, a pseudoplastic material with a yield value; and F, a dilatant material with a yield value. \( \tau_0 \) is the yield value. These authors classify Newtonian,
Figure 2. Types of Fluid Equilibrium Viscosity Curves.
pseudoplastic, and dilatant bodies as liquids because they do not have a yield value, and plastic substances (those with a yield value) as either liquids or solids because they exhibit the properties of solids at stresses below the yield value and the properties of liquids at greater stresses. In their opinion true yield values are never found in single-phase liquids but are always associated with emulsions or slurries, in which one or more phases are dispersed as particles or bubbles in a continuous phase. In their words:

The yield value is due to interference between the dispersed particles. As the concentration of the dispersed phase is reduced, the yield value decreases, finally to zero.

In their opinion:

Non-Newtonian flow is found only in colloidal and other particulate systems (in which the concept of a colloidal particle includes large molecules).

By this definition most polymer melts would be classed as colloids. Concerning thixotropy, they say:

Thixotropic breakdown can vary from a nearly instantaneous to an extremely slow process. Measurement is limited on one hand by the response of the viscometer and, on the other, by the patience of the invesigator.

On the subject of rate of decline of viscosity of thixotropic materials, they suggest that the apparent viscosity of a thixotropic fluid decreases logarithmically with time from an initial value, \( \mu_{t=0} \), to a final value, \( \mu_{t=\infty} \). This can be contrasted with Weltmann's use of plastic viscosity.

Hermans (10) gives a concensus of opinion concerning the
properties of gels and suspensions:

It is generally accepted nowadays that a gel owes its solid character to the fact that one or more of the components forms a coherent structure, or network, throughout the system. In the majority of gels the coherence is brought about by short range forces between the constituent parts. These may be real chemical bonds or else Van der Waals forces.

Hermans noted that:

Many suspensions can undergo a considerable amount of elastic deformation before flow commences. Elastic shear strains as high as 0.5 have been obtained before the stress reaches the yield value.

He felt that this high deformability is more likely to be caused by the looseness of the liquid structure than by long range forces.

Mack (11) and Gillespie (12) illustrate the continuance of the opinion that thixotropy is related to fluid structure. To quote Mack:

It is generally agreed that anomalous (non-Newtonian) flow is associated with a change in the internal structure of the system.

According to Gillespie:

It is generally recognized that the rheology of colloidal systems is connected with the state of flocculation and possible changes in it with changes in shear rate. The precise manner in which aggregation affects flow properties will not be known until much more pertinent experimental evidence is available.

Vinogradov has a large number of publications (13,14) on all phases of rheology. Of particular interest to us is the concept of thixotropy he adopted as a result of experimental observations on various greases (14). The concept is best illustrated with a diagram. In Figure 3 the data are taken at various shear rates but in any given experiment the shear rate is held constant. When the shear rate is
Figure 3. General Concept of Plastic Fluids.
below A, the initial and equilibrium shear rates are the same (i.e., level 1). Above this (say, level 2) the curve ABH represents the maximum values of shear stress at the corresponding shear rates. The curve ACDH represents the equilibrium values of shear stress at the corresponding shear rates. At high shear rates, the fluid structure is either completely broken down almost immediately after shearing action is initiated or has negligible effect on shear stress values (i.e., level 3). Consequently, the fluid is Newtonian in this region. At very low shear rates, 0 to A, creep flow is the dominant mechanism, and the structure is not broken further by increasing the duration of shearing. Between A and H the structure breaks down as a function of time and shear rate with the result as shown in the diagram (arrow at level 2). Of particular interest is the portion of the equilibrium curve from A to C. This is a region in the flow curve where breakdown of the structure is slow enough that the flow mechanism appears to tend toward a solid-like creep flow. Ultimately, as shear rate is lowered below A (i.e., level 1), structural breakdown rate becomes nil compared to structural build-up rate, and flow apparently takes place along slip planes. If shearing action is halted when in this flow regime, materials capable of exhibiting a yield value show a residual shear stress or yield value that is fixed at or nearly at the shear stress during the shearing action. For most fluids of interest, it is difficult to observe this region of the flow curve because this behavior occurs at shear rates too
Dintenfass (15) studied thixotropy of concentrated pigment solutions. His experimental approach is of interest to us because he studied the time required for recovery of viscosity in thixotropic systems. In general, he believed that:

The thixotropic recovery may take place between two equilibrium levels of stress or rates of shear, both these levels corresponding to some fixed and specified pigment structure.

In a typical experiment the material was sheared at 600 rpm until equilibrium was reached, then the rotational speed was reduced to 2 rpm and the amount of time required to reach equilibrium at this rate was measured.

Of his several conclusions, the ones of interest to us are:

1. The times of thixotropic recovery depend on the values of rates of shear used in the breakdown of the pigment network and on the values of rates of shear used during observation of the thixotropic recovery. Thixotropic recovery is very rapid in the regions of high rates of shear and relatively slow at low rates of shear.

and:

2. The time of thixotropic recovery between various consecutive levels of rates of shear are additive.

Defining an equilibrium rate of shear as any shear rate at which shear stress no longer varies with time, Dintenfass also deduced that an unspecified, non-equilibrium rate of shear could cause the same degree of structural breakdown as a lower equilibrium value. These conclusions mean that if a material is sheared at a high shear
rate until equilibrium is established, and then sheared at a very low shear rate until equilibrium is once more established, the time required to reach equilibrium at the low shear rate is the same as the sum of the times required if the material were sheared to equilibrium at a number of intermediate shear rates before reaching equilibrium at the final low shear rate. Also, viscosity recovery is faster at higher shear rates during the recovery cycle.

Bujake (16) suggests that two types of bonds, primary and secondary, are responsible for thixotropic and non-Newtonian behavior. His hypothesis is that the primary bonds are strong, hard to break, and slow in reforming after shearing action ceases, while the secondary bonds are weak, easy to break, and reform rapidly when shearing action stops. His theory suggests that thixotropic behavior is the result of breaking primary bonds and that non-Newtonian behavior without thixotropic behavior is due to the secondary bonds.

DeWaele (17) studied thixotropic paints in an effort to determine "thixotropic coefficients". His experimental procedure was to first shear the material until the stress was stabilized ($\tau_1$). Then the shearing action was arrested for various intervals of time before shearing once again was resumed at the same level. The high, but temporary stress level ($\tau_2$) was recorded. The log of the difference, $\tau_2 - \tau_1 = \tau_r$, was plotted versus log time and a straight line resulted. The equation is

$$\log \tau_r - n \log t = \log k$$

3)
where $k$ and $n$ are constants (his thixotropic coefficients). The equation can be differentiated to

$$\frac{d\tau_r}{dt} = n \frac{\tau_r}{t} \quad (4)$$

which in turn can be simplified to

$$\frac{d\tau_r}{dt} = nk \quad (5)$$

at unit time, since at unit time $\tau_r = k$.

In another paper (18) DeWaele suggests that the indicated yield value for a liquid (determined by extrapolating the straight line portion of a stress versus shear rate plot to zero shear rate) is due to flocculation in the liquid material, and that therefore total shearing stress is the sum of deflocculating stress and viscous stress, where deflocculating stress is that part supplied to overcome flocculation.

His concept of rigidity is the following:

Rigidity, however, is not a function of viscosity and functions solely as an elastic modulus, exhibiting an elastic unit with a characteristic tangential displacement at which a break of the elastic component takes place. At this elastic limit or breaking point, displacement causes destruction of the structure. Thus, it is clear that any dynamic method of measurement is ineffective if displacement is carried beyond this point. He further comments:

This elasticity differs from that found in materials which exhibit no self-healing properties in being progressively recoverable with time of rest.
Essentially the same concept is brought forth by Roller and Stoddart (19).

Jankovics (20) showed that a polymer flocculated suspension could be degraded to primary particles by vigorous agitation.

Eissenberg (21) studied an aqueous thoria slurry, concluding that the limiting (minimum) viscosity of the solution was equal to the chemically dispersed Newtonian suspension viscosity. He considered a good first estimate of the limiting viscosity of a shear thinning (lower viscosity at higher shear rates) non-Newtonian suspension to be one equal to or greater than that of the suspending medium.

Foster, Savins, and Waite (22), on the other hand, concluded that montmorillonite clay-water systems exhibited higher viscosities and were more thixotropic as they became more dispersed. They believed that certain exchange ions affect the size of the clay micelles, with smaller micelles allowing a higher degree of anomalous rheological behavior.

At first examination, the studies of Eissenberg, and Foster, Savins, and Waite appear to be contradictory. The problem is resolved by understanding that these authors have different definitions of the term dispersion. Eissenberg considers dispersion to be the breaking down of flocs while Foster, Savins, and Waite use the term to describe an alteration of the size of the micelles. The subsequent flocculation and deflocculation of these micelles is not
considered by them in terms of dispersion. Thus a system such as described by Eissenberg probably has no change in the size of the micelles due to his chemical treatment of it. The entire resulting viscosity effect is therefore probably due to deflocculation.

Worrall and Tuliani (23) found that:

Consistency of clay-water suspensions is not constant but changes with time. In general, the viscosity of a clay suspension starts to increase from the moment it is made up, and this process goes on indefinitely.

They concluded that:

Changes in clay suspensions due to ageing complicate measurement of flow properties.

that:

There is a marked deviation from linearity (Bingham's law), particularly with flocculated suspensions, at low shear rates.

and that using the width of the hysteresis loop obtained when the applied shear is increased to a maximum and then decreased back to zero is unsatisfactory for quantitative determinations of thixotropy in liquids.

With fresh (newly prepared) sample, they found that clockwise thixotropic loops occurred when using Green's (6) method of obtaining data, which was the reverse of the expected behavior. Therefore, they developed a procedure for obtaining "reasonably stable suspensions". This was to prepare a fresh sample of suspension, and determine upcurves and downcurves until; (1) the clockwise loops disappeared, (2) there were no perceptible changes in the flow curves
after further ageing and, (3) a counterclockwise thixotropic loop appeared.

No discussion of thixotropy is complete without a mention of rheopexy, the occasionally observed increase in the rate of build-up of viscosity due to shearing action. According to Freundlich (24):

Rheopexy is probably due to a certain coagulation of the particles as soon as they have been made to approach each other by movement of the liquid.

We interpret this to mean that shearing action can on occasion physically orient the particles in such a way as to promote reactions which would either occur more slowly or not at all without shearing action.

Summary of literature on thixotropy

This completes the review of literature on thixotropic behavior. The most noteworthy items obtained from it are:

1. Thixotropic behavior is often associated with a yield value,
2. Apparent viscosity of thixotropic fluids decreases logarithmically with time,
3. Thixotropic behavior is apparently related to a liquid structure of some type,
4. The duration of thixotropic behavior and amount of viscosity change with time varies widely for different liquid systems,
5. Thixotropic behavior is usually associated with shear thinning non-Newtonian equilibrium behavior.
From our review it is apparent that thixotropy is not well understood. The early experimental techniques that were developed for the purpose of quantitatively measuring thixotropy did not provide information that is useful in developing theoretical concepts. Furthermore, the great need for understanding and characterizing the flow properties of polymers has distracted from rheological research on other types of liquids. Since most polymer melts and polymer solutions do not exhibit appreciable thixotropic behavior, the subject has not received much recent attention. Consequently, only a few studies on a few liquids are of any real value for research purposes.

Rate Theories

The characteristics of combined thixotropic behavior and shear thinning non-Newtonian equilibrium behavior suggests that some kind of reversible chemical or physical reaction is responsible for the deviation from ideal (Newtonian) flow. Consequently, a number of theories have been developed in an attempt to use the concepts of chemical kinetics to account for viscometric behavior.

In the following pages the rate theories considered most directly applicable to our work are presented. We have chosen to deal only with rate theories based on classical chemical reaction kinetics. This excludes the works of Eyring and co-workers (25,26,27), and others, in which the absolute reaction rate theory is adapted to treating rheological data.
Goodeve (28) developed one of the earliest rate theories to account for non-Newtonian behavior. His approach is important in that it has served as a basis for several other efforts. To Goodeve the term "thixotropic system" included both time dependent and shear thinning non-Newtonian systems. He was primarily concerned with fluids exhibiting yield values and for which the experimental data follow fairly closely the relation

\[ \tau = \mu_\infty S + \tau_0 \]

where \( \tau \) is shear stress, \( S \) is shear rate, \( \mu_\infty \) is an upper Newtonian viscosity (limiting viscosity at high shear rates), and \( \tau_0 \) is a yield value. To account for the \( \tau_0 \) term, Goodeve proposed that this stress is due to link formation between particles with first a stretching and breaking and then a reformation of the links. This stress is given by

\[ \tau_0 = \frac{1}{2} f_c n z \]

where \( f_c \) is the breaking force at a link, \( z \) is the distance between two velocity planes (constant and always less than the extended length of the two linked particles), and \( n \) is the number of links/cc. By this equation, \( \tau_0 \) is constant if \( n \) is constant. To account for the Newtonian term, Goodeve once again hypothesized link breakage and formation. In this case he proposed that the links are made and broken primarily by thermal effects, giving, at constant tem-
perature, a resistive force directly proportional to the rate of shear. This force is \( \mu_\infty S \). In this approach, if \( n \) varies with shear rate, \( \tau_0 \) can vary. Thus, thixotropy can be accounted for by a change of \( n \) with time which causes a change in \( \tau_0 \). Goodeve proposed the rate equation

\[
\frac{dn}{dt} = -\frac{HzS}{f_c} + k'' (2n_0 - 2n)^2 S
\]  

(8)

where \( H \) is a Hook's law constant, \( k'' \) is the reaction rate constant for rate of formation of links, \( n_0 \) is the maximum number of possible links/cc, and \( (2n_0 - 2n) \) is the concentration of potential partners to a link. In this equation, at equilibrium, when \( dn/dt = 0 \), \( n \) is not dependent on shear rate. Goodeve made no attempt to apply his rate equation to the rate of change of viscosity with time.

Gillespie

Using similar reasoning, Gillespie (12) extended Goodeve's analysis in order to develop a theory applicable to pseudoplastic systems. Gillespie's rate equation is

\[
\frac{dy}{dt} = KN - By
\]  

(9)

where \( \gamma \) is the average number of links involving a given particle, \( t \) is time, \( N \) is total number of particles in a given volume, and \( K \) and \( B \) are rate "constants". \( K \) and \( B \) are not really constants, since
\[ K = (K_0 + K_1 S) n_L \]

and

\[ B = B_0 + B_1 S \]

where \( K_0 \) is the contribution due to Brownian movement, \( K_1 S \) is the contribution of shear, \( n_L \) is the number of links formed when two particles come in contact (presumably constant for a single fluid system), and \( B_0 \) and \( B_1 S \) are descriptive of thermal and shear induced rupture, respectively. Following Goodeve's arguments, Gillespie obtained the final equilibrium equation

\[
\tau = \mu_\infty S + \frac{E_A N^2 (K_0 + K_1 S) S}{2[(B_0/B_1) + S]^2} = \mu_\infty S + \theta
\]

where \( E_A \) is the total binding energy between two particles. In this equation \( \theta \) is analogous to Goodeve's \( \tau_0 \), but no longer represents a yield value. Using his equations Gillespie obtained a fairly good correlation of equilibrium data on a polymer solution at several concentrations over a fairly narrow range of shear rates. No attempt was made to analyze any rate data.

**Storey and Merrill**

Storey and Merrill (29) used an approach similar to that of Goodeve in that they assumed that deviation from Newtonian behavior is due to formation of links between particles. Their basic equation
\[ \mu = \tau / S = a n + \mu_\infty \]

where \( a \) is a proportionality constant, \( n \) is the number of links/cc, \( \mu \) is apparent viscosity, and \( \mu_\infty \) is the viscosity if no links are present. Their rate equation is

\[ \frac{dn}{dt} = -k_1 n S + k_2 (n_o - n) \]

where \( k_1 \) and \( k_2 \) are rate constants for destruction and reformation of links, respectively, and \( n_o \) is the number of links/cc at equilibrium under no shear. The assumption of a first order reformation reaction was based on the idea that each link rupture frees only one effective reacting particle. This is equivalent to assuming that there are a large excess of sites for links to form compared to the number of particles available for forming links.

Storey and Merrill applied their equations to some data of aqueous solutions of amylose and amylopectin. The agreement for the equilibrium curve was good but their range of shear rates was apparently less than two decades. They did obtain rate data but did not attempt to make an independent check on the correctness of their theory by obtaining the two rate constants from rate studies and then comparing them with constants obtained from equilibrium data. This was probably due to an inability to obtain data over the necessary ranges of shear rates.
Krieger and Dougherty (30) also used a rate theory to develop an equation for non-Newtonian flow. Their proposed mechanism is the association and dissociation of spherical particles which they referred to as singlets and doublets. Letting \( n_1 \) and \( n_2 \) be the number of singlet and doublet particles per unit volume, they wrote the overall rate equation

$$\frac{dn_2}{dt} = k_f n_1^2 - (k_b + k_s) n_2$$  \hspace{1cm} (14)$$

where \( k_f \) and \( k_b \) represent the specific rate constants for the formation and dissociation of singlets and doublets, respectively, and \( k_s \) is the specific rate constant for shear-induced dissociation. At steady state,

$$\frac{n_2}{n_1^2} = \frac{k_f}{k_b + k_s}$$  \hspace{1cm} (15)$$

and at zero shear

$$\bar{n}_2 / \bar{n}_1^2 = k_f / k_b$$  \hspace{1cm} (16)$$

where \( \bar{n}_2 \) and \( \bar{n}_1 \) refer to the zero shear rate. Their relation between \( n_1, n_2, \) and \( \mu \) is

$$\mu / \mu_s = f_1 n_1 + f_2 n_2 = f_1 n + (f_2 + 2f_1) n_2$$  \hspace{1cm} (17)$$

where \( f_1 \) and \( f_2 \) are functions of \( n \) (independent of \( S \)), \( \mu_s \) is the
viscosity of the continuous medium, such as constant solvent viscosity, and

\[ n = n_1 + 2n_2 \quad \text{18)} \]

where \( n \) is the total concentration of spheres. Using the boundary conditions \( \mu \) approaches \( \mu_\infty \) as \( S \) approaches \( \infty \), and \( \mu \) approaches \( \mu_0 \) as \( S \) approaches 0, they arrived at the relation

\[ \frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = \frac{n_2}{n_2} \quad \text{19)} \]

Then, using the Einstein (31) approach to relate number of particles to shear stress for a flowing liquid, they obtained the equation

\[ \frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = (1 + \frac{1}{\tau C})^{-1} \quad \text{20)} \]

where \( \tau_C \) is a material constant. They made no attempt to apply their equations to rate data but did use them to correlate concentration effects.

**Worrall and Tuliani**

As a flow mechanism, Worrall and Tuliani (23) suggested that the marked deviation of their data for various clay suspensions from Bingham plastic behavior is due to the breaking down by shearing of an internal thixotropic structure and its subsequent reformation upon resting. With this concept as a basis they developed a rate theory
to account for their clay-water data. As in most rate approaches, they assumed a mechanism and adjusted their equations until they were able to fit the data.

They let $X$ be the fraction of particle-particle links existing in the internal structure at any time. For complete buildup, $\gamma = 1.0$ and for complete breakdown, $\gamma = 0$. No flow is presumed to occur in the suspension until the stress exceeds a yield value, $\tau_0$. If no breakdown of the internal structure occurred, shear would take place only via slip planes and viscosity would be high (see the dotted line in Figure 4). However, progressive breakdown starts to occur at the initiation of shearing action and consequently the flow curve follows the illustrated experimental curve which has a limiting slope of $1/\mu_{op}$, where $\mu_{op}$ is a point viscosity and equals the slope of the curve corresponding to $\lambda = 0$. Based on this reasoning, they concluded that $\tau$ is a function of $S$ and $\lambda$. They assumed that the value of $\lambda$ for a rested liquid is less than unity and let it equal $\lambda_0$. Their rate equations are $-aS\lambda$ for breakdown rate and $b(\lambda_0 - \lambda)$ for buildup rate. The overall rate equation therefore is

$$\frac{d\lambda}{dt} = b(\lambda_0 - \lambda) - aS\lambda$$  \hspace{1cm} (21)$$

where $a$ and $b$ are constants. At equilibrium, $\frac{d\lambda}{dt} = 0$, and

$$\lambda = \frac{b\lambda_0}{aS + b}$$ \hspace{1cm} (22)$$

Then, by trial and error, they related $\tau$ to $S$ and $\lambda$ by the equation
Experimental curve
limiting slope = \frac{1}{\mu_{op}}

Figure 4. Theoretical Flow Curves.
where $h$ is a constant. Substituting for $\lambda$ in Equation 23 they obtained the equilibrium equation

$$\tau = \mu_0 S + \tau_0 + hS\lambda \quad 23)$$

where $g = h\lambda$. Worrall and Tuliani used their equation to correlate equilibrium data on several clay-water suspensions. The agreement was excellent over their total shear rate range of 2 to 3 decades. They also took some rate data and obtained rate constants from these. However, equilibrium data were also used in this determination so the constants were not independently determined.

Denny, Kim, and Brodkey

Denny and Brodkey (1), Denny (2), Denny, Kim, and Brodkey (3), Kim (4), and Kim and Brodkey (32) have presented a general theory relating thixotropic behavior to general non-Newtonian characteristics. Their theory is based on three assumptions: (1) non-Newtonian behavior, including thixotorpy, is caused by changes in the internal fluid structure, (2) the structural change can be described by the rate equation

$$-\frac{dF}{dt} = k_1 F^m - k_2 (1-F)^n \quad 25)$$

where $F$ is the fraction of the property (structure) unchanged, $k_1$ is the forward reaction rate constant, $k_2$ is the reverse reaction rate constant, $m$ and $n$ are the orders of the forward and reverse reactions, respectively, and $1-F$ is the fraction of the structure.
changed, (3) $F$ can be related directly to viscosity by an equation of the type

$$ F = \frac{f(\mu) - f(\mu_o)}{f(\mu_o) - f(\mu_\alpha)} \quad 26) $$

where $f(\mu)$ refers to a function of apparent viscosity, $f(\mu_o)$ refers to a function of the lower Newtonian viscosity, and $f(\mu_\alpha)$ refers to a function of the upper Newtonian viscosity.

In an early attempt to apply this approach to viscometric data (1), the equations

$$ F = \frac{\mu_p - \mu_\alpha}{\mu_\alpha - \mu_\alpha} \quad 27) $$

and

$$ k_1 = k_1 S_p \quad 27) $$

were used, where the subscript $p$ refers to point viscosities, and $S_p$ is shear rate to the power $p_1$, where $p_1$ is a material property.

In this case, the rate equation is

$$ -\frac{dF}{dt} = k_1 S_p F^m - k_2 (1-F)^n \quad 28) $$

Application of these equations to the steady state (equilibrium) situation gives the equation

$$ K = \frac{k_1}{k_2} = \frac{(\mu_\alpha - \mu_\alpha)^m}{(\mu_p - \mu_\alpha)^n S_p (\mu_\alpha - \mu_\alpha)^{m-n}} \quad 29) $$
This equation was applied successfully to equilibrium data on several polymer systems over a limited range of shear rates, but failed for some attempted applications to data where the range of shear rates was very wide. These authors also studied time dependent viscosity behavior using data reported in the literature on a heavy mineral oil and reported a good agreement between the constants obtained from equilibrium data and those obtained independently from data on the rate of change of viscosity with time. In our knowledge, this was the first case reported where rate data were checked independently with equilibrium data. It should be noted here that the rate data in this case were not of high quality for the type of comparison made by Denny and Brodkey.

This theory was later modified (2,3) to allow correlation of data on polymer systems over a wider range of shear rates. The modification consisted of three parts. The first was a change in the rate constants to

\[ k_1' = k_1^{P_1} \]

and

\[ k_2' = k_2^{P_2} \]  \hspace{1cm} (30)

Instead of

\[ k_1' = k_1^{S_1} \]

and

\[ k_2' = k_2 \]
In these equations $p_1$ and $p_2$ are constants and $k_1$ and $k_2$ are true forward and reverse rate constants for a given system at a given temperature. The second change was in using apparent viscosities instead of point viscosities, and the third was in the relationship between $F$ and $\mu$ to give

$$F = \frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty}$$  \hspace{1cm} (31)$$

although the linear relation of Equation 32

$$F = \frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty}$$  \hspace{1cm} (32)$$

was later found to be adequate also.

The rate equation is then

$$- \frac{dF}{dt} = k_1 \tau^p F^m - k_2 \tau^p (1-F)^n$$  \hspace{1cm} (33)$$

At equilibrium, this equation reduces to

$$\frac{k_1}{k_2} \tau^p = \frac{(1-F)^n}{F^m} = k_\tau^p$$  \hspace{1cm} (34)$$

where

$$p = p_1 - p_2$$  \hspace{1cm} (35)$$

A log-log plot of $(1-F)^n / F^m$ vs. $\tau$ will yield a straight line of slope $p$ and intercept $k_1/k_2$ for the proper values of $m$ and $n$. This
equation was applied (2,3) to a number of systems, apparently obtaining the best results with \( m = 1, n = 2 \), and \( p \) ranging from 1.5 to 2.5.

Denny (2) made a major effort to obtain rate data and compare rate constants calculated from those with constants calculated from equilibrium data. He reported some success in this but there are a number of questions concerning the general applicability of his results. These will be dealt with later.

Kim and co-workers (3,5,32) further modified the theory to allow its application to polymer solutions as well as pure melts. The rate equation in this case was

\[
- \frac{d(CF)}{dt} = k_1 \tau^p (CF)^m - k_2 \tau^p [C(1-F)]^n
\]

At equilibrium, the resulting equation is

\[
\frac{k_1}{k_2} \tau^{p_1-p_2} = \frac{k_1}{k_2} \tau^p = \frac{(1-F)^n}{f^m} \xi^{n-m}
\]

In this development, the definition of \( F \) has not been changed.

Equation 37 allowed a fairly good correlation of data on ten solutions of polymethyl methacrylate in diethyl phthalate with concentrations up to 55%. Once again, the values \( m = 1 \) and \( n = 2 \) appeared to give the best results. Kim made no attempt to obtain or use rate data, primarily because of anticipated experimental difficulties. As a consequence, he missed an important point in his theoretical development. This will be presented later.
Cross

A very recently developed rate theory, in some ways quite similar to that of Denny and Brodkey, is that of Cross (33). He assumed that flocculation involves groups of linked particles, and that under steady shear conditions there is an average group size dependent on the magnitude of the applied shear. The groups are assumed to take the form of random kinked chains.

To develop his theory, he let $S =$ applied shear rate, $P =$ total number of single particles in a unit volume, $L =$ average number of links per chain at shear rate, $S$, $L_0 =$ average number of links per chain at $S = 0$, $\mu =$ viscosity, $\mu_o =$ viscosity at $S = 0$, and $\mu_\infty =$ viscosity at $S = \infty$. He presumed that $L$ approaches 0 and $\mu$ approaches $\mu_\infty$ as $S$ approaches $\infty$. The rate aspects of his theory arise from the assumed relation between $L$ and $S$. The rate of linkage rupture is given by $(k_0 + k_1 S^n) L$, where $k_0$ is due to the contribution of Brownian movement, $k_1 S$ is the contribution of shear, and $n$ must be even because the rate of breakdown must be independent of the direction of shear. The rate of linkage formation is given by $k_2 P$. Therefore, the rate equation is

$$\frac{dL}{dt} = k_2 P - (k_0 + k_1 S^n) L$$

In this equation, $k_2 P$ is a constant. At any given shear rate $k_0 + k_1 S^n$ is also constant. At equilibrium,
\[
\frac{dL}{dt} = 0
\]

and

\[
L = \frac{k_2p}{(k_0 + k_1S^n)}
\]

By letting \( L = L_0 \) when \( S = 0 \), we see that

\[
\frac{L}{L_0} = \frac{k_0}{k_0 + k_1S^n} = \frac{1}{1 + aS^n}
\]

where \( a = k_1/k_0 \). This is the relationship between \( L \) and \( S \) for equilibrium conditions. Still needed is a relationship between \( L \) and \( \mu \). Cross used an expression developed by Bueche (34) in developing the equation

\[
\mu = \mu_\infty + DL
\]

where \( D \) is a constant. When \( \mu = \mu_\infty \), \( L = L_0 \). Therefore

\[
\mu_\infty - \mu_\infty = DL_0
\]

Thus

\[
\frac{\mu - \mu_\infty}{\mu_\infty - \mu_\infty} = \frac{L}{L_0}
\]

This is the required relationship between \( \mu \) and \( L \). It is identical to Denny and Brodkey's \( F \) and Krieger and Dougherty's \( \bar{n}_2 / \bar{n}_2 \). By combining the equations relating \( L \) to \( S \) and \( \mu \), the equation
\[ \mu = \mu_\infty + \frac{\mu_0 - \mu_\infty}{1 + aS^n} \]

is obtained. According to Cross, this equation should be applicable to all equilibrium viscosity data on pseudoplastic liquids. Cross applied his equation to several fluid systems with the data covering a range of shear rates of between 3 and 4 decades. Equation 43 allowed an excellent match of the data in all cases. Although his equations appear well suited for the attempt, Cross made no attempt to relate thixotropic behavior in his fluids to equilibrium flow curves.

Summary of literature on rate theories

Each of the theories discussed here is similar to all of the others in two respects. The first common element is the assumption of the occurrence of a rate process consisting of the breaking and reforming of some kind of bond between particles or molecules in the liquid. The second common element is the designation of a relationship between the number of existing bonds and the viscosity of the liquid. Since the type of reaction actually occurring was unknown, the various theorists used simple combinations of forward and reverse reactions in their rate equations and fairly simple equations to relate viscosity to the number of bonds present. The agreement between theory and experimental results was encouraging in every case.
inasmuch as equilibrium curves could be described with the equilibrium equations developed from the rate theories. However, with the single exception of Denny and Brodkey (1,2), no serious efforts were made to use data on the rate of change of viscosity with time to check the validity of the rate theories.
III.

THEORY

A number of rate theories proposed by various authors were presented in the literature section. In this section they are analyzed in terms of the relationships they imply between thixotropy, structure, and equilibrium. The order of presentation is the same as in the literature section. A more extended analysis of the works of Denny, Kim, and Brodkey (1, 2, 3, 4, 5) was made because of the relationship between their work and ours. This is presented at the end of the section.

Analysis of Rate Theories

Goodeve

The equations of interest to us in Goodeve's theory (28) are the relationship between viscosity and $n$, given by

$$\tau = \mu_\infty S + \frac{1}{2} n z f_c$$

and the rate equation

$$\frac{dn}{dt} = -\frac{nHzS}{f_c} + k''(2n_o - 2n)^2 S$$

In these equations $\mu_\infty$, $z$, $f_c$, $H$, $n_o$, and $k''$ are constants.

At equilibrium, $n$ is independent of shear rate and
\[ \tau = \mu_\infty S + \tau_0 \quad \text{(6)} \]

indicating that at equilibrium there is only one yield value. Also, at high shear rates, as \( n \) approaches 0, viscosity tends toward an upper Newtonian viscosity, \( \mu_\infty \).

From Equation 44 it is apparent that for a given pair of values of \( \tau \) and \( S \),
\[ \frac{\tau}{S} = \mu = \mu_\infty + \frac{\eta z f C}{2S} \]

and \( n \) is set at one value. If \( n \) and \( S \) are set, from Equation 8, \( \frac{dn}{dt} \) has a single possible value. From Equation 44 it follows that \( \frac{du}{dt} \) also has only one possible value. However, at a given value of \( n \), \( \mu \) does vary with \( S \).

Gillespie

Gillespie's (12) equilibrium equation is
\[ \tau = \mu_\infty S + \frac{E_A N^2 (K_0 + K_1 S) S}{2(B_0 / B_1 + S)^2} = \mu_\infty S + \theta \quad \text{(11)} \]

By inspection it is apparent that as \( S \) approaches 0, \( \mu \) approaches a constant, and that as \( S \) approaches \( \infty \), \( \mu \) approaches \( \mu_\infty \). Thus, at low shear rates a lower Newtonian viscosity is postulated while at high shear rates the equation is similar to Goodeve's equilibrium equation which allows for the existence of an upper Newtonian viscosity. No allowance is made for a yield value.
To make the point we wish to make concerning the rate equation, it is necessary to examine Gillespie's analysis in more detail.

From his paper,

\[
\theta = \frac{C_2 S n_c}{B} \quad (45)
\]

where \( C_2 \) is constant for a given fluid and \( n_c \) is the number of links per cc. \( n_c \) is related to \( \gamma \) by the relation \( n_c = N\gamma \). Since

\[
\tau = \mu_\infty S + \theta = \mu_\infty S + \frac{C_2 S n_c}{B} \quad (46)
\]

the apparent viscosity is given by

\[
\mu = \frac{\tau}{S} = \mu_\infty + \frac{C_2 n_c}{B} \quad (47)
\]

Thus, at a given apparent viscosity and shear rate, the number of links, \( n_c \), is the same in all cases and does not depend on history. Since \( K \) and \( B \) are presumably functions of shear rate, temperature, and concentration only, and since \( N \) is constant if the concentration is constant, from the rate equation

\[
\frac{dv}{dt} = KN - B\gamma \quad (9)
\]

it follows that if shear rate, concentration, temperature, and viscosity are the same for any two cases, the rate of change of viscosity with time will also be the same. As in Goodeve's theory, at a set value of \( \gamma \) or \( n_c \), \( \mu \) varies with \( S \).
Storey and Merrill

The equation of Storey and Merrill (29) which relates viscosity to the number of existing bonds is

\[ \mu = \alpha n + \mu_\infty \]  

Their rate equation is

\[ \frac{dn}{dt} = -k_1 nS + k_2 (n_0 - n) \]  

At equilibrium

\[ n = n_0 / (1 + \frac{k_1}{k_2} S) \]  

Then

\[ \frac{T}{S} = \mu = \frac{\alpha n_0}{1 + \frac{k_1}{k_2} S} + \mu_\infty \]  

As \( S \) approaches \( \infty \), \( \mu \) approaches \( \mu_\infty \), an upper Newtonian viscosity, and as \( S \) approaches \( 0 \), \( \mu \) approaches \( \alpha n_0 + \mu_\infty \). When shearing action is initiated, and the structure is entirely built up,

\[ \mu = \alpha n_0 + \mu_\infty = \mu_\infty \]  

the maximum possible viscosity of the liquid at the existing environmental conditions. These equations do not allow for a yield value, either initially or when the liquid is at equilibrium.

In the Storey and Merrill approach, when \( n \) is a given value, \( \mu \) cannot vary. When \( n \) and \( S \) are set values, \( \frac{dn}{dt} \) cannot vary. Therefore,
once again, the possibility of different rates of change of viscosity with time at the same $n$, $S$, and $\tau$ values is denied.

**Krieger and Dougherty**

In Krieger and Dougherty's (30) equation,

$$\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = (1 + \frac{1}{\tau/\tau_c})^{-1}$$

as $\tau$ approaches 0, $\mu$ approaches $\mu_0$, and as $\tau$ approaches $\infty$, $\mu$ approaches $\mu_\infty$. This is to be expected since they used these boundary conditions in developing the equations. This equation applies either for equilibrium or non-equilibrium conditions. At constant concentrations, $n$, the total concentration of spheres, is constant and

$$n = n_1 + 2n_2$$

Their equation relating these terms to viscosity,

$$\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = \frac{n_2}{n_2}$$

says that at a given viscosity, $n_2$ and $n_1$ can each have only one value. Therefore, at a given association level, the fluid is Newtonian.

In their rate equation,

$$\frac{dn_2}{dt} = k_f n_1^2 - (k_b + k_s) n_2$$
at any given \( \mu \), since \( n_2 \) and \( n_1 \) are set, \( \frac{dn_2}{dt} \) has only one possible value and therefore \( \frac{d\mu}{dt} \) has only one possible value. Once again, at a given viscosity and shear rate, only one rate of change of viscosity with time is allowed.

Worrall and Tuliani

The approach of Worrall and Tuliani (23) provides an interesting equilibrium curve represented by the equation

\[
\tau = \mu_{op} S + \tau_o + \frac{gbS}{aS + b}
\]

By inspection, when \( S = 0 \), \( \tau = \tau_o \), the yield value, which therefore is always the same when the liquid is at equilibrium. When \( S \) becomes large, the equation reduces to

\[
\tau = \mu_{op} S + \tau_o + \frac{gb}{a}
\]

which is equivalent to the equation describing a Bingham plastic since \( \mu_{op} \) is a point viscosity. Although they don't mention it, as \( S \) becomes small, the equation reduces to another straight line,

\[
\tau = S (\mu_{op} + g) + \tau_o
\]

They probably neglect this range because of the difficulty of obtaining data in this region of the curve.

Their other two equations which are of interest to us are the rate equation,
\[ \frac{d\lambda}{dt} = b(\lambda_0 - \lambda) - aS\lambda \]

and the equation relating viscosity to \( \gamma \),

\[ \tau = \mu_{op}S + \tau_0 + hS\lambda \]

The latter can be rewritten

\[ \frac{\tau}{S} = \mu = \frac{\mu_{op}}{S} + \frac{\tau_0}{S} + h\lambda \]

This equation allows \( \mu \) to vary at a single value of \( \lambda \). However, if \( \mu \) and \( S \) are set, \( \lambda \) has a single value. If \( \lambda \) and \( S \) are set, \( \frac{d\lambda}{dt} \) has a single possible value and consequently so does \( \frac{d\mu}{dt} \).

**Denny and Brodkey**

The Denny and Brodkey (1,2,3) effort is more ambitious than any of the other attempts to develop rate theories because these authors allow, and attempt to perform, an independent check on the values of the rate constants.

In the Denny and Brodkey approach, \( F \) can vary from 0 to 1. From their equation,

\[ F = \frac{\mu_{o.29} - \mu_{\infty.29}}{\mu_{o.29} - \mu_{\infty.29}} \]

it can be shown that as \( F \) approaches 0, \( \mu \) approaches \( \mu_{\infty} \), and \( S \) approaches \( \infty \). Also, as \( F \) approaches 1, \( \mu \) approaches \( \mu_{o} \), and \( S \) approaches 0. This allows for an equilibrium curve such as expected
for pseudoplastic liquids. Also, according to this equation, at any set structural level the fluid will exhibit Newtonian behavior.

From the equation for $F$ and their rate equation,

$$-\frac{dF}{dt} = k_1 \tau F^n - k_2 \tau (1 - F)^n \quad (33)$$

If $\mu$, $S$, and $F$ are set, $\tau$ has a single value and there is only one possible value of $-\frac{dF}{dt}$. From Equations 31 or 32 it is obvious that there is also only one possible value of $\frac{d\mu}{dt}$.

Cross

For our purposes the theory of Cross (33) can be represented by the rate equation

$$\frac{dL}{dt} = k_2 P - L \left( k_o + k_1 S^n \right) \quad (38)$$

the equilibrium equation

$$L = \frac{k_2 P}{k_o + k_1 S^n} \quad (39)$$

and the relationship between $L$ and $\mu$,

$$\frac{\mu - \mu_0}{\mu_o - \mu_\infty} = \frac{L}{L_o} \quad (42)$$

The latter equation indicates that at constant $L$, $\mu$ is constant. Equations 38 and 42, when combined, indicate that at given values of $\mu$ and $S$ there is a single value of $L$, a single value of $\frac{dL}{dt}$, and therefore a single value of $\frac{d\mu}{dt}$. At equilibrium, as $S$ approaches
Analysis of the results of Denny and Kim

Denny and Kim were our immediate predecessors on this project and their works (2,5) have had a great deal of influence on our own efforts. For this reason it is both desirable and necessary for us to analyze and evaluate their results and conclusions.

Denny was primarily concerned with correlating the rates of viscosity decline, observed for his polymer melt at constant shear rates, with the equilibrium curve. Since the polymer was very viscous at the operating temperatures, the instrument response was slower than he desired, and much of his experimental effort was directed at minimizing response time. His solution to the problem was to use a fairly light torsion bar, which he prestressed so as to minimize the movement of the bar during torque rise and then stopped before allowing much total movement to take place. This procedure is described in detail by Denny (2). The curves obtained by him were similar to the one shown in Figure 5. This ingenious experimental procedure did limit the total movement of the torsion bar. Consequently, greatly improved instrument response was observed while the ability for taking fairly accurate measurements of the rate of decline of torque or viscosity at constant shear rates was maintained.

Unfortunately, Denny's experimental procedure masked a more
Figure 5. Transducer Core Deflection Versus Time - Movement Limited. (Adapted from Reference 2)
important problem, the occurrence of an elastic component in the polymer melt. The failure to account for this component throws some doubt on the validity of Denny's conclusions regarding the relationship between thixotropy and the equilibrium curve of his material. The magnitude of this problem is best illustrated by the curve shown in Figure 6, which was taken on the rheogoniometer with another sample of polymethylmethacrylate. For this experiment shear stress is directly proportional to transducer core displacement. In obtaining this curve the time required for instrument response was minimized by using the heaviest torsion bar available for the machine and a solid stainless steel lower platen holder. With this equipment in place, at the viscosity of this material, the calculated time required for the machine to allow the torsion bar to rotate 98% of the total expected amount is less than 0.5 seconds. Actual response was checked as described in Appendix B. Therefore, for practical purposes, the data are free of instrument problems. The resulting curve is a typical illustration of viscoelastic response. A comparison of this curve with that of Denny shows immediately that his curve would have the same characteristics if he had not prestressed the bar and stopped its movement as he did. The early portion, A, in his curve (see Figure 5), corresponding to A' in Figure 6, is due to the relaxing of his prestressing bar as force is removed from it by the application of torque through the melt to the torsion bar. The free movement of the torsion bar, B, corresponding to B', occurs as the
Figure 6. Transducer Core Deflection - Movement Unlimited.
bar travels freely during the time when no contact is made with either the prestressing bar or the stop. Part C, corresponding to C', shows the truncation of the stress curve when the torsion bar is stopped. D, corresponding to D', shows free movement of the bar as torque becomes lower than that at the stopping point. The point we wish to make is that the torque versus time curve is essentially the same for both cases. The only difference is that Denny did not measure the entire curve. From this comparison it is apparent that Denny's stress-time relationship was not what he believed it to be during early time periods.

However, stress-time curve misinterpretation notwithstanding, Denny did obtain close agreement between constants calculated from rate data and constants calculated from equilibrium data. However, it should be pointed out that the range of shear stresses covered for the rate data was small, $2.35 \times 10^6$ to $3.22 \times 10^6$ dynes/cm$^2$.

Another item worthy of note is that at low shear stresses Denny's predicted (theoretical) forward reaction rate is very low, and that the initial predicted forward reaction rate is the maximum which could be achieved. Therefore, the system should not approach equilibrium very rapidly. Denny did not report this to be the case, but instead found that thixotropic effects disappeared at lower shear rates. This can be demonstrated numerically at his data point; $\tau = 1.99 \times 10^5$ dynes/cm$^2$, $S = 4 \times 10^{-2}$ sec$^{-1}$, and $\mu = 4.99 \times 10^6$ poise. Using Equations 31 and 33 and his reported values of $k_1$, $m$, and $p_1$,
\[ F = \left( \frac{4.99}{5.82} \right)^{.29} = 0.952 \]

and initial rate is

\[ -\frac{dF}{dt} = (1.1 \times 10^{-20})(1.99 \times 10^5)^{2.96} = 8.45 \times 10^{-5} \]

When \( \frac{dF}{dt} \) is constant

\[ -\frac{dF}{dt} \times t = \Delta F \]

or

\[ -0.048 = (8.45 \times 10^{-5})t \]

and the time required to reach equilibrium at this shear level is 570 seconds, even at the highest possible rate of viscosity decline. In 285 seconds, \( F \) would be 0.976, and \( \mu/\mu_\infty \) would be 0.92, giving a viscosity of 5.45 \( \times 10^6 \) poise. Therefore, even after 285 seconds, the viscosity should still have to drop 8\% before reaching equilibrium if Denny's theory and results are correct. There was no evidence of such a long term effect in Denny's data. Since viscoelastic effects appear to last less than a minute at this shear rate, it doesn't appear probable that they would mask such a long term thixotropic effect, if it were present.

This analysis has left us with a dilemma. Denny's excellent agreement between theory and experimental results must be balanced against the knowledge that viscoelastic effects were overlooked and
that the theory predicts improbable results at low shear stresses. The simplest way to settle the question would be to isolate thixotropy from viscoelasticity and measure these effects separately.

In an attempt to observe thixotropy in polymer melts in the absence of viscoelastic effects, we obtain rough data on a number of polymer melts within 10°F to 50°F of their glass transition temperatures. In each case both thixotropic and viscoelastic effects increased as the temperature approached the glass transition region, and thixotropy in polymer melts was never found without also observing viscoelasticity. An obvious inference is that thixotropy and viscoelasticity are somehow related. From this we concluded that polymer melts are unsatisfactory for use in making thorough studies of thixotropic behavior.

Kim (5) was concerned primarily with the effects of concentration changes on the shape of equilibrium curves for his polymer solutions. Consequently, he did not look at the rates of change of viscosity at constant shear rate. However, some of his data do show thixotropic behavior and these data can be used to make a most important point concerning his rate equation.

Kim's rate equation is

\[ - \frac{d(FC)}{dt} = k_1 \tau^p_1 (CF)^m - k_2 \tau^p_2 [(1-F)C]^n \]  

where all terms are those of Denny (2) except for C, which is concentration on a gms/cc basis. The only change from Denny's rate equation
is the addition of $C$. For any given concentration, $C$ is constant, and

$$\frac{d(FC)}{dt} = C \frac{dF}{dt}$$

Also, if $m = 1$, as Kim and Denny reported, the forward reaction rate is

$$k_1^P_1C_F = Ck_1^P_1F$$

Therefore, initial rate of change of viscosity is given by

$$-\frac{dF}{dt} = k_1^P_1F$$

just as it was for the pure melt. Thus, for a given value of $F$, initial rates should be identical for all concentrations when $\tau$ is constant. As $\tau$ is lowered, equilibrium should once again be reached more slowly.

In Figures 7, 8, and 9, data from three experiments performed by Kim are shown. The characteristics of the polymer solutions used in these experiments are given in Table 1. For our purposes, it is

**TABLE 1**

**CHARACTERISTICS OF KIM'S POLYMER SOLUTIONS**

<table>
<thead>
<tr>
<th>Solution</th>
<th>Concentration (wt%)</th>
<th>Approximate lower Newtonian viscosity (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-4</td>
<td>38.5</td>
<td>$4 \times 10^4$</td>
</tr>
<tr>
<td>C-5</td>
<td>42.5</td>
<td>$2 \times 10^2$</td>
</tr>
<tr>
<td>C-7</td>
<td>47.4</td>
<td>$1 \times 10^6$</td>
</tr>
</tbody>
</table>
Figure 7. Thixotropic Behavior of Kim's C-4 Solution.
Figure 8. Thixotropic Behavior of Kim's C-5 Solution.
Figure 9. Thixotropic Behavior of Kim's C-7 Solution.
best to consider only the initial rate observed in these figures because this eliminates the problem of considering variable \( F \) values.

Shear stresses for the experiments with the C-4 and C-7 solutions were almost identical but shear stress for the experiment with the C-5 solution was slightly higher. However, according to the theory, this should increase the observed initial rate for the C-5 solution and consequently does not detract from our argument, which is that, according to Kim's theory, at equal shear stresses the initial rates of viscosity decline should be the same. From these figures, this is obviously not the case.

Judging by these data, thixotropy in the solutions might be related to shear rate and to concentration but any relationship with shear stress seems to be relatively unimportant. Apparently these data contradict Kim's rate equation if it is presumed that the same mechanism is responsible for both thixotropic behavior and non-Newtonian equilibrium effects. However, the effects of viscoelasticity noted in the data on the melt are undoubtedly also present here and may be of sufficient importance that the rate behavior is affected.

The plate, cone, torsion bar, and other equipment used to obtain these data were the same as described in Appendix B when cold glycerine was used in the determination of response. Therefore, at a viscosity of \( 10^5 \) poise, if the liquid were Newtonian, the system should respond fast enough to give the maximum reading in 0.5 seconds or less. Therefore, mechanical response was not a detrimental factor in these experiments.
IV.

EXPERIMENTAL PROCEDURES

Preparation of samples

After the decision was made to work with a thixotropic liquid which recovered viscosity slowly after shearing, a number of liquids were surveyed. The desired fluid characteristics were:

1. Easily measurable rate of change of viscosity with time while shearing at constant shear rate.

2. Fairly slow recovery of viscosity after shearing so that a structure curve could be obtained at each structural level.

3. Complete recovery of initial viscosity within a matter of hours upon standing.

4. Chemical and physical stability.

One liquid, approximately 2.75% colloidal "Baymal" in water, by weight, had many of the desired properties. "Baymal", manufactured by E. I. Dupont de Nemours & Co., is a powder consisting of clusters of minute particles of alumina. The surface of the particles is modified by adsorbed acetate ions which, according to the manufacturers, play an important role in the behavior and useful properties of "Baymal" suspensions. The chemical composition of the powder is given in Table 2.
TABLE 2
CHEMICAL COMPOSITION OF "BAYMAL"

<table>
<thead>
<tr>
<th>Component</th>
<th>Per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>AlOOH</td>
<td>83.1</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>9.8</td>
</tr>
<tr>
<td>SO$_4$</td>
<td>1.7</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>5.0</td>
</tr>
<tr>
<td>NH$_4$</td>
<td>0.2</td>
</tr>
<tr>
<td>Na</td>
<td>0.07</td>
</tr>
<tr>
<td>Fe</td>
<td>0.02</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Unfortunately, upon standing, a film invariably formed over the top of the sample, making determination of initial values impossible, and determination of viscosities at low shear rates nearly so, since the motion of the plate was too slow to prevent film formation. The film formation was apparently due to evaporation, which cannot be avoided while the machine is running because the air from the air bearing sweeps around the plate and cone. In order to avoid this problem, the "Baymal" was dispersed in propylene glycol instead of water. The reasoning was that the low vapor pressure of propylene glycol would prevent evaporation and film formation. The procedure for doing this was to mix 600 ml of a suspension of 2.75% "Baymal" in water with 600 ml of propylene glycol of greater than 99% purity and then boil off the water under vacuum at less than 50°C. The procedure facilitates sample preparation because "Baymal" can only be dispersed
in highly polar solvents. Even in propylene glycol it is difficult to obtain complete dispersion except in the manner described above.

Upon viscometrically testing this approximately 2.72% suspension of "Baymal" in propylene glycol, two undesirable characteristics were observed. First, the rates of fall-off and build-up of viscosity were too high, and second, the sample absorbed water from the atmosphere with an attendant drop in viscosity. The first problem was solved by doubling the amount of propylene glycol in the suspension, and the second was circumvented by allowing the entire suspension to "stabilize" by exposing it to the atmosphere for two days. This liquid was then placed in bottles and sealed with rubber stoppers.

The amount of water in the sample was determined by the Karl Fischer method for water determination (35). Since no interfering compounds were present, a direct titration was possible.

Two titrations were made, one with 1.0 ml of sample and one with 0.30 ml. The titration of the 1.0 ml sample indicated 0.0236 ml of water was present in 1.0 ml of suspension. For the 0.30 ml sample, the titration gave 0.0245 ml water/ml of suspension. An average value of 0.0240 ml water/ml suspension is close enough for practical purposes.

The weight of solids in the sample was determined by weighing a known volume of the suspension and then heating it in an oven at 250°C to drive off the propylene glycol. The boiling point of
propylene glycol, 189°C, is high enough so that the acetic acid in "Baymal" will be lost at the same time. Therefore, the remaining solids represent only 85% of the original weight of "Baymal". For a 5 ml sample, the weight of the sample was 5.190 grams and the solids remaining weighed 0.060 grams. The original charge of "Baymal" therefore was 0.0705 grams and the weight per cent of "Baymal" in our suspension was 1.36%. By back calculation, the weight per cent of "Baymal" in the original 600 ml of "Baymal"-propylene glycol suspension was 2.72%. By adjusting for the difference in densities of water and propylene glycol, the weight per cent of "Baymal" in the "Baymal"-water suspension was calculated as being 2.75%.

Description of the rheogoniometer

The Weissenberg rheogoniometer was used to obtain all of our data. This instrument is basically a rotational viscometer with plate and cone or couette capabilities. Only the major elements are discussed here. A complete description is given in references 2, 5, 9, and 37, and the reader is referred to these for detail.

The Weissenberg rheogoniometer consists of three major parts. These are a drive unit, a measuring head, and the recording system. The drive unit and measuring head are shown in Figure 10. The drive unit consists of a 1/2 horsepower synchronous motor and a gear box with 60 output speeds ranging from $5.68 \times 10^{-4}$ to $4.50 \times 10^{2}$ rpm. The measuring head consists of the measuring faces, base, air bearing,
Figure 10. Weissenberg Rheogoniometer. (Adapted from Reference 5)
torsion rod and torque sensor, and a constant temperature chamber. A special feature of the measuring head is the use of an air bearing to minimize frictional effects. Torsion bars are supplied in a range of diameters. The clamp at the lower end of the torsion bar carries a 3.5 inch radius arm. At the outer end of this is the armature of the torsion head transducer. Another transducer, which is used to measure the gap between the top and bottom plates, is mounted on the column. Plates and cones, couette cylinders, and Mooney cups are supplied in a number of different diameters, sizes, and cone angles. These, coupled with the different torsion bars, provide the capability to measure a wide range of stress versus shear rate. The recording instruments consist of transducer meters, filter, and recorder. The transducer meter has six different sensitivity ranges, which vary from $0.25 \times 10^{-3}$ to $100 \times 10^{-3}$ inches of deflection at full scale. An Offner type 461 R.S. Dynograph is used to record the output.

Experimental procedure

All of the measurements on "Baymal" suspensions were taken using the 10 cm 1° Mooney cup. The reasons for using this cup were the need to obtain considerable deflection of the torsion bar during measurements, the relatively non-viscous nature of the liquid samples which required some sort of reservoir holding device, the desire to cut the amount of surface area exposed to air to a minimum, and the desire to eliminate the need for correcting every torque value because
of use of a large cone angle. For measurements on the "Baymal"-propylene glycol system the 1/8 inch torsion bar was used, and the 1/16 inch bar was used for the less viscous "Baymal"-water system. The choice of torsion bars was dictated by the need for both fast response and a reasonable amount of deflection when stepping down to lower shear rates to obtain structure curves.

The measurements on polymethyl methacrylate melts and solutions were taken with a plate and cone and heavier torsion bars.

The data taking procedures used in each experiment are described in the results section. In general, the data were taken over the broadest possible range of shear rates, with enough intermediate points to allow reasonable interpolation between them. The lowest available shear rate with the Mooney cup we were using is \(35.25 \times 10^{-4}\) sec\(^{-1}\) and this shear rate was used when practical. The highest shear rate used was 1762.0 sec\(^{-1}\). Theoretically, the equipment is capable of slightly higher values. However, it is very hard on the equipment to operate it above this shear rate and this was not done.

In order to record the results obtained when stepping down to lower speeds from equilibrium at high shear rates, it was necessary to amplify the output signal using the equipment available with the measuring system. Within our ability to read the chart, amplified signals agreed with unamplified ones. However, as the amount of amplification is increased, the noise level eventually increases to the point where the signal is unreadable. An amplification of 40 times
the signal on the lowest transducer range was arbitrarily chosen as the cut-off point. Consequently, for step-downs from equilibrium at high shear rates, the minimum shear rate reached was 8.81x10^{-2} \text{sec}^{-1}.

In step-downs from equilibrium at lower shear rates, lower minimum shear rates were reached.

**Calculation procedures**

**Plate and cone.** Calculation procedures for the plate and cone are well known (2, 36, 37). The equations are summarized below:

\[
\tau = \frac{3kT\Delta T}{2\pi R^3} \tag{55}
\]

\[
S = \frac{\pi (\text{rpm})}{30 \sin \theta} \tag{56}
\]

\[
\mu = \frac{\tau}{S} \tag{57}
\]

where \(k_T\) = the torsion constant of the torsion bar in dyne-cm per milli-inch of transducer core deflection

\(\Delta T\) = the transducer core deflection in milli-inches

\(R\) = radius of the cone

\(\theta\) = angle between the plate and cone

**Mooney cup.** The Mooney Cup is a combination plate and cone and Couette cylinder designed to allow accurate measurements on slightly viscous materials. Reference 37 describes its use in detail. Calculations are made by determining an equivalent plate
and cone. The torque produced by a Couette cylinder is \( \frac{6h}{d} \) times that produced by a plate and cone at the same diameter, \( d \). \( h \) is the elevation of the Couette cylinder. Thus, for the combined system (Mooney),

\[
\text{total torque} = T \left(1 + \frac{6h}{d}\right)
\]  

where \( T \) = torque of the equivalent plate and cone.

The torque of the equivalent plate and cone is then

\[
T = \left(\text{total torque}\right) \times \frac{1}{1 + \frac{6h}{d}}
\]  

Thus, since \( \text{total torque} = k \Delta T \),

\[
T = \left(k \Delta T\right) \times \frac{1}{1 + \frac{6h}{d}}
\]

Shear rate is determined in the same manner as for the plate and cone.

Possible sources of error

There are numerous sources of possible errors in the measurements. These are:

1. Viscosity changes due to a change in the amount of water in the sample.
2. Reading errors.
4. Variations of shear rate with time at low shear rates.
5. Errors in taking slopes.
6. Viscosity changes due to temperature variation during testing.
7. Skin formation on "Baymal"-water suspension.
8. Shift of zero point on the highest sensitivity range.
10. Problems arising from operating at shear stresses below the yield value.

After it was first prepared, the "Baymal"-propylene glycol suspension was exposed to the atmosphere for a few days in hopes that the amount of water in it would stabilize so that no differences in viscosity readings would occur due to changes in water content. Since our concern was with the viscometric properties of the suspension rather than its composition, the actual composition was of no concern to us as long as it did not change. In practice, it was found that the water content of the suspension is a function of relative humidity. The rate of change of the water content is very slow, and the effect of the change is not noticeable over the period of one day, but the effect can be appreciable if the sample is exposed to the atmosphere for long periods of time. This was discovered by making duplicate experimental observations on both fresh samples and samples that had been exposed to the air for several days. Viscosity values of exposed samples were usually
lower, indicating that the sample had absorbed some water from the air. The problem was solved by a combination of procedures. The sample was isolated by placing a plastic bag around the entire measuring head. This eliminated all fresh air except that introduced through the air bearing during an experiment. The amount of air in the bag was small enough so that equilibrium could be established without noticeably affecting the viscometric results. After each experiment, the sample was sheared to equilibrium at a shear rate of $27.95 \text{ sec}^{-1}$. When a difference from the results obtained with a fresh sample could be observed the sample was changed.

Whenever data are recorded on chart paper and the values are read from these charts, reading errors of one or two per cent are normal. In these experiments, at shear stress levels of $2.0 \text{ dynes/cm}^2$ and lower, the signal was greatly amplified in order to obtain a reading. Although the amplification was linear, the noise level was also greatly magnified, and as a consequence reading errors were greater in these cases.

We were informed by W. E. Lewis (38) that shear rates cannot be maintained constant with the rheogoniometer at values below $8.81 \times 10^{-2} \text{ sec}^{-1}$ for our experimental procedure. This is probably due to very slow meshing of gear teeth at these low rotational speeds. The variation in shear rate is hardly noticeable at a shear rate of $8.81 \times 10^{-2} \text{ sec}^{-1}$ but is possibly as high as 50% at a shear rate of $35.25 \times 10^{-4} \text{ sec}^{-1}$. The effect of this variation on our data
is not as large as might be expected, since shear stress does not change greatly with shear rate at these very low values, except when stepping down to low shear rates from higher shear rates. Fortunately, not many of our readings were taken at these extremely low shear rates.

The errors in taking slopes occur both because of the difficulty in determining the straight line portion of the curves, and because of difficulties in recording and reading shear stress when shear stress changes rapidly with time.

The experimental data presented here were taken at temperatures between 28°C and 29°C. This was essentially room temperature. Some control was obtained by judicious use of fans, doors, windows, and the heating elements associated with the rheogoniometer. The variation of temperature introduces a variation of viscosity, particularly at high shear rates. If it is presumed that the suspension behaves almost like propylene glycol when the structure is completely broken down, the difference in viscosity between 28°C and 29°C should be about 3%. Our experimental observations on duplicate experiments indicate that the difference is slightly less than this. At shear rates of \(8.81 \times 10^{-1}\) sec\(^{-1}\) and lower and in the initial stress studies, we were unable to discern any differences due to minor temperature variations. From this we conclude that the liquid structure is affected very little by temperature changes in the temperature range of our experiments.
In some ways, "Baymal"-water suspensions are easier to work with than "Baymal"-propylene glycol suspensions. The rate of change of viscosity is lower at higher concentrations of "Baymal" in water than in propylene glycol and the non-Newtonian characteristics are more outstanding. Unfortunately, in order to allow the structure to rebuild, it is necessary to allow the suspension to sit for several days. We were totally unable to prevent evaporation of water from the sample during the rest period. When even a slight amount of evaporation occurs, a viscous film develops over the surface of the liquid. The large added resistance due to the film makes interpretation of any data impossible. It is possible to perform experiments on new samples which have not been exposed to the atmosphere before the experiment. A few of these are reported in the results section. The experimental procedure is to pour some sample, which has been previously prepared, aged, and kept in a closed bottle, into the cup and start shearing immediately. The liquid structure is partially broken down in the loading process. Therefore, the only meaningful experiments are those at high shear rates where the equilibrium structure is more broken down than the structure which is left after the loading process. Obviously, it is impossible to obtain initial stress values and initial rates. This problem is not present with the "Baymal"-propylene glycol suspension because the vapor pressure of propylene glycol is so low at room temperature that almost no evaporation takes place and no
film is formed.

When taking data at the highest sensitivity range of the transducer meter, $0.25 \times 10^{-3}$ inches deflection at full scale, the zero (base) level changes slightly from time to time, primarily as a result of changes in the room temperature. The magnitude of this variation can be as much as 5% of the full scale deflection at room temperatures and much greater at high temperatures. With the set of gear we used in obtaining the data for the "Baymal"-propylene glycol suspension, this represents a possible variation in shear stress of $0.5 \text{ dynes/cm}^2$. If not accounted for, this could be a source of considerable error in the stepdown experiments, since the readings in many cases are much lower than 1.0 dynes/cm$^2$. Fortunately, at high shear rates, the liquid structure is broken down to the point where shear stress falls almost immediately to zero when shearing action is halted. This gives a base level from which the readings are made. At lower shear rates, shear stress values are higher when step-downs are made, and the variation in shear stress due to base level variation is not as important. Nevertheless, at the end of each step-down sequence, the shear rate was stepped up and the base level was checked at that time and adjustments were made in the data to account for the change.

In addition to the problems discussed above, there are the normal problems associated with making duplicate measurements when using the rheogoniometer. These include adjustments of the
flatness of the plate and cone, the setting of the gap between the plate and cone, and the introduction of exactly the same amount of sample. Under normal conditions variations of up to 2% are common in readings of duplicate experiments when a new sample of a viscosity standard has been used in each case.

Discussion with Savins (39) leads us to believe that the equilibrium data taken and reported in Table 3, for shear rates of $27.95 \times 10^{-3}$ sec$^{-1}$ and lower, may be misleading due to incomplete breaking down of the solid structure. In these three experiments, after initial fracturing of the solid structure, the shear stress is constantly below the yield stress. Therefore, it appears to be possible that a portion of the solid structure may be unbroken and cling to either the plate or cone, making interpretation of this data impossible. This condition does not affect in the slightest the data obtained by stepping down from higher shear rates. Considering the facts that only four data points are affected by this situation, that there are other problems associated with obtaining data at these low shear rates, that the importance of our results is not altered by errors in this range of shear rates, that the data may be fairly accurate as it stands, and that there are no known methods for dealing with this problem, it was decided to leave the solution of this problem as a matter for future research.

Our estimate is that the accuracy of the experimental data is about $\pm 5\%$, except at shear rates of $27.95 \times 10^{-3}$ sec$^{-1}$ and lower,
where the possibility of error becomes progressively greater as the shear rate is lowered, as noted in the previous discussion. This estimate is supported by the duplicate experiments, which fell within this range whenever the sample was still good. The accuracy of the rate data is estimated to be on the order of ±15%, due to the problems associated with taking slopes and making accurate readings of rapidly changing values.

Normal force measurement developmental work

In addition to the experimental work required to obtain the data reported in the main body of this dissertation, an effort was made to develop a new normal force measuring device, specifically designed to allow measurement of transients of short duration. The immediate need for this device was later eliminated, but the project was carried on to a logical stopping point. The findings are reported in detail in Appendix A.

Determination of mechanical response

A problem that arose both in analyzing Denny's data and in measuring normal stresses was the need to know that the mechanical response of the measuring system was sufficiently fast so as to have negligible effect on the transient stress data. This problem was particularly acute in the normal stress work because there was no logical way to calculate the effects on response of the various
diaphragms. The solution to the problem consisted of finding a Newtonian liquid with a viscosity of $10^5$ poise. The details of this work are reported in Appendix B.
V.

RESULTS

In presenting and discussing the results, in all cases the symbol \( \tau \) is used for shear stress in dynes/cm\(^2\) and \( S \) is used for shear rate in sec\(^{-1}\). The ratio, \( \tau/S \), is therefore apparent viscosity, \( \mu \), in poise. The units are occasionally left out in discussion, but the above rules are always followed.

Results Associated with Equilibrium Conditions

Stepping up and down in shear rate from equilibrium

Figure 11 shows a typical sequence of the experimental procedure for obtaining step-down results. The sample was sheared at a shear rate of \( 8.81 \times 10^2 \) sec\(^{-1}\) until equilibrium was established (A). Then the shear rates were alternated as shown, first at \( 8.81 \times 10^2 \) sec\(^{-1}\) for equilibrium (A), then to the lower shear rate for the reading (B), then back to \( 8.81 \times 10^2 \) sec\(^{-1}\) to reestablish equilibrium (C), then to the next lower shear rate in the sequence (D), etc. Step-up results are obtained in a similar manner, except that only one step-up can be made in each experiment since the higher shear rate destroys the structure present at equilibrium. In Figure 11 it can be seen that there is a tendency to rebuild viscosity or "structure" rapidly at higher shear rates (B), and
Figure 11. Typical Step-down Sequence.
that the rebuilding rate lessens as shear rate is lowered (D).

In Tables 3 and 4 are given the shear stress and viscosity values thus obtained for a large number of experiments. The values of shear stress are plotted in Figure 12 versus the corresponding shear rates. We refer to the curves drawn through the points as "structure curves".

There are several items of importance to note in these data. First, at each structural level, as defined by the equilibrium viscosity, the liquid is non-Newtonian. The same non-Newtonian characteristics are exhibited at no two levels, except possibly at the two highest shear rates, $8.81 \times 10^2$ sec$^{-1}$ and $1.762 \times 10^3$ sec$^{-1}$.

Second, equilibrium stress levels are progressively lower at lower shear rates until shear rates of $8.81 \times 10^{-1}$ sec$^{-1}$ and $2.795 \times 10^{-1}$ sec$^{-1}$ are reached. Experiments at these two shear rates along with the shear rate $8.81 \times 10^{-2}$ sec$^{-1}$ were performed several times because the behavior in that region of shear appears anomalous. However, with fresh samples, the results are reproducible within our experimental measuring accuracy of $\pm 5\%$, and we concluded that the data are correct. Third, the liquid is progressively more non-Newtonian at lower shear rates. Fourth, while the curves in Figure 12 appear to tend toward a yield value in most cases, particularly at low equilibrium shear rates, the yield value apparently would not be the same for any two structural levels except at the highest shear rates, where the yield value is zero.
<table>
<thead>
<tr>
<th>Shear Rates to which Shear Rate was Changed (sec⁻¹)</th>
<th>Shear Rates at which Equilibrium was Attained (sec⁻¹)</th>
</tr>
</thead>
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<tr>
<td></td>
<td>3.525x10⁻³  8.81x10⁻³  2.795x10⁻²  8.81x10⁻²  2.795x10⁻¹  8.81x10⁻¹  2.795  8.81  2.795x10¹  8.81x10¹  2.795x10²  8.81x10²  1.762x10³</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)</td>
</tr>
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<td>3.525x10⁻³</td>
<td>E1.85⁵</td>
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<tr>
<td>8.81x10⁻³</td>
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</tr>
<tr>
<td>2.795x10⁻²</td>
<td></td>
</tr>
<tr>
<td>8.81x10⁻²</td>
<td></td>
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</tr>
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<td>2.795</td>
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</tr>
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<td>8.81</td>
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</tr>
<tr>
<td>2.795x10¹</td>
<td></td>
</tr>
<tr>
<td>8.81x10¹</td>
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</tr>
<tr>
<td>1.762x10³</td>
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</tr>
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</table>

⁵The tabulated values are shear stress, τ, in dynes/cm², for the indicated experiments.

⁶E denotes equilibrium values.
# TABLE 4

STEP-UP, STEP-DOWN, AND EQUILIBRIUM VISCOSITIES

<table>
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<tr>
<th>Shear Rates to which Shear Rate was Changed (sec⁻¹)</th>
<th>Shear Rates at which Equilibrium was Attained (sec⁻¹)</th>
</tr>
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<td>3.525 x 10⁻³</td>
<td>3.525 x 10⁻³ 8.81 x 10⁻³ 2.795 x 10⁻² 8.81 x 10⁻² 2.795 x 10⁻¹ 8.81 x 10⁻¹ 2.795 8.81 2.795 x 10¹ 8.81 x 10¹ 2.795 x 10² 8.81 x 10² 1.762 x 10³</td>
</tr>
<tr>
<td>(1)</td>
<td>(2)   (3) (4) (5) (6) (7) (8) (9) (10) (11) (12) (13) (14)</td>
</tr>
</tbody>
</table>

| 3.525 x 10⁻³                                    | E532⁹ |
| 8.81 x 10⁻³                                    | E307  |
| 2.795 x 10⁻²                                    | E277  |
| 8.81 x 10⁻²                                    | E153  |
| 2.795 x 10⁻¹                                    | E53.0  |
| 8.81 x 10⁻¹                                    | 32.1  |
| 2.795                                           | 18.0  |
| 8.81                                           | E2.65  |
| 2.795 x 10¹                                    | 4.33  |
| 8.81 x 10¹                                    | 4.19  |
| 2.795 x 10²                                    | 3.93  |
| 8.81 x 10²                                    | 3.0  |
| 1.762 x 10³                                    | E1.32  |
| 8.81 x 10³                                    | 0.985  |
| 2.795 x 10⁴                                    | 0.910  |
| 8.81 x 10⁴                                    | 0.665  |
| 1.762 x 10⁵                                    | 0.430  |

*The tabulated values are viscosity, μ, in poise, for the indicated experiments.

*E denotes equilibrium values.
Figure 12. Step-up, Step-down, Equilibrium, and Initial Shear Stresses.
Results Obtained from Rate Studies

Initial stress and viscosity values

These were obtained when the sample was sheared at a constant shear rate after allowing the sample to sit for eight hours or more after it had been sheared nearly to equilibrium at a shear rate of 27.95. Some results were obtained after allowing the sample to sit for lengths of time much greater than eight hours, but no differences were observed in the initial values which could be attributed to the longer durations of build-up. Some other results were obtained after allowing the material to build up from structural levels other than that represented by equilibrium at a shear rate of 27.95. Again, we were unable to discern any differences.

The initial values of $\tau$ and $\mu$ are given in Table 5 and the $\tau$ values are shown in Figure 12. Once again, non-Newtonian behavior is observed.

Viscosity decline at constant shear rates

To obtain these results, the sample was allowed to rest as described for obtaining initial values. After the rest period, the liquid was sheared at the chosen constant shear rate. Shear stress was recorded as a function of time, as measured from the occurrence of the peak value of shear stress, and these values, along with viscosities, are given in Table 6. No rate data were
TABLE 5
INITIAL STRESS AND VISCOSITY VALUES

<table>
<thead>
<tr>
<th>Shear Rate (sec⁻¹)</th>
<th>Initial Shear Stress (dynes/cm²)</th>
<th>Initial Viscosity (poise)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.525 x 10⁻³</td>
<td>11.0</td>
<td>3120.0</td>
</tr>
<tr>
<td>8.81 x 10⁻³</td>
<td>9.6</td>
<td>1100.0</td>
</tr>
<tr>
<td>2.795 x 10⁻²</td>
<td>16.8</td>
<td>600.0</td>
</tr>
<tr>
<td>8.81 x 10⁻²</td>
<td>21.5</td>
<td>244.0</td>
</tr>
<tr>
<td>2.795 x 10⁻¹</td>
<td>30.9</td>
<td>111.0</td>
</tr>
<tr>
<td>8.81 x 10⁻¹</td>
<td>40.5</td>
<td>45.0</td>
</tr>
<tr>
<td>2.795</td>
<td>71.0</td>
<td>25.4</td>
</tr>
<tr>
<td>8.81</td>
<td>91.2</td>
<td>10.35</td>
</tr>
<tr>
<td>2.795 x 10¹</td>
<td>128.0</td>
<td>4.55</td>
</tr>
<tr>
<td>8.81 x 10¹</td>
<td>190.0</td>
<td>2.16</td>
</tr>
<tr>
<td>2.795 x 10²</td>
<td>287.0</td>
<td>1.03</td>
</tr>
<tr>
<td>8.81 x 10²</td>
<td>605.0</td>
<td>0.688</td>
</tr>
<tr>
<td>$t$ (sec)</td>
<td>$\tau$ (dynes/cm²)</td>
<td>$\mu$ (poise)</td>
</tr>
<tr>
<td>----------</td>
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<td>-------------</td>
</tr>
<tr>
<td>(S = 8.81 \times 10^2 \text{ sec}^{-1})</td>
<td>(S = 2.795 \times 10^1 \text{ sec}^{-1})</td>
<td>(S = 8.81 \text{ sec}^{-1})</td>
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<td>0.0</td>
<td>605</td>
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TABLE 6--Continued

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</tbody>
</table>
taken at the shear rate $1.762 \times 10^3$, and the rate was not monitored long enough at the shear rate $3.525 \times 10^{-3}$ to measure the portion of the curve not affected by viscoelasticity.

In Figures 13, 14, 15, and 16, viscosity is plotted versus log time, as is suggested in the literature (9). Occasionally the first point or two on a curve is low due to viscoelastic effects or slow instrument response. After discarding these points, it is apparent that viscosity varies linearly with log time until viscosity approaches equilibrium viscosity. As viscosity approaches the equilibrium value the linearity disappears. The slopes during the linear portion of the curve were measured and these were plotted versus $1/S$ on log-log paper, since it was apparent that there was a simple relationship between slope and the reciprocal of the shear rate. This plot gave a straight line, as shown in Figure 17, from which the expression

$$\frac{d\mu}{d\log(t)} = \frac{10.95}{S^{2/3}}$$

or

$$\frac{d\mu}{dt} = \frac{4.76}{ts^{2/3}}$$

was obtained. All of these data, and the agreement between $\frac{d\mu}{d\log(t)}$ values calculated by Equation 61 and the experimental values, are given in Table 7.
Figure 13. Viscosity Decline at Constant Shear Rates.
Figure 14. Viscosity Decline at Constant Shear Rates.
Figure 15. Viscosity Decline at Constant Shear Rates.
Figure 16. Viscosity Decline at Constant Shear Rates.
Figure 17. Relationship of Viscosity Decline to Shear Rate.
TABLE 7
COMPARISON OF ACTUAL AND CALCULATED SLOPES

<table>
<thead>
<tr>
<th>$S$</th>
<th>Slope $\frac{d\mu}{d\log(t)}$</th>
<th>$\frac{1}{S}$</th>
<th>Slope Calculated by $\frac{10.95}{S^{2/3}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$8.81 \times 10^{-3}$</td>
<td>270/cycle</td>
<td>113.5</td>
<td>260.0/cycle</td>
</tr>
<tr>
<td>$2.795 \times 10^{-2}$</td>
<td>110</td>
<td>35.8</td>
<td>130.0</td>
</tr>
<tr>
<td>$8.81 \times 10^{-2}$</td>
<td>55</td>
<td>11.35</td>
<td>58.0</td>
</tr>
<tr>
<td>$2.795 \times 10^{-1}$</td>
<td>25</td>
<td>3.58</td>
<td>26.5</td>
</tr>
<tr>
<td>$8.81 \times 10^{-1}$</td>
<td>11</td>
<td>1.135</td>
<td>12.0</td>
</tr>
<tr>
<td>$2.795$</td>
<td>7</td>
<td>0.358</td>
<td>5.60</td>
</tr>
<tr>
<td>$8.81$</td>
<td>2.6</td>
<td>0.1135</td>
<td>2.60</td>
</tr>
<tr>
<td>$2.795 \times 10^{1}$</td>
<td>1.35</td>
<td>0.0358</td>
<td>1.20</td>
</tr>
<tr>
<td>$8.81 \times 10^{1}$</td>
<td>0.6</td>
<td>0.01135</td>
<td>0.54</td>
</tr>
<tr>
<td>$2.795 \times 10^{2}$</td>
<td>0.18</td>
<td>0.00358</td>
<td>0.240</td>
</tr>
<tr>
<td>$8.81 \times 10^{2}$</td>
<td>0.08</td>
<td>0.001135</td>
<td>0.137</td>
</tr>
</tbody>
</table>
Time from clutch engagement to peak shear stress

These were obtained from the same experiments used to obtain the data given in Table 6. At high shear rates the peak shear stress was obtained after approximately 0.06 seconds. This is apparently the response time of the rheogoniometer with the particular Mooney cup and torsion bar we were using. At a shear rate of 8.81 the time required changed to 0.16 seconds and after that it increased each time the shear rate was lowered. The data are given in Table 8.

TABLE 8

<table>
<thead>
<tr>
<th>S (sec⁻¹)</th>
<th>t (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.762 x 10³</td>
<td>0.06</td>
</tr>
<tr>
<td>8.81 x 10²</td>
<td>0.06</td>
</tr>
<tr>
<td>2.795 x 10²</td>
<td>0.06</td>
</tr>
<tr>
<td>8.81 x 10¹</td>
<td>0.06</td>
</tr>
<tr>
<td>2.795 x 10¹</td>
<td>0.06</td>
</tr>
<tr>
<td>8.81 x 10⁰</td>
<td>0.16</td>
</tr>
<tr>
<td>2.795 x 10⁻¹</td>
<td>0.32</td>
</tr>
<tr>
<td>8.81 x 10⁻¹</td>
<td>1.0</td>
</tr>
<tr>
<td>2.795 x 10⁻¹</td>
<td>3.5</td>
</tr>
<tr>
<td>8.81 x 10⁻²</td>
<td>7.0</td>
</tr>
<tr>
<td>2.795 x 10⁻²</td>
<td>16.0</td>
</tr>
<tr>
<td>8.81 x 10⁻³</td>
<td>50.0</td>
</tr>
<tr>
<td>3.525 x 10⁻³</td>
<td>75.0</td>
</tr>
</tbody>
</table>
Rates of viscosity rise upon stepping down to lower shear rates

In obtaining the data given in Table 3, each time the shear rate was lowered, the viscosity of the liquid rose. Ultimately it reaches the equilibrium viscosity at the new shear rate. The rate at which the viscosities rose was measured, where possible or practical, and the results are given in Table 9.

Except at high shear rates there is considerable room for error in these values, since in each case the small difference between two large numbers is read from the chart, and, in many cases, high signal amplification was necessary.

To illustrate the use of Table 9, from equilibrium at a shear rate of $2.795 \times 10^1$, the shear rate was lowered to $8.81$, at which the rate of viscosity rise was 0.055 poise/sec.

Viscosity build-up at zero shear rate

The build-up of viscosity at zero shear rate (rest) was studied by shearing the liquid to equilibrium at shear rates of $8.81 \times 10^1$, $2.795$, and $8.81 \times 10^{-2}$, and then allowing the liquid to rest for various measured periods of time before resuming shear. Upon the resumption of shear, the maximum value of shear stress was measured. The following experiments were performed:

1. $S = 8.81 \times 10^1$ to $8.81 \times 10^1$
2. $S = 8.81 \times 10^1$ to $2.795$
TABLE 9  

RATES OF VISCOITY RISE UPON STEPPING DOWN TO LOWER SHEAR RATES

<table>
<thead>
<tr>
<th>Shear Rates to which Shear Rate was Lowered (sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Shear Rates at which Equilibrium was Attained (sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.81 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>8.81 x 10&lt;sup&gt;2&lt;/sup&gt; 2.795 x 10&lt;sup&gt;2&lt;/sup&gt; 8.81 x 10&lt;sup&gt;1&lt;/sup&gt; 2.795 x 10&lt;sup&gt;1&lt;/sup&gt; 8.81 2.795 8.81 x 10&lt;sup&gt;-1&lt;/sup&gt; 2.795 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>2.795 x 10&lt;sup&gt;2&lt;/sup&gt;</td>
<td>.004&lt;sup&gt;a&lt;/sup&gt; .00135 .0076</td>
</tr>
<tr>
<td>8.81 x 10&lt;sup&gt;1&lt;/sup&gt;</td>
<td>.0045 .0118</td>
</tr>
<tr>
<td>2.795 x 10&lt;sup&gt;1&lt;/sup&gt;</td>
<td>.0025 .0075 .055</td>
</tr>
<tr>
<td>8.81 x 10&lt;sup&gt;1&lt;/sup&gt;</td>
<td>.0117 .043 .100</td>
</tr>
<tr>
<td>2.795 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>.0086 .040 .062 .091</td>
</tr>
<tr>
<td>8.81 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>.025 .192 .174 .172</td>
</tr>
<tr>
<td>2.795 x 10&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>.454 .490 .550 .455</td>
</tr>
<tr>
<td>8.81 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>1.79 1.43 1.43</td>
</tr>
<tr>
<td>2.795 x 10&lt;sup&gt;-2&lt;/sup&gt;</td>
<td>5.60 4.55</td>
</tr>
<tr>
<td>8.81 x 10&lt;sup&gt;-3&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>The tabulated values are rates of viscosity rise in poises/sec.
An explanation of these is needed. For experiment 1, the liquid was sheared at the shear rate $8.81 \times 10^1$ until equilibrium was attained. Then the liquid was allowed to rest for one of the time intervals shown in Table 10, after which shearing action was resumed at the shear rate $8.81 \times 10^1$. The peak value was recorded. Shearing action was continued until equilibrium was attained once more. Then the liquid was allowed to rest once again, and the procedure was repeated for a different time interval. For experiment two, the liquid was sheared at the shear rate $8.81 \times 10^1$ until equilibrium was attained, then allowed to rest for a time interval, and then sheared, but at the shear rate $2.795$ instead of $8.81 \times 10^1$. The rest of the experiments were of a similar nature. In practice it was convenient to intermingle the experiments. For example, all three experiments where equilibrium was attained at the shear rate $8.81 \times 10^1$ and shearing action was resumed after approximately 60 seconds rest were performed in succession.

In Table 10, the rates of increase of shear stress with time for the various intervals are also given. These were calculated by dividing the difference in shear stress from the end of one interval to the end of the next by the difference in time from the end of one
### TABLE 10

**VISCOSITY BUILD-UP AT ZERO SHEAR**

<table>
<thead>
<tr>
<th>$t_r^a$ (sec)</th>
<th>$\tau$ (dynes/cm$^2$)</th>
<th>$d\tau/dt$ (dynes/cm$^2$/min)</th>
<th>$t_r$ (dyne cm$^{-2}$)</th>
<th>$d\tau/dt$ (dyne cm$^{-2}$/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S = 8.81 \times 10^1$ to $8.81 \times 10^1$</td>
<td></td>
<td></td>
<td>$S = 2.795$ to $2.795$</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>70.5</td>
<td>1.7</td>
<td>0</td>
<td>18.0</td>
</tr>
<tr>
<td>64 sec</td>
<td>72.2</td>
<td>1.7</td>
<td>62 sec</td>
<td>19.4</td>
</tr>
<tr>
<td>140 sec</td>
<td>74.0</td>
<td>1.35</td>
<td>120 sec</td>
<td>21.6</td>
</tr>
<tr>
<td>5 min</td>
<td>80.0</td>
<td>2.0</td>
<td>5 min</td>
<td>27.0</td>
</tr>
<tr>
<td>20 min</td>
<td>97.5</td>
<td>1.17</td>
<td>11 min</td>
<td>33.3</td>
</tr>
<tr>
<td>63 min</td>
<td>128.0</td>
<td>0.7</td>
<td>26 min</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>74 min</td>
<td>56</td>
</tr>
</tbody>
</table>

| $S = 8.81 \times 10^1$ to $8.81 \times 10^2$ | | | $S = 2.795$ to $8.81 \times 10^{-2}$ | |
| 0 | 2.86 | 0.16 | 0 | 3.69 |
| 67 sec | 3.02 | 0.16 | 61 sec | 4.21 | 0.56 |
| 150 sec | 3.36 | 0.23 | 122 sec | 5.21 | 1.0 |
| 7 min | 5.7 | 0.52 | 6 min | 8.4 | 0.80 |
| 20 min | 15.8 | 0.77 | 19 min | 13.75 | 0.415 |
| 59 min | 30.3 | 0.37 | 61 min | 19.5 | 0.14 |

| $S = 8.81 \times 10^1$ to $8.81 \times 10^{-2}$ | | | $S = 8.81 \times 10^{-2}$ to $8.81 \times 10^{-2}$ | |
| 0 | 0.100 | 0 | 0 | 13.5 |
| 80 sec | 0.117 | 0.013 | 32 sec | 14.8 | 2.5 |
| 155 sec | 0.143 | 0.021 | 80 sec | 15.4 | 0.75 |
| 7 min | 0.353 | 0.047 | 4 min | 16.1 | 0.26 |
| 21 min | 4.55 | 0.30 | 10 min | 17.5 | 0.23 |
| 60 min | 11.7 | 0.185 | 33 min | 20.8 | 0.145 |

$^a t_r$ is the duration of the rest period after reaching equilibrium.
interval to the end of the next. Thus, at \( t \) of 80 seconds for the

\[ S = 8.81 \times 10^{-2} \]

experiment, the rate given is shear stress at 80 seconds minus shear stress at 32 seconds, divided by

\( 48/60 \) minutes.

**Viscosity build-up while shearing**

In Figure 18 several plots of \( \tau_e - \tau \) versus log time for stress build-up while shearing are shown. \( \tau_e \) is equilibrium shear stress. These data were obtained by first shearing the liquid to near equilibrium at a shear rate of \( 2.795 \times 10^2 \) and then lowering the shear rate to successively lower values while observing the build-up for various lengths of time at each shear rate. If values obtained immediately after the shear rates were changed are neglected, the plots all approximate straight lines. The build-up rate is higher at higher shear rates. Obviously, plots of \( \mu_e - \mu \) versus log time would also be straight lines. At shear rates of \( 8.81 \times 10^{-1} \) and lower, the slopes of these curves would vary directly with shear rate since there is no appreciable variation of the slopes in the \( \tau_e - \tau \) versus log time plots.

**Unexpected rate behavior**

One phenomenon, which to our knowledge is previously unreported, was observed numerous times in various situations. The fact can be stated quite simply: For our material, rate of change
Figure 18. Stress Recovery while Shearing.
of viscosity at a given shear rate is not uniquely determined by viscosity. This will be illustrated in a number of ways. First, let us consider Figures 19, 20, and 21. Figure 19 shows a typical rate curve. This was obtained by changing to a shear rate of $8.81 \times 10^1$ from near equilibrium at a shear rate of $2.795$. This curve is nearly identical to the initial rate curve for the shear rate $8.81 \times 10^1$. Note the rate of decline when the chart speed is changed to 5 mm/sec at a reading of 30 mm, or a viscosity of 1.15 poise. Figures 20 and 21 show rates of viscosity decline at the same 30 mm reading, the same chart speed, and the same shear rate of $8.81 \times 10^1$. The rate of decline of viscosity is at least three times greater than in Figure 19 in both cases. The results shown in Figure 20 were obtained after shearing the liquid to equilibrium at the shear rate $8.81 \times 10^1$, allowing it to sit for 20 minutes, and then resuming the shearing action at the shear rate $8.81 \times 10^1$. To obtain the results shown in Figure 21, the liquid was sheared to equilibrium at the shear rate $8.81 \times 10^1$ and allowed to sit for 20 minutes. The liquid was then sheared at the shear rate 2.795 for approximately 20 seconds, and then the shear rate was raised to $8.81 \times 10^1$.

Figure 22 shows an even more enlightening example of this phenomenon. To obtain these results the liquid was sheared at the shear rate $2.795 \times 10^2$ and then the viscosity was allowed to build back up for a short time at a shear rate of 2.795. It was still far
Figure 19. Expected Viscosity Decline.
Figure 20. Unexpected Viscosity Decline.

Scale refers to transducer range.
G.B. refers to gear ratio.
Temp. = 29°C.
Figure 21. Unexpected Viscosity Decline.
Figure 22. Unexpected Rate Behavior.

Scale refers to transducer range.
G.B. refers to gear ratio.
Temp. = 28.7°C
Chart speed = 1 mm/sec.
from equilibrium at this shear rate. Then the shear rate was set at $2.795 \times 10^{-1}$ for a time, during which the viscosity rose by a factor of two. Then the shear rate was set once more at 2.795 with the resulting curve shown in Figure 22. It is apparent that structure built up at a lower shear rate is not necessarily stable at higher shear rates, even though the viscosity is lower than the equilibrium viscosity.

The "Baymal"-water system allows another example of rate variation at a given viscosity level. The sample was sheared at a shear rate of $2.795 \times 10^1$ until equilibrium was reached at a viscosity of 0.397 poise. When the shear rate was changed to $2.795 \times 10^2$, the shear stress was 66.7 and the rate of change of shear stress with time was 1.62 dynes/cm²/sec. Then a new sample was sheared at a shear rate of $2.795 \times 10^2$ until shear stress was 68.7, the idea being to try to match the shear stress obtained from the step-up from equilibrium at the shear rate of $2.795 \times 10^1$. The rate of change of shear stress with time at the shear stress of 68.7 was approximately 0.0133 dynes/cm²/sec. In this case the rate of change of viscosity varied by a factor of more than 100 at approximately the same viscosity level.

**Relation of rate variation to structure curves**

The discovery that rates of change of viscosity with time can vary at a single viscosity level and shear rate in two experiments
suggests the possibility that the structure is different and that the structure curves might be different in such cases. In Table 11 the results of several experiments performed to test this hypothesis are presented. Columns 2, 3, 4 and 5 are data for "Baymal"-water sheared to equilibrium as indicated in the figure. In columns 6 and 7 are given the results from shearing a "Baymal"-water sample at a shear rate of \(2.795 \times 10^2\) until the shear stress was 68.7, and the results from step-downs in shear rate from that point. The object was to try to stop the break-down of structure for the shear rate \(2.795 \times 10^2\) at the same shear stress that would be obtained by stepping up to a shear rate of \(2.795 \times 10^2\) from equilibrium at the shear rate \(2.795 \times 10^1\). Comparison of columns 5 and 7 shows that the structure curves are almost identical, although, as previously indicated, the rates of change of viscosity when the shear rate was \(2.795 \times 10^2\) was greatly different in the two cases. In columns 8 and 9 are given the results of the same experiments with the "Baymal"-propylene glycol system. Comparison of column 8 with column 10 of Table 3 shows that, once again, the structure curves are the same. However, in this case the rates of change of viscosity at the shear rate \(2.795 \times 10^2\) for the two experiments were approximately the same. In columns 10 and 11 are given the results of a truly non-equilibrium experiment, in the sense that not one value is at any of the studied equilibrium states. Comparison of column 10 with columns 8 and 9 of Table 3 shows that the shear stress
### TABLE 11

RELATION OF RATE VARIATIONS TO NON-NEWTONIAN BEHAVIOR

<table>
<thead>
<tr>
<th>S (sec⁻¹)</th>
<th>(\tau^a)</th>
<th>(\mu^b)</th>
<th>(\mu^c)</th>
<th>(\tau^d_A)</th>
<th>(\mu_A)</th>
<th>(\tau^e_B)</th>
<th>(\mu_B)</th>
<th>(\tau^e_C)</th>
<th>(\mu_C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.81 x 10⁻²</td>
<td>0.101</td>
<td>0.362</td>
<td>0.220</td>
<td>0.785</td>
<td>0.67</td>
<td>2.40</td>
<td>2.50</td>
<td>8.95</td>
<td></td>
</tr>
<tr>
<td>2.795 x 10⁻¹</td>
<td>0.292</td>
<td>0.332</td>
<td>0.605</td>
<td>0.685</td>
<td>0.615</td>
<td>1.70</td>
<td>1.93</td>
<td>6.7</td>
<td>7.62</td>
</tr>
<tr>
<td>8.81 x 10⁻¹</td>
<td>0.775</td>
<td>0.277</td>
<td>1.62</td>
<td>0.580</td>
<td>1.72</td>
<td>0.615</td>
<td>13.4</td>
<td>4.80</td>
<td></td>
</tr>
<tr>
<td>2.795</td>
<td>2.40</td>
<td>0.275</td>
<td>4.25</td>
<td>0.483</td>
<td>4.55</td>
<td>0.517</td>
<td>13.4</td>
<td>26.9</td>
<td>3.05</td>
</tr>
<tr>
<td>8.81 x 10¹</td>
<td>5.65</td>
<td>0.202</td>
<td>11.1</td>
<td>0.397</td>
<td>11.25</td>
<td>0.402</td>
<td>67.5</td>
<td>2.41</td>
<td></td>
</tr>
<tr>
<td>2.795 x 10¹</td>
<td>13.7</td>
<td>0.156</td>
<td>28.2</td>
<td>0.320</td>
<td>27.5</td>
<td>0.313</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.81 x 10¹</td>
<td>33.4</td>
<td>0.120</td>
<td>66.7</td>
<td>0.238</td>
<td>68.7</td>
<td>0.246</td>
<td>282</td>
<td>1.01</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\)Shear stress is in dynes/cm².

\(^{b}\)Viscosity in poise.

\(^{c}\)In \(\tau_A\) and \(\mu_A\) the subscript A indicates shear rate was maintained at \(2.795 \times 10^2\) until \(\tau = 68.7\).

\(^{d}\)Subscript B indicates shear rate maintained at \(2.795 \times 10^2\) until \(\tau = 255\).

\(^{e}\)Subscript C indicates shear rate maintained at \(2.795 \times 10^1\) until \(\tau = 67.5\).

\(^{f}\)B.W. refers to the "Baymal"-water suspension.

\(^{g}\)B.P.G. refers to the "Baymal"-propylene glycol suspension.

\(^{h}\)E denotes equilibrium values.
values all lie in the expected positions, somewhere between the
values of columns 8 and 9.

Analysis of the data using the Brodkey-Denny theory

Although it is recognized that the theory was not designed for
use with a liquid having a yield value, it is perhaps still useful
to use the theory of Denny and Brodkey (1,2) to analyze that portion
of our data obtained for structure levels where no yield value is
indicated and nearly Newtonian behavior is observed. The reason for
doing this is that this theory attempts to tie thixotropic behavior
to the equilibrium curve. It is therefore of value to see if the
theory applies to that portion of the data which fits the boundary
conditions required by the theory.

As given in the literature section, the Brodkey-Denny theory
can be described by two equations, the rate equation,

\[- \frac{dF}{dt} = k_1 \tau^{p_1} F^n - k_2 \tau^{p_2} (1-F)^n \quad (33)\]

and the equation defining \( F \),

\[ F = \frac{f(\mu) - f(\mu_\omega)}{f(\mu_0) - f(\mu_\omega)} \quad (26) \]

The equation for \( F \) used most extensively by Denny and Brodkey was
Equation 31 which was developed for polymers. This equation was
found unsuccessful for correlating our data. The more recently
reported Equation 32 shows more promise, and some results obtained
using this definition of $F$ are presented in the following pages.
The data used in this effort are those taken at shear rates of
27.95 and above, since non-Newtonian characteristics at a single
structure and yield values become excessive below this level.

At equilibrium

\[ k_1 \tau^p F^m - k_2 \tau^p (1-F)^n = 0 \]

and

\[ K \tau^p F^m = (1-F)^n \]

where $K = k_1/k_2$ and $p = p_1-p_2$. From previous work (2,3,5) it is
apparent that the combination of values $m = 1$ and $n = 2$ is the most
likely to correlate this data. Therefore the equilibrium equation
becomes

\[ K \tau^p F = (1-F)^2 \]

By plotting $\mu$ versus $\frac{1}{S}$ as shown in Figure 23, $\mu_\infty$ was determined to
be 0.400 poise. $\mu_0$ was chosen, somewhat arbitrarily, as 250 poise.
Using these values, Table 12 was developed. Log $\tau_e$ is plotted versus
log $(1-F)^2/F$ in Figure 24. The resulting line should have a slope
of $p$ and an intercept of $K$. Any number of lines can be drawn through
the points and the analysis is pursued further using the results from
two of these, curves A and B in Figure 24. Using curve A, the values
$p = 1.36$ and $K = 2.181$ are obtained. Curve B indicates that $p = 1.0$
and $K = 10.0$. These are nearly at the two possible extremes and
should bracket all possibilities for $p$ and $K$. 
Figure 23. Estimation of Upper Newtonian Viscosity.
Figure 24. Determination of $p$ and $K$. 

\[ \tau_e \text{ (dynes/cm}^2) \]

\[ \frac{(1-F)^2}{F} \]


TABLE 12
VALUES USED IN DETERMINING p AND K

<table>
<thead>
<tr>
<th>S (sec⁻¹)</th>
<th>τₑᵃ (dynes/cm²)</th>
<th>μₑᵇ (poise)</th>
<th>F</th>
<th>(1-F)²</th>
<th>(1-F)²/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.762 x 10³</td>
<td>760</td>
<td>0.430</td>
<td>0.00012</td>
<td>1.0</td>
<td>8.33 x 10³</td>
</tr>
<tr>
<td>8.81 x 10²</td>
<td>410</td>
<td>0.465</td>
<td>0.00026</td>
<td>1.0</td>
<td>3.85 x 10³</td>
</tr>
<tr>
<td>2.795 x 10²</td>
<td>155</td>
<td>0.555</td>
<td>0.00062</td>
<td>1.0</td>
<td>1.61 x 10³</td>
</tr>
<tr>
<td>8.81 x 10¹</td>
<td>69.5</td>
<td>0.79</td>
<td>0.00156</td>
<td>0.999</td>
<td>6.4 x 10²</td>
</tr>
<tr>
<td>2.795 x 10¹</td>
<td>36.9</td>
<td>1.32</td>
<td>0.00368</td>
<td>0.993</td>
<td>2.59 x 10²</td>
</tr>
</tbody>
</table>

ᵃτₑ is equilibrium shear stress.
ᵇμₑ is equilibrium viscosity.

The agreement between equilibrium curves calculated with these values of p and K and experimental data is shown in Figure 25. As might be expected, calculated and experimental curves match fairly well at high shear rates and poorly at low shear rates. Better agreement at low shear rates could be obtained by using different values for p and K, but this would be accomplished at the expense of agreement at high shear rates where the assumptions used in developing the equations more nearly fit the experimental facts.

With p and K determined, the rate data can be considered. The best possible data for analysis would appear to be that taken
Figure 25. Actual versus Calculated Equilibrium Curves.
when yield values and viscoelasticity are not present. For this reason initial rate data is not considered in the following analysis. The lack of usable initial rate data prevents a completely independent determination of $p_1$, $p_2$, $k_1$, and $k_2$. However, if the theory is valid for this liquid, all of the rate data should be consistent, and this requirement allows a valid check of the theory.

In order to analyze the type of data available, it is necessary to rewrite the rate equation. By substituting $p = p_1 - p_2$ and $K = k_1/k_2$ into Equation 33, the equation

$$- \frac{dF}{dt} = k_2 p^2 \left[ k^P F - (1-F)^2 \right]$$

is obtained. Since $(1-F)^2 \approx 1.0$, the equation can be rewritten

$$\log \frac{df}{dt} = p^2 \log \tau + \log \left[ k^P (1-K^P F) \right]$$

Thus

$$\log \left[ \frac{df}{dt} / (1-K^P F) \right] = p^2 \log \tau + \log k^P$$

and a log-log plot of $df/dt / (1-K^P F)$ versus $\tau$ should give a straight line with a slope of $p^2$ and an intercept of $k^P$.

Various data are available for use in testing the validity of this approach. The first used are rate data obtained when stepping up to a higher shear rate from equilibrium at a lower shear rate. Although no particular effort was made to obtain this data, some are available as a consequence of obtaining the data presented in Table 3. The data are processed using the equations given above.
and the results are given in Table 13. The results obtained using 
p = 1.0 and K = 10.0 are plotted in Figure 26. The results obtained 
using p = 1.36 and K = 2.181 are similar and are not plotted. In 
Table 13, data set A was obtained after stepping up from equilibrium 
at the shear rate 27.95 to the shear rate 8.81 x 10^2, data set B was 
obtained after stepping up from equilibrium at the shear rate 
8.81 x 10^1 to the shear rate 8.81 x 10^2, data set C was obtained 
after stepping up from equilibrium at the shear rate 2.795 x 10^2 
to the shear rate 8.81 x 10^2, and data set D was obtained after 
stepping up from equilibrium at the shear rate 27.95 to the shear 
rate 2.795 x 10^2.

Theoretically, all of the rate data should fall on the same 
straight line whether they are obtained during viscosity build-up 
after stepping down to lower shear rates, or during viscosity fall- 
off after stepping up to higher shear rates. The next data con- 
sidered are those obtained after stepping down from equilibrium at 
the shear rate 8.81 x 10^1 to the shear rate 27.95. The results are 
given in Table 14 and those obtained using p = 1.0 and K = 10.0 are 
plotted in Figure 26. In Table 14, the values of 10F_T exceed 1.0 
at the higher values of shear stress, and instead of calculating 
\( \frac{dF}{dt} / (1.0 - K \tau F) \), the values of \( \frac{dF}{dt} / (1.19 - K \tau F) \) were determined. 
The reason 10F_T exceeds 1.0 is because the equilibrium value at the 
shear rate 27.95 deviates from the curve drawn for p = 1.0 and 
K = 10.0. Therefore, as the shear stress approaches equilibrium,
TABLE 13
ANALYSIS OF RATE DATA OBTAINED BY STEPPING UP TO A HIGHER SHEAR RATE

<table>
<thead>
<tr>
<th>Data Set</th>
<th>( \tau ) (dynes/cm²)</th>
<th>( \frac{dF}{dt} )</th>
<th>2.18( \tau )^{1.36}</th>
<th>10( \tau ) (poise)</th>
<th>F</th>
<th>( \frac{dF}{dt} ) (1-( \tau )( \mu ))</th>
<th>( \frac{dF}{dt} ) (1-( \tau )( \mu ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>550</td>
<td>-0.00132</td>
<td>11200</td>
<td>5500</td>
<td>0.625</td>
<td>0.0009</td>
<td>10.1</td>
</tr>
<tr>
<td>A</td>
<td>510</td>
<td>-0.000907</td>
<td>10450</td>
<td>5100</td>
<td>0.580</td>
<td>0.00072</td>
<td>7.5</td>
</tr>
<tr>
<td>A</td>
<td>485</td>
<td>-0.0001135</td>
<td>9780</td>
<td>4850</td>
<td>0.550</td>
<td>0.00060</td>
<td>5.85</td>
</tr>
<tr>
<td>B</td>
<td>510</td>
<td>-7.56x10⁻⁴</td>
<td>10450</td>
<td>5100</td>
<td>0.580</td>
<td>0.00072</td>
<td>7.50</td>
</tr>
<tr>
<td>B</td>
<td>492</td>
<td>-5.0x10⁻⁴</td>
<td>10000</td>
<td>4920</td>
<td>0.558</td>
<td>0.000633</td>
<td>6.33</td>
</tr>
<tr>
<td>B</td>
<td>473</td>
<td>-1.54x10⁻⁴</td>
<td>8680</td>
<td>4730</td>
<td>0.537</td>
<td>0.000548</td>
<td>4.75</td>
</tr>
<tr>
<td>C</td>
<td>435</td>
<td>-3.4x10⁻⁴</td>
<td>8480</td>
<td>4350</td>
<td>0.494</td>
<td>0.000376</td>
<td>3.19</td>
</tr>
<tr>
<td>C</td>
<td>420</td>
<td>-1.68x10⁻⁴</td>
<td>7940</td>
<td>4200</td>
<td>0.477</td>
<td>0.000308</td>
<td>2.44</td>
</tr>
<tr>
<td>D</td>
<td>242</td>
<td>-1.5x10⁻³</td>
<td>3840</td>
<td>2420</td>
<td>0.865</td>
<td>0.00186</td>
<td>7.14</td>
</tr>
<tr>
<td>D</td>
<td>228</td>
<td>-1.25x10⁻³</td>
<td>3460</td>
<td>2280</td>
<td>0.815</td>
<td>0.00166</td>
<td>5.75</td>
</tr>
<tr>
<td>D</td>
<td>215</td>
<td>-0.56x10⁻³</td>
<td>3230</td>
<td>2150</td>
<td>0.770</td>
<td>0.00148</td>
<td>4.79</td>
</tr>
<tr>
<td>D</td>
<td>209</td>
<td>-0.288x10⁻³</td>
<td>3085</td>
<td>2090</td>
<td>0.747</td>
<td>0.00139</td>
<td>4.28</td>
</tr>
</tbody>
</table>
TABLE 14
ANALYSIS OF RATE DATA OBTAINED BY STEPPING DOWN TO LOWER SHEAR RATES

<table>
<thead>
<tr>
<th>( \tau ) (dynes/cm(^2))</th>
<th>( \frac{dF}{dt} )</th>
<th>( F )</th>
<th>( 2.181\tau^{1.36} )</th>
<th>( 10\tau )</th>
<th>( \frac{dF/dt}{(1-K\tau^pF)} )</th>
<th>( \frac{dF/dt}{(1.19-K\tau^pF)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.0</td>
<td>1.93x10^{-6}</td>
<td>0.00341</td>
<td>0.932</td>
<td>1.19</td>
<td>2.84x10^{-5}</td>
<td>-</td>
</tr>
<tr>
<td>33.5</td>
<td>4.37x10^{-6}</td>
<td>0.00322</td>
<td>0.832</td>
<td>1.07</td>
<td>2.60x10^{-5}</td>
<td>3.64x10^{-5}</td>
</tr>
<tr>
<td>32.2</td>
<td>5.3x10^{-6}</td>
<td>0.00303</td>
<td>0.733</td>
<td>0.965</td>
<td>1.99x10^{-5}</td>
<td>2.35x10^{-5}</td>
</tr>
<tr>
<td>30.9</td>
<td>6.43x10^{-6}</td>
<td>0.00282</td>
<td>0.657</td>
<td>0.870</td>
<td>1.87x10^{-5}</td>
<td>2.00x10^{-5}</td>
</tr>
<tr>
<td>29.5</td>
<td>8.47x10^{-6}</td>
<td>0.00262</td>
<td>0.568</td>
<td>0.773</td>
<td>1.95x10^{-5}</td>
<td>2.03x10^{-5}</td>
</tr>
<tr>
<td>28.2</td>
<td>1.26x10^{-5}</td>
<td>0.00244</td>
<td>0.503</td>
<td>0.688</td>
<td>2.54x10^{-5}</td>
<td>2.5x10^{-5}</td>
</tr>
<tr>
<td>26.8</td>
<td>1.49x10^{-5}</td>
<td>0.00224</td>
<td>0.410</td>
<td>0.600</td>
<td>2.53x10^{-5}</td>
<td>2.87x10^{-5}</td>
</tr>
<tr>
<td>25.5</td>
<td>1.865x10^{-5}</td>
<td>0.00205</td>
<td>0.368</td>
<td>0.522</td>
<td>2.95x10^{-5}</td>
<td>2.79x10^{-5}</td>
</tr>
<tr>
<td>24.1</td>
<td>1.95x10^{-5}</td>
<td>0.00185</td>
<td>0.306</td>
<td>0.436</td>
<td>2.81x10^{-5}</td>
<td>2.58x10^{-5}</td>
</tr>
<tr>
<td>22.8</td>
<td>1.995x10^{-5}</td>
<td>0.00166</td>
<td>0.255</td>
<td>0.378</td>
<td>2.68x10^{-5}</td>
<td>2.46x10^{-5}</td>
</tr>
</tbody>
</table>
Figure 26. Correlation of Rate Data.
the discrepancy in $K\tau^p$ occurs, and since the rate is a function of the difference between shear stress and equilibrium shear stress, the values of $\frac{dF}{dt} / (1.19 - K\tau^p)$ were used. This is approximately equivalent to redrawing the curve nearly through the equilibrium point at the shear rate 27.95. This problem is less severe for the data at higher shear rates since the theoretical curve is closer to the equilibrium points.

The last data that we wish to consider are those presented in Table 9 for shear rates of 27.95 and above. In this case, only one rate is available for each experiment, but the range of experiments makes these possibly the most important rate data available. The results are given in Table 15 and those obtained using $p = 1.0$ and $K = 10.0$ are plotted in Figure 26.
### Table 15

**Analysis of Rate Data Obtained by Stepping Down to Various Shear Rates**

<table>
<thead>
<tr>
<th>Data Point</th>
<th>τ (dynes/cm²)</th>
<th>μ (poise)</th>
<th>F</th>
<th>2.181F₁^{1.36}</th>
<th>10τF</th>
<th>( \frac{dF}{dt} ) (1-K^pF)</th>
<th>( \frac{dF}{dt} ) (1-K^pF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>134</td>
<td>0.481</td>
<td>0.000324</td>
<td>0.555</td>
<td>0.435</td>
<td>3.6x10^{-5}</td>
<td>2.83x10^{-5}</td>
</tr>
<tr>
<td>F</td>
<td>44.5</td>
<td>0.505</td>
<td>0.000420</td>
<td>0.163</td>
<td>0.187</td>
<td>0.645x10^{-5}</td>
<td>0.565x10^{-5}</td>
</tr>
<tr>
<td>G</td>
<td>49.6</td>
<td>0.563</td>
<td>0.000652</td>
<td>0.287</td>
<td>0.323</td>
<td>4.5x10^{-5}</td>
<td>4.72x10^{-5}</td>
</tr>
<tr>
<td>H</td>
<td>15.9</td>
<td>0.580</td>
<td>0.000720</td>
<td>0.068</td>
<td>0.114</td>
<td>1.93x10^{-5}</td>
<td>2.03x10^{-5}</td>
</tr>
<tr>
<td>I</td>
<td>23.3</td>
<td>0.833</td>
<td>0.00173</td>
<td>0.274</td>
<td>0.403</td>
<td>0.65x10^{-5}</td>
<td>0.79x10^{-5}</td>
</tr>
</tbody>
</table>
VI.

DISCUSSION OF RESULTS

Results Associated with Equilibrium Conditions

Step-up and step-down studies

The object of these studies was to determine the behavior of the liquid at various "structural" levels, with these levels being determined by shearing the liquid until equilibrium was established at the various shear rates. By choosing a liquid in which structure rebuilds slowly after shearing and by returning to the original shear rate and shearing until equilibrium was reestablished after each step-down, we have assured that, for all practical purposes, the data were obtained at set structural levels.

We are not aware of another complete study of this type, although, by accident more than design, a number of isolated down-curves have been reported which were probably obtained at a single structural level. Downcurves are obtained following the determination of upcurves by progressively lowering the shear rate in a stepwise manner and measuring the shear stress at each step until the lowest desired point on the downcurve is obtained. Therefore, the determination of a downcurve usually requires a minute or more, during which the structure may change. For a downcurve to represent
a single structural level, it is necessary that a stable structure be present at the end of the determination of the upcurve. This is not often the case because upcurves and downcurves are ordinarily obtained on liquids which show considerable variation of viscosity in short periods of time. Furthermore, in obtaining an upcurve, no attempt is made to attain equilibrium at the highest shear rate. Therefore, this point is difficult to define in terms of basic experimental procedures. For these reasons, structure curves are more useful than downcurves for defining relationships between structure and viscometric behavior.

The fact that the liquid at a set structural level is non-Newtonian has important theoretical implications. This can be considered as one of the boundary conditions that any theory must satisfy if it is to be useful in describing the rheological behavior of liquid systems such as the ones considered here.

The similarity of the structure curves obtained for equilibrium shear rates (shear rate at which equilibrium was attained) of $8.81 \times 10^2$ and $1.762 \times 10^3$ (see Figure 12) suggests that the liquid structure is almost completely broken down at equilibrium for both of these shear rates and that results obtained at all higher shear rates would be almost identical. The viscosity of propylene glycol at the operating temperatures is approximately 0.30 poise. Apparently the suspension is still non-Newtonian when the structure is completely broken down, but the viscosity tends toward an upper Newtonian
viscosity slightly above that of propylene glycol. Therefore, an acceptable phenomenological theory for our liquid would have to allow for an upper Newtonian viscosity.

At low shear rates, shearing apparently promotes formation of a stronger structure. This can be seen by looking at Table 3. The shear stress obtained upon stepping down to a lower shear rate from equilibrium at a higher shear rate normally is higher when the equilibrium shear rate is lower. For example consider the following data extracted from Table 3:

<table>
<thead>
<tr>
<th>Previous equilibrium shear rate (sec(^{-1}))</th>
<th>Shear stress (dynes/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.762x10(^3)</td>
<td>1.68</td>
</tr>
<tr>
<td>27.95</td>
<td>5.36</td>
</tr>
<tr>
<td>2.795</td>
<td>18.3 (equilibrium)</td>
</tr>
</tbody>
</table>

These data illustrate the expected behavior. They were obtained at a shear rate of 2.795 upon lowering the shear rate to that value from the stated equilibrium shear rates. Next consider the following data, also extracted from Table 3:

<table>
<thead>
<tr>
<th>Previous equilibrium shear rate (sec(^{-1}))</th>
<th>Shear stress (dynes/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.81x10(^{-1})</td>
<td>3.03</td>
</tr>
<tr>
<td>8.81x10(^{-2})</td>
<td>10.6</td>
</tr>
<tr>
<td>8.81x10(^{-3})</td>
<td>2.70 (equilibrium)</td>
</tr>
</tbody>
</table>

The above data were obtained at a shear rate of 8.81x10\(^{-3}\).
These were also obtained after stepping down from the given equilibrium shear rates. These data show a marked deviation from the expected behavior, indicating that a stronger structure was present at the two higher equilibrium shear rates.

Two more illustrations of this tendency are the facts that at shear rates of $8.81 \times 10^{-1}$ and $2.795 \times 10^{-1}$ the same equilibrium shear stress is observed, and that, upon stepping down to the shear rate $8.81 \times 10^{-3}$ from equilibrium at the shear rate $8.81 \times 10^{-2}$, a shear stress of 10.6 is observed, which is almost as high as the initial shear stress observed at the shear rate $8.81 \times 10^{-3}$. Another facet of this tendency is not apparent from any of the data presented here. At the shear rate $2.795 \times 10^{-2}$, when shearing was initiated, the shear stress decreased to a level lower than the shear stress at equilibrium and then rose to the equilibrium level gradually over a period of several hours.

The structure curves in Figure 12 show more deviation from Newtonian behavior at lower shear rates. This is particularly true for structure curves obtained after low equilibrium shear rates ($8.81$ and lower). This suggests that the curves tend toward yield values. If this is the case, the yield value is most certainly not the same for each curve. If true, this is another boundary condition that a rate theory applicable to ours or similar liquids must satisfy.
Results Obtained from Rate Studies

Initial stress studies

Theoretically, initial stress values also represent a single structural level, since the structure should be almost completely built up and at equilibrium after the liquid has rested eight hours. Once again non-Newtonian behavior is apparent. However, viscoelasticity and instrument response obscure these values to the point where no reliance can be placed on their representation of the viscosity of the liquid with the structure completely intact. The same thing is true of the step-up values given in Table 4. When the shear rate is stepped up to higher levels, be it from zero shear rate or from finite value, the effective shear rate while the instrument responds and during the period when viscoelastic behavior can be observed is unknown and in some portion of the liquid is higher than the preceding equilibrium shear rate.

Viscosity decline at constant shear rates

In reference 9 it was suggested that a plot of viscosity versus log(t) would give a straight line for thixotropic liquids. We found this to be true, except when the viscosity approaches the equilibrium value.

The fact that the rates of viscosity decline in the straight line portion of the curves are describable by a single equation is a
very intriguing result. If studies of other liquids of a similar nature should produce similar results, this relation should be studied as a possible clue to the mechanism of thixotropy.

**Time from clutch engagement to peak shear stress**

The time required to reach the peak shear stress (neglecting the data at high shear rates) is not quite linear with shear rate. However, it is close enough to it to allow us to point out that if a solid which obeys Hook's law was sheared between the plates, the shear stress would reach a peak value at times almost linear with shear rate. There is at least a similarity between the behavior of our liquid before the structure breaks and a solid obeying Hook's law.

**Rate of viscosity rise upon stepping down to lower shear rates**

While there is obviously much scatter in these data, several trends are apparent.

At high equilibrium shear rates (8.81x10², 2.795x10², and 2.795x10¹) the rate at which viscosity rises when the shear rate is stepped down to lower levels is highest when the level to which the shear rate is lowered is highest. This can be best illustrated
by the following data extracted from Table 9:

<table>
<thead>
<tr>
<th>Level to which shear rate was lowered and at which data were obtained (sec(^{-1}))</th>
<th>Rate of viscosity rise (poise/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8.81 \times 10^1)</td>
<td>0.0076</td>
</tr>
<tr>
<td>(2.795 \times 10^1)</td>
<td>0.0045</td>
</tr>
<tr>
<td>8.81</td>
<td>0.0025</td>
</tr>
</tbody>
</table>

The shear rate at which equilibrium was attained prior to these determinations was \(2.795 \times 10^2\). Next consider the following data, also extracted from Table 9:

<table>
<thead>
<tr>
<th>Level to which shear rate was lowered and at which data were obtained (sec(^{-1}))</th>
<th>Rate of viscosity rise (poise/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(8.81 \times 10^{-1})</td>
<td>0.091</td>
</tr>
<tr>
<td>(2.795 \times 10^{-1})</td>
<td>0.174</td>
</tr>
<tr>
<td>(8.81 \times 10^{-2})</td>
<td>0.490</td>
</tr>
<tr>
<td>(2.795 \times 10^{-2})</td>
<td>1.79</td>
</tr>
</tbody>
</table>

The shear rate at which equilibrium was attained prior to these observations was 2.795. Obviously, for low equilibrium shear rates the trend is reversed. A note of caution should be injected here. Remember that the liquid is highly non-Newtonian at low shear rates, and that an apparent rate of viscosity rise at one shear rate does not necessarily correspond to the same rate of viscosity rise at another shear rate.

Another highly significant trend in these data is the slower rate of viscosity rise when the liquid has been sheared at high shear
rates. For example, consider the following data extracted from Table 9:

<table>
<thead>
<tr>
<th>Previous equilibrium shear rate (sec(^{-1}))</th>
<th>Rate of viscosity rise (poise/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.795 \times 10^2</td>
<td>0.0025</td>
</tr>
<tr>
<td>2.81 \times 10^1</td>
<td>0.0075</td>
</tr>
<tr>
<td>2.795 \times 10^1</td>
<td>0.055</td>
</tr>
</tbody>
</table>

These data were obtained when the shear rate was stepped down to 8.81 after equilibrium was attained at the stated shear rates. The rate of viscosity rise was 22 times smaller when the liquid had been previously sheared to equilibrium at a shear rate of 2.795\times10^2 than it was when the previous equilibrium shear rate was 2.795\times10^1.

A third trend, which is not apparent from Table 9, is that when the liquid is sheared to equilibrium at a low shear rate, upon stepping down to lower shear rates, \(\frac{dT}{dt}\) appears to reach an almost constant value of approximately 0.045 dynes/cm\(^2\)/sec. In this case the rate of viscosity rise varies inversely with shear rate. This compares favorably with values for \(\frac{dT}{dt}\) of 0.01 to 0.04 dynes/cm\(^2\)/sec when the liquid viscosity builds up at rest.

**Viscosity build-up at zero shear rate**

In only one of these experiments, \(S = 8.81\times10^{-2}\) to \(S = 8.81\times10^{-2}\), did the rates of viscosity rise decrease uniformly
with time (see Table 10). In each of the other five experiments, the rates went through a maximum. Of particular interest are the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^1$, $S = 8.81 \times 10^1$ to $S = 2.795$, and $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^{-2}$ experiments. In these experiments it can be seen that shearing at high rates apparently either retards the build-up of structure at rest or breaks down the structure to the point where a period of time is required before it rebuilds enough to greatly affect viscosity measurements. The latter seems more likely, since the maximum rebuilding rate occurs at different (longer) times for the $S = 8.81 \times 10^1$ to $S = 2.795$, and $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^{-2}$ experiments than for the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^1$ experiment.

This brings up another point. It appears probable that structure which affects readings at a shear rate of $8.81 \times 10^{-2}$ has less effect on readings obtained at a shear rate of $8.81 \times 10^1$ and vice versa. This is shown by a comparison of $\frac{dT}{dt}$ observed at different shear rates for the same intervals of rest after the same equilibrium point. Supposedly, the amount of structure rebuilt in the interval from five or seven to twenty minutes should be about the same. However, the effect of this structural change on the change in shear stresses during the interval is much different in the three cases. If the comparison is made on the basis of the ratio of final to initial reading, then, for the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^1$ experiment, the ratio of the 20 minute reading to the 7 minute reading...
is approximately $\frac{97.5}{84.0} = 1.15$. The value, $\tau = 84.0$, at 7 minutes was obtained by extrapolating the rate during the prior interval for two more minutes. For the $S = 8.81 \times 10^1$ to $S = 2.795$ experiment the ratio is 2.78. For the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^{-2}$ experiment the ratio is approximately 12.0. Probably a better way to compare the readings is to divide the difference in readings during the interval by the difference between the minimum reading and the maximum possible reading (the initial value; see Table 5). Then, for the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^1$ experiment the ratio is $\frac{13.5}{190-70.5} = 0.113$, for the $S = 8.81 \times 10^1$ to $S = 2.795$ experiment the ratio is 0.148, and for the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^{-2}$ experiment the ratio is 0.181. If the comparison is made for the interval from 0 to 7 minutes, the difference is more striking. The ratios are then 0.126 for the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^1$ experiment, 0.042 for the $S = 8.81 \times 10^1$ to $S = 2.795$ experiment, and 0.012 for the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^{-2}$ experiment. In data from any of these experiments the errors can be large since in some cases the reading is a small difference between fairly large numbers. However, the trend suggested by the above ratios should be correct.

One other noteworthy comparison can be made using the $S = 8.81 \times 10^1$ to $S = 2.795$ and $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^1$ experiments. The value of shear stress after 59 minutes of rest for the $S = 8.81 \times 10^1$ to $S = 2.795$ experiment is 30.3. The corresponding shear stress for the $S = 8.81 \times 10^1$ to $S = 8.81 \times 10^1$ experiment is
approximately 125.0. In an experiment where the shear rate was changed directly from 2.795 to \(8.81 \times 10^1\) with no build-up time, the final shear stress at the shear rate 2.795 was 20.0 and a reading of 151.0 was obtained for shear stress at the shear rate 8.81x10^1. This indicates a cross-over in the two curves and suggests the possibility that two samples with different histories can exhibit different non-Newtonian curves after having the same apparent viscosity at the same shear rate. However, viscoelastic effects are an unknown quantity in these experiments and may account for this behavior.

**Viscosity build-up while shearing**

These studies were not designed for any purpose. The results just occurred in the course of events and were analyzed for content. It is interesting to note that the plotting procedure described by De Waele (17) for viscosity build-up at zero shear rate worked for these results but not for our results on viscosity build-up at zero shear rate.

**Unexpected rate behavior**

These results indicate one thing very clearly. More than one rate of viscosity rise or decline can occur at a single shear rate and viscosity. In fact it appears probable that an infinite number of rates of both viscosity rise and decline can occur at a single
shear rate and viscosity, depending on the shear history of the liquid. We hesitate to call this a 'memory' as is done for highly viscoelastic liquids. Instead, we believe that there are either many different "structures" or bonds between the particles in the liquids or many different sized and shaped particles or flocs with similar types of bonds, or possibly a combination of both. In any case, structure which is stable at one shear rate is not necessarily stable at another, even though the shear stress at the second shear rate is not as high as the equilibrium level. Therefore, it is possible to observe rates varying from negative to positive at the same shear rate and viscosity. However, if the liquid is sheared long enough, the viscosity will always tend toward the equilibrium level at the rate of shear being administered.

The variability of rate of change of viscosity at a given shear rate and viscosity is a most difficult boundary condition to satisfy with a rate theory. The observer can only measure three variables, shear rate, shear stress, and time. With the rate of change of viscosity having apparently an infinite number of degrees of freedom at a given set of $S$, $\tau$, and $t$ values, the development of a rate theory to describe the experimental results becomes a needle in the haystack proposition of trying to include shear history as a variable. In our opinion, this is a well nigh impossible task to perform with only viscometric data. The necessary further information can possibly be supplied by other physical chemical studies.
We will leave the choice of the type of studies to be used to the next researcher, but would like to suggest that a knowledge of particle size and shape distribution in colloids or molecular weight distribution in polymers might be helpful. If a single size and shape of colloidal particle, or a very narrow range of molecular weights of polymer were used, this would eliminate a number of possibilities for causes of extraneous rate effects.

**Relation of rate variations to structure curves**

These results show that when the viscosity at a given shear rate is the same in two experiments, similar structure curves can be obtained upon stepping down to lower shear rates, even though the rate of change of viscosity is very dissimilar in the two cases. However, when the viscosity was allowed to build up at zero shear rate, we observed contradictory behavior. This suggests that if the history of the sample in two experiments is extremely dissimilar, different structure curves will be observed upon stepping up or down in shear rate from a given viscosity at a given shear rate. If the history is not too different, the difference in the structure curves will be undetectable.

**Analysis of the data using the Brodkey-Denny theory**

At first glance, the results shown in Figure 26 appear to show a trend toward a straight line with a wide scatter in the points.
However, upon closer analysis, this apparent trend appears to be more the result of chance than anything else. The data were obtained from studies of viscosity fall-off after stepping up to higher shear rates from equilibrium at low shear rates and studies of viscosity rise after stepping down to lower shear rates from equilibrium at high shear rates. These are two different types of experiments and the results fall into two groups on the figure, with the results from fall-off on the right. Viscosity fall-off data are subject to considerable error, but the trend for a single set should be fairly representative. It is apparent that the curve for each set of this data has an almost infinite slope. If the duration of the data taking had been extended, in all likelihood this trend would have continued and the plots would show more vertical extension, thus giving a series of four almost vertical lines of considerable length, one for each set of data. The results from viscosity build-up data, on the left in Figure 26, are noteworthy for the lack of a trend. Build-up data in general are more accurate than fall-off data because the viscosities change much more slowly and slopes therefore are more easily determined. The more meaningful of these results are points E, F, G, H, and I. These cover a fairly wide range of shear stresses and show no trend at all. For example, it is not possible to dismiss the difference in points F and G as being due to data scatter. The slopes might be off 20%, but not by a factor of 10. Since $\mu_0$ was chosen somewhat arbitrarily, different values could be tried in the
attempt to find a better match. However, from the equilibrium equation, since \((1 - F)^2 \approx 1.0\), unless \(\mu_o\) is chosen very small, it is apparent that this would change \(K\) but not \(p\). Also, the change in \(K\) would be a direct result of the offsetting change in \(F\). Consequently this would not reduce the scatter of the results shown in Figure 26.

If all the rate data had been found to be consistent with the theory of Denny and Brodkey, this would not have provided proof of the applicability of the theory but would have indicated that it might be generally applicable. However, since the data are not consistent, we have valid proof that the theory in the form tested is not applicable to the data used in this analysis.
VII.
GENERAL DISCUSSION

In this work, an early decision was made to make a thorough study on a single thixotropic liquid rather than to try to relate data on different liquids or different concentrations of the same liquid system. Few, if any, other studies of the relationship between viscosity, rate of change of viscosity, and non-Newtonian behavior have been made with liquids specifically designed to allow simultaneous examination of all of these items. Therefore, the experimental techniques used here are uncommon, and in some cases unique. The data presented here are to date the most comprehensive ever obtained on a single thixotropic liquid. As such, they provide more information regarding some of the problems associated with interpreting such data than has previously been available. The results suffer from a lack of breadth, but it is hoped that this shortcoming is outweighed by the greater detail provided by a more penetrating, but narrower study of thixotropy.

In the following pages, the general behavior of thixotropic liquids is discussed using our results as a basis. Naturally, the applicability of these comments to any other liquid system depends upon the similarity of that system to the "Baymal"-propylene glycol system. However, we suspect that many colloidal systems exhibiting
a yield value will have some, if not most, of the characteristics reported here.

The suspension of "Baymal" in propylene glycol represents an acceptable compromise of the desired experimental characteristics for a thixotropic liquid. The rates of fall-off and recovery of viscosity with time are a little higher than convenient. The several hours required for recovery of initial viscosity is a little more than ideal, but to reduce the viscosity fall-off and recovery rates would require a suspension with even slower recovery of initial viscosity. The low vapor pressure of propylene glycol prevents film formation, but at the same time this liquid contributes to sample instability through the tendency to absorb water. Undoubtedly, any number of other thixotropic systems could be produced which would function as well in allowing the taking of these types of data. At present however, for the purpose of studying thixotropy, it is much easier to adapt the liquid to the machine than vice versa, and much care should be taken in choosing the liquid.

The tolerance of the possible error levels of ± 5% for viscosity data, and ± 15% for rate data is easily justified by the fact that the conclusions based on the trends shown by the large amount of data presented would not be affected if the data were slightly in error.

Beyond saying that liquid structure may be due to ionic or molecular attractions, or to physical entanglement, we prefer not to discuss it except in terms of rheological behavior. Our own
definition of liquid structure is any situation in which a liquid exhibits viscoelastic or thixotropic behavior or both.

Our concept is that thixotropy reflects the progressive destruction of structural masses in the liquid. The amount of thixotropy observed in a liquid is a function of the amount of structure present, the effect of this structure on rheological behavior, the amount of structural alteration due to shearing action, and the rates of structural change when a shear rate is imposed on the liquid. The last item is important because it is entirely possible that much or most of the structural alteration in a liquid takes place during the time required for instrument response or viscoelastic response of the liquid.

Three general types of structure seem to occur in liquids. One of these is solid-like in nature, where a certain amount of stress, which we consider to be a true yield value, is required to break the structure. Such a structure extends throughout the liquid. After the structure is broken, flow takes place. Prior to breaking, the material is a solid and regains its original form if the stress is removed. A second type of structure is that such as exhibited by the polymethylmethacrylate melt of Denny (2). This type of structure extends throughout the liquid and the liquid is viscoelastic but has no yield value. Any measurable stress will cause flow to take place. However, upon sudden application of high shear rates, the flow mechanism cannot relieve the resulting stress rapidly enough, and
the structure apparently breaks down over a period of time with resulting thixotropic behavior. This is not to say that breaks in the structure occur only when thixotropy is observed. Thixotropic behavior is the result of structural breakdown but structural breakdown can undoubtedly occur without the observation of thixotropic behavior. A third type of liquid structure is due to isolated flocs in the liquid. No yield values or viscoelasticity are present, but, upon shearing, progressive breakdown of the flocs occurs and thixotropic behavior is observed.

As might be expected, real liquids do not always neatly fit into one class. For example, in the "Baymal"-propylene glycol system the first type of structure breaks down upon shearing to give the third type.

The terms yield or yield value are often not clearly defined in the literature. We prefer to use the term initial yield to describe the stress at which the solid structure first breaks or yields to allow flow. If shearing action is stopped prior to reaching this value of shear stress, the torsion bar remains fixed in the stressed position rather than relaxing back to its original location. Thus the fluid behaves as a solid. The terms yield or residual yield are used here to mean any point other than zero displacement to which the torsion bar relaxes after shearing action is stopped. Other authors use the terms in various ways. The most common usage is to describe the point obtained by extrapolating the
curve of $\tau$ versus $S$ to $S = 0$. This is also often referred to as Bingham yield.

In the past, the relationship between yield value and thixotropy has been the subject of considerable debate. Many of the differences of opinion on this subject are probably due to the use of different definitions of yield value or to a lack of knowledge concerning the differences between the various definitions. In order to observe an initial yield some type of solid structure must be present in the liquid. It is difficult to conceive that such a liquid would not be thixotropic. On the other hand, the occurrence of a Bingham yield does not require the presence of a solid structure or thixotropic behavior.

Yield values are not reported here because they are difficult to obtain and even more difficult to interpret. Both of these difficulties are the result of a single problem. After equilibrium is obtained at low shear rates and shearing action is halted, it can take a long time for the torsion bar to relax to a set point corresponding to the yield value. Meanwhile, the zero on the lowest transducer range can shift with no way available to check whether any change in reading is due to drift or to further relaxation. Also, during the relaxation period, structure rebuilds continuously with the result that the yield value finally observed does not represent the structure present at the time shearing action was halted. These two factors destroy the quantitative usefulness of this information.
One noteworthy aspect of our data is the indication that thixotropic liquids have a different yield value associated with each structural level. This is true no matter what definition of yield is used. As equilibrium shear rate increases or structure decreases, the yield value falls. This is shown in Figure 12 where each structure curve has its own characteristics and there appears to be no tendency toward lower Newtonian viscosities. Therefore, the use of a single yield value to correlate equilibrium data is invalid from a theoretical standpoint and can be justified only for the sake of convenience. No single yield value or even a series of yield values will give a constant plastic viscosity when the equation

$$\frac{\tau - \tau_o}{S} = \mu$$

is applied to the data represented by the structure curves. In Equation 63, $\mu$ is plastic viscosity and $\tau_o$ is the yield value.

Some of the weaknesses of using hysteresis loops to define the amount of thixotropy in liquids have been discussed in the literature section. Originally it was hoped that hysteresis loops would provide a measure of the amount of structure present in liquids. From our data, it is apparent that the width of these loops is also very much a function of the experimental procedure. If many points (as opposed to few) are taken on the upcurve, the liquid structure is broken down farther than if only a few points are taken, and
therefore a wider hysteresis loop is observed. Furthermore, as the top shear rate of the upcurve is increased, the width of the loop should increase, since structural breakdown occurs much faster at higher shear rates. The width of the loop is also a function of how fast the structure rebuilds. Once again, this varies with shear rate and duration of shear. With all of these variables affecting the data, quantitative interpretation of hysteresis loops is impossible at the present time.

Thixotropic behavior can occur in the absence of a yield value. An example of this is the experiment described in the results section where the liquid was sheared to equilibrium at a shear rate of 27.95, at which no residual yield value was observed. Then the shear rate was raised to a shear rate of 279.5 with resulting thixotropic behavior.

The data of Table 9 show that in some situations shearing promotes higher rates of viscosity recovery than occur at zero shear rate. This is not unreasonable. Since the viscosity of the liquid tends toward equilibrium at any shear rate from any structural level, it is only logical that the tendency to recover structure is promoted by shearing action. If no shearing takes place, the structural recovery depends partly on liquid diffusion, a slow process at best. The movement induced by shear allows much more rapid contact of re-acting particles, and those bonds that can endure the shearing action are formed much more quickly. It is reasonable to expect that most
thixotropic liquids would exhibit this tendency at some shear rates.

We can only speculate as to reasons why the liquid shows higher viscosities than expected at equilibrium for shear rates of \(8.81 \times 10^{-1}\), \(2.795 \times 10^{-1}\), \(8.81 \times 10^{-2}\), and \(2.795 \times 10^{-2}\). This was particularly noticeable at the shear rate \(2.795 \times 10^{-2}\), where the viscosity went through a minimum before reaching the equilibrium level. One possibility is that shearing action orients the particles in such a way that flocs are formed which have more resistance to flow than those which form when the liquid is at rest. Another possibility is that the structure which forms at rest traps some particles in positions where only weak bonds can form.

It is of interest to note that upon stepping up to a shear rate of \(27.95\) from equilibrium at shear rates of \(8.81 \times 10^{-2}\) and \(3.525 \times 10^{-3}\), the resulting shear stress is about the same. This indicates that the different structures as represented by the difference between initial and flowing viscosities under the same conditions at low flow rates, had little effect on the results at high shear rates. This leads to the conclusion that factors which are important at one shear rate are not necessarily important at other shear rates.

At high shear rates, the viscosity of the "Baymal"-propylene glycol suspension appears to tend toward the viscosity of propylene glycol, as suggested by Eissenberg (21). This suggests that at very high shear rates, the structure can be degraded to primary particles as suggested by Jankovics (20).
Our results indicate that the conclusions of Dintenfass (15) are only partially correct. Upon stepping down from equilibrium at high shear rates, thixotropic recovery is indeed rapid in the regions of high shear rates and relatively slow at low rates of shear. However, this tendency is reversed when the original equilibrium shear rate is relatively low. These data are given in Table 9. Furthermore, time of thixotropic recovery is by no means additive. Shearing action, at shear rates lower than the original shear rate, promotes the viscosity recovery process with higher shear rates promoting faster recovery. Obviously, as the liquid approaches equilibrium, the recovery rate slows down greatly. Therefore, there is some optimum experimental procedure to promote the most rapid recovery of viscosity or structure. Even this discussion is an oversimplification of the situation, because at low shear rates, the rate of increase of shear stress, not viscosity, is almost independent of shear rate, and probably is a more meaningful piece of information.

It is also true that an unspecified, non-equilibrium rate of shear can cause structural breakdown which will give the same viscosity as a lower equilibrium rate of shear when the shear rate is changed to the lower value. However, this is by no means proof that the resulting structures are the same. In fact, judging from the rate studies performed here, it is almost certain that the two structures are not identical in most cases.
The findings of Worrall and Tuliani (23) on their clay-water suspensions are entirely consistent with the results given here. The structure in their solution was probably harder to break down while shearing and slower to recover when shearing action was halted. It is entirely possible to observe clockwise thixotropic loops with our suspension if it is sheared vigorously before determining the upcurve and downcurve. The rest of their results are easily explained as being due to rate phenomena.

The question arises as to which of the various theories or empirical equations are best for correlating viscometric data. The answer appears to be that each of them can be useful, depending on the liquid system and the type of data taken. For example, the plots of viscosity versus log time for viscosity fall-off shown in the results section give a straight line during the early portion of the curve, but deviate as viscosity approaches the equilibrium point. The same type of plot does not work for viscosity build-up data. There appears to be no single theory or equation that will correlate all rate data.

In our opinion, the general concept of plastic fluids as described by Vinogradov (14) (see Figure 3) is representative of the behavior of the "BaymaII"-propylene glycol liquid system. Although A is shown in the diagram as being less than H, this is not a necessary requirement. As shear rate approaches point A, the equilibrium stress values approach the initial yield value because the shear rate is so
low that the structure does not break down beyond the initial fracture plane, and the flow is due to slip across planes rather than normal viscous flow. The data given here does not extend far enough to observe the lower portion of the curve, A to C. One possibility that is not presented in Figure 3 is that from point A, the curve may extend straight downward, possibly almost to $S = 0$, before curving off toward the origin. The extension toward the origin should not occur until the shear rate is low enough that shear stress, calculated by the equation

$$\tau = \mu_c S$$

is not greater than the initial yield value. In this equation, $\mu_c$ is the creep viscosity of the material when the structure is fully formed. If shear stress, as calculated by this equation, exceeds the initial yield value, flow should occur along slip planes as previously mentioned.

The two bond hypothesis of Bujake (16) does not go far enough. A multi-bond hypothesis would probably be more nearly correct. Considering the complexity of the rate behavior, it is probable that many different types of bonds occur and that any one of these bonds can vary in strength due to physical orientation of the particles. Furthermore, even if all the bonds were of similar strength, the shear stress required to break the bonds could vary with particle size because the viscous drag could vary with particle size. Also, it appears possible that a structural level obtained by a certain
shear rate history could consist of flocs with a certain statistical size distribution. At the same viscosity and shear rate, but with a different shear rate history, the structure might consist of a different size distribution of flocs.

This suggests a possible next step for this type of research. A study of the effects of particle size, particle size distributions, and molecular interactions on structure in similar experiments would prove fruitful. Also, by judiciously choosing a solution and a concentration, it might be possible to produce a liquid which would permit an independent measurement of the amount and type of structure present at various shear rates and times.

Some of the mathematical implications of the various rate theories were discussed in the theory section. Based on the data presented in the results section, it appears that a number of conditions must be met before a rate theory can possibly apply to a liquid such as the "Baymal"-propylene glycol system. A tabulation of which of these conditions are met by each theory is given in Table 16. No criticism of any of the theories is intended in presenting this table. For example, only two of them were developed to consider liquids with a yield value. The rest were developed primarily for polymers, or polymer solutions, which undoubtedly have a different type of structure than those liquids which have a yield value, such as the "Baymal"-propylene glycol system. The purpose of the tabulation is to illustrate the difficulties of
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- Allows for non-Newtonian behavior at one structural level.
- Allows for promotion of viscosity recovery by shearing action.
- Allows for a single yield value.
- Allows for more than one rate at one structure and one shear rate.
- Allows for an upper Newtonian viscosity.
- Allows for multiple yield values.
- Allows for viscosity to pass through a minimum and rise again.

Table 16: Properties of Butyl Alkyl Glycol Suspension
developing a rate theory for liquids such as ours.

The easiest way to allow for non-Newtonian behavior at one structural level is to assign a yield value to the liquid or a set of yield values with one yield value being associated with each of the various structural levels. This proposal can be dismissed for our liquid by pointing out that no yield value will give a single plastic viscosity for the data for any given structure, and that the liquid is non-Newtonian even when the structure is broken down to the point where no yield can be observed. Therefore, this condition is not an easy one to satisfy for our liquid.

The occurrence of an upper Newtonian viscosity limit was recognized as a probable situation by most of those trying to develop a rate theory. Consequently, they built this condition into their theories as an integral part.

The fact that rate of viscosity fall-off is a function of shear rate or shear stress has long been recognized. Promotion of viscosity recovery by shearing action has also been recognized as probable by some of the theorists. To account for these conditions, they let the rate constants for structural changes be dependent on shear rate or shear stress.

The occurrence of more than one rate of change of viscosity at a single structural level and a single shear rate indicates that more than one mechanism is involved in the rate process. No one has yet attempted to present a rate theory with more than one
mechanism for the very good reason that viscometric studies do not provide enough variables to allow pursuit of this approach. In attempting to devise a satisfactory theory based on chemical reaction kinetics, it is necessary to define a concentration of structure, no matter what concept of structure is used. If only viscometric results are to be used, this concentration of structure must be deduced indirectly from shear stress or viscosity since these are the results obtained from the viscometer. When more than one rate of change of viscosity can be observed at a single viscosity and shear rate, it is obvious that these readings do not supply sufficient information to completely define the system.

The fact that viscosity can pass through a minimum and rise again at a single shear rate shows once more that more than one mechanism is operative in the rate process. Apparently, part of the structure breaks down and reforms into a stronger aggregate. This indicates that even a two mechanism approach, such as suggested by Bujake, would be insufficient.

The construction of a general rate theory to account for the behavior of this suspension and any other similar to it appears to be an unrewarding pursuit at this time. More basic information is needed in order to define the nature of the reactions taking place and the effect of these reactions on viscometric results.

Care must be taken in attempting to apply the results and conclusions of this study to other systems. Clearly, we cannot say
that the types of mechanisms implied by the authors of the various rate theories are not present and are not the controlling factors in determining the behavior of their materials. However, this study does indicate the possibilities that other mechanisms are present and that the mechanism responsible for thixotropic behavior is not entirely responsible for all observed non-Newtonian behavior. A great deal more research will be required to answer these questions satisfactorily.
VIII.

CONCLUSIONS

Some of the results reported here are unexpected and thought provoking. The rate processes which occur in the "Baymal"-propylene glycol suspension are much more complex than anticipated. Viscometric studies alone do not provide sufficient information for determining the nature of these processes. While there can be little doubt that the occurrence of liquid structure is responsible for the non-Newtonian thixotropic behavior observed in this liquid, a great deal more research will be required in order to obtain an adequate understanding of the changes which occur during and after shearing action. Until these are understood, it is unlikely that an adequate theory to account for the rheological behavior of the "Baymal"-propylene glycol suspension or similar liquids can be developed.

A number of our experimental findings are important enough so that they need to be emphasized:

1. Examination of the structure curves shows that at a single structural level the liquid is non-Newtonian and that there is a different yield value associated with each structural level.

2. Factors which affect results at one shear rate are not necessarily important at greatly different shear rates. This is illustrated by observing that even though the viscosity declined
to one half or less of the initial viscosity at low shear rates, the viscosity obtained when the shear rate was increased to a high value was at or nearly at the initial viscosity level.

3. The various studies of rates of viscosity change were used to test the Brodkey-Denny rate theory. Like all others, it could not be used to explain the observed experiments. Rate data is a most powerful tool to test ideas that attempt to predict thixotropic behavior or associate thixotropic behavior with equilibrium results.

4. The liquid viscosity eventually tends toward the same equilibrium point at a given shear rate whether viscosity is below or above that point when the shear rate is first imposed. This tendency was observed every time the shear rate was changed.

5. The results from viscosity fall-off studies (at constant shear rate and when the liquid structure was initially completely built up) show that the liquid has an elastic component when structure is present throughout the liquid. During the early portion of viscosity fall-off, a plot of viscosity versus log time yields a straight line. The slopes of these straight lines can be correlated with the equation

\[-\frac{d\mu}{dt} = \frac{2}{4.76/t(s)^3}\]

6. The studies of rates of viscosity change at other structural levels show that more than one rate of change of viscosity can
occur at a given shear rate and viscosity. The rate of change of viscosity is a function of the shear history of the liquid. The rheological theories based on chemical kinetics cannot be used to explain this condition nor can they be easily altered to permit describing this type of rheological behavior.

7. It was also found that shearing action promotes viscosity recovery when the viscosity is considerably lower than the equilibrium viscosity at the shear rate in effect (rheopexy). This indicates that particle orientation or the proximity of particles to each other, or both, are important factors in the rebuilding of structure.
IX.

RECOMMENDATIONS

The "Baymal"-propylene glycol suspension studied here is a different type of liquid than the more commonly studied polymer solutions. Insomuch as the viscosity transient is longer and the structural recovery rate is lower it is an easier fluid to work with than most polymer solutions. We recommend that an experimental program be established to further investigate the rheological behavior of this type of liquid. If necessary, this should be done at the price of exclusion of further theoretical developments.

Based on the results of our work, a number of specific suggestions concerning future studies can be made. To begin with, we worked with only one system and tried to avoid any alterations in the chemical composition of the liquid. A very natural extension of our work would be to study the changes in rheological behavior resulting from variations in the concentrations of the components. It would also be very useful to do a screening study on a number of liquids in order to determine the chemical requirements for producing liquid systems with rheological behavior such as reported here.

A study of the effects of physical dimensions of particles on rheological behavior, as contrasted to studies of chemical
variables as suggested above, might yield even more meaningful results. Studies of the effects of different particle size and shape distributions on viscometric behavior appear to be a particularly promising area of research for the immediate future. It might well be that the number of particles present in the liquid and their dimensions are more important factors than weight per cent in determining rheological behavior.

In order to determine structure curves with the present equipment it is necessary that the structure rebuilds slowly when the liquid is not being sheared because approximately ten seconds are required to change gears. This limits the number of liquids and concentrations that can be studied. An attempt should be made to alter the rheogoniometer so that the shear rate can be changed at least an order of magnitude faster.

The combination of results from viscometric studies with other physical chemical measurements such as x-ray diffraction, birefringence, and light scattering will ultimately be needed in order to determine the operative mechanisms in the rate processes which occur when a structured liquid is sheared.
APPENDIX A

NORMAL FORCE MEASUREMENT DEVELOPMENT WORK

Introduction

The development of a new normal force measuring device, specifically designed to allow measurement of transients of short duration, was undertaken at a time when it was anticipated that this information would be needed to extend the work of Denny, Kim, and Brodkey (1, 2, 3, 5, 32) on polymers. Subsequent to most of this development the decision was made to study a thixotropic colloidal system without normal stresses; thus the need for these latter measurements was eliminated. However, since the device should ultimately prove useful, the project was pursued to a logical stopping point. In this section we report our findings, describe some of the problems encountered in working with this system, give our current thoughts on the subject, and make recommendations for future work in this area.

Farol Normal Force Equipment

The normal force measuring equipment provided with the rheogoniometer is shown in Figure 27. The basic difference between the system without the normal force equipment in place and with it in
Figure 27. Diagrammatic Layout of Normal Force System.
place is that when the normal force equipment is not in, the weight of the platen is supported by the bearings of the driving member, and when it is in, the weight of the normal force platen assembly and the platen is supported by the normal force measuring device. The normal force platen assembly is free to move in the vertical direction but is located rigidly in the horizontal direction and driven in rotation through a diaphragm. Of particular interest to us is the bottom end of the lower platen shaft where a hardened steel ball rests in the normal force pivot bearing. This pivot bearing is attached to the normal force leaf spring assembly and is adjusted on each spring, so that the normal force platen holder has no tilt and the diaphragm is flat. The terms "no tilt" and "flat" are relative, depending on the type of measurement being taken.

The key element in the taking of measurements is the normal force spring. On its "free" end the cantilever leaf spring has a steel ball which provides a pickup point for the spring plunger and micrometer which position this "free" end. During measurements of normal force it is necessary to keep the gap between the two platens nearly constant. This is accomplished by driving the micrometer either by hand or with the servo system. As the normal force increases, the normal force spring bends and the lower platen moves downwards. This is detected by the transducer under the normal force pivot bearing and its deflection seen on the appropriate transducer meter (see Figure 27). The normal force is determined
by replacing the pivot bearing to its zero position by lifting the "free" end of the spring. The amount of movement of the "free" end is calibrated with the normal force at the pivot bearing.

For more detailed information, the reader is referred to the Farol literature (37).

**Difficulties in normal force measurement**

Of the measurements that can be made on the Weissenberg Rheogoniometer, normal force measurements are the most difficult to obtain. This is particularly true when investigating materials of high viscosity, especially when the normal forces are relatively low and the electronic equipment is being used on a sensitive range.

The most serious problem is that of servo system overshooting and oscillating. Under a normal force the lower platen moves downwards and this causes the servo system to move the "free" end of the normal force spring upward to attempt to replace the lower platen in its original position. However, if the material is very viscous it will not flow readily and the lower platen moves very slowly to its original position. This means that the servo system has a positive signal for too long a period and overshoots, eventually causing the lower platen to move upwards too far with a consequent negative signal on the servo system. The oscillations of the system caused in this way may or may not die out to give a reliable steady state reading of normal force.
Upon looking at the design of the system provided with the rheogoniometer, and upon looking at measurements taken with it, it becomes apparent that the system was not designed for taking accurate measurements with highly viscous fluids in place. In particular, short duration transients can not be measured because the system cannot respond to them. Our opinion was, and still is, that the response problem can only be eliminated by eliminating most of the vertical movement of the lower platen. With this in mind we set about designing a system which would allow accurate measurement of stress with almost no vertical movement.

Kistler Piezoelectric Load Cells

After some investigation, we concluded that a Kistler Model 912 piezoelectric load cell would be best suited to serve our purpose. Quoting from Kistler (40) literature, this load cell:

> is a compact, fast-response force transducer for measuring forces in either tension or compression. The inherent rigidity of this piezoelectric instrument has a deflection under load equivalent to a stainless steel washer with the same overall dimensions.

The extreme operating ranges (5000 lb compression and 500 lb tension) provides the load cell with a capability for high-level force measurements in temperature environments from -400°F to +500°F. The load cell is shown in Figure 28.
Figure 28. Piezoelectric Load Cell.
Installation

The load cell must be carefully installed to avoid transverse loading which results in erroneous output signals. The transducer must be mounted on a flat surface perpendicular to the axis of the force applied. For static measurements such as ours, the transducer must be insulated to avoid rapid temperature variations. Figure 29 shows an application of the Model 912 load cell similar to ours.

A mounting problem that was encountered which is not specifically mentioned in the Kistler brochure was the following. Upon using the beryllium-copper studs for mounting the cell to a load bearing plate we found that if a sudden force was exerted on the system by tapping on the plate, the cell, or anywhere else such that force could be transmitted to the measuring system, the charge output would jump and remain set in the new position. The amount and direction of the jump was random. This caused us much consternation because we found that the magnetic clutch on the rheogoniometer engages with enough force to cause a jump as described above. Also, the measurements were affected by such minor things as someone slamming a door down the hall. This problem was solved for us by Mr. Raymond Gogolick of Sterling Company, the manufacturers' representative. He suggested that the offset was caused by minute changes in the metal to metal contact position, and suggested placing a washer of plastic film between the metal parts. This procedure
Mounting Studs (Must not "bottom")

Figure 29. Load Cell Mounted for Tension or Compression.
eliminated the problem with no apparent loss of accuracy or response.

**Associated equipment**

Required for use with the load cell in order to make useful measurements are a high quality charge amplifier, associated insulated lead in wires, an electronic filter, and a recorder. For our system we purchased a Kistler Model 503 Universal Dial Calibration Charge Amplifier and used the same filter and Offner Dynograph recorder used with the rheogoniometer.

A description of the charge amplifier is best obtained from the Kistler (41) brochure. Its function is to convert the electrostatic output signal from the load cell to voltage (or current) outputs which can be displayed on indicating or recording equipment (see Figure 30). The charge amplifier has a SHORT-MEDIUM-LONG Time Constant switch which permits selection of extremely high input resistance (nominally $10^{14}$ ohms) for short-term static response when calibrating with quartz crystal transducers, or either of two lower input resistances ($10^{11}$ ohms and $10^{9}$ ohms) for dynamic operation. A GND pushbutton switch, when depressed, removes residual charges from the measuring system and restores the output to zero. These two features of the charge amplifier are vital to our use. Without the variable time constant we would not be able to take static readings and could not use a load cell for our type of measurements. The short button allows removal of the charge from
Figure 30. Charge Amplifier.
the crystal at any time. This capability for disposing of any charge due to constant loads arising from mounting procedures allows the measuring and amplifying of the variable normal force signal without overloading the circuits.

**Signal drift**

The system, here referring to the cell, amplifier, and recorder, has a number of drift problems. These can be classified as; (1) charge decay, (2) charge output drift or variation due to temperature changes, and (3) electronic drift.

Drift, in general, is not a function of the size of the input signal. Therefore, large signals are measured with ease and small ones with difficulty. The following discussions apply only to the case where the investigator is trying to accurately measure small or intermediate signals. In our terms a large signal represents a force of 200 gm wt or more and small signals represent 2 to 20 gm wt or so. In the following discussions we will always refer to signal intensity in terms of gm wt. From a practical standpoint it is not important to know the absolute value of the charge on the crystal. It is only necessary to know what the reading on any scale represents in terms of vertical force exerted on the plate.

In working with the load cell, drift due to charge leakage in the charge amplifier when on long time constant was found negligible for periods of a few minutes for measurements in the range of interest.
Therefore, this is not a limiting factor when using the equipment.

Drift due to temperature change is important. Minor temperature fluctuations cause large variations in charge output. To minimize this problem it is necessary to isolate the load cell from stray air currents in the room in order to cut down heat transfer by convection, and to minimize conduction heat transfer effects by connecting the load cell to a large heat sink. Even with these precautions appreciable drift occurs, but, since the heat transfer is normally unidirectional and at a fairly constant rate over any short period of time, the amount of drift can be accounted for in ordinary short term measurements. However, if it were desired to observe a transient for 5 to 10 minutes or longer, it would be necessary to take considerable care in order to obtain a drift small enough and predictable enough so as to be calibratable.

While electronic drift in the recorder is negligible, that in the charge amplifier is not, and special procedures must also be taken to minimize this item. When the charge amplifier is first turned on the drift is so great that only large signals can be measured accurately. After a minute or two the drift decreases to the point where the pen will stay on scale for intermediate measurements, and several minutes later it is possible to measure short term transients on small signals. To use the data, the rate of drift before and after a run must be noted and accounted for when the data is reduced. To reach minimum drift, the charge amplifier should be left on 24 hours
or more. Since the electronic components are of a solid state variety, it is not particularly harmful to leave the amplifier on continuously and this is recommended if measurements are to be taken frequently.

**Measuring capability of the system**

The ability to measure forces is limited on one end by the maximum load cell capacity of 5000 lbs force, and on the other by noise problems in the mechanical system. The cell seems capable of responding to a feather touch, and the amplifying system is capable of handling very small charges, perhaps down to a load of tenths of grams, without having too much drift. However, as will be described later, the mechanical system limitation seems to be on the order of several grams so the potential range of measuring capability is from a few gm wt up to 5000 lbs force. A typical measurement system is shown in Figure 31.

**Various Attempts to Measure Normal Forces with the Piezoelectric System**

We tried, with varying degrees of success, a number of procedures for measuring normal forces in polymer solutions using the piezoelectric crystal. Not all of the problems were solved to our satisfaction but some fairly good data were obtained with one set-up, and what is considered a usable system was developed for taking transient normal force data on viscous liquids. Having shown the feasibility
Figure 31. Typical Measurement System.
of using this radically different transducer system and having outlined most of the problems involved in its use, we halted development work on it and pursued our other work to its conclusion. In this section most of our experiments are outlined and recommendations are given for further development of the system. The primary value of this work will be for directing someone who wishes to take such measurements.

The load cell was first tested with no fluid present. The system in this case is shown schematically in Figure 32. The only difference between this set-up and the original rheogoniometer normal force unit is at the bottom. To make this arrangement, the normal force bar and center transducer were removed. Then two stainless steel pieces were machined, one, a support, being slip fitted for the lower clamp, with a 10 - 32 x 1/8" deep threaded mounting hole drilled in the top, and the other a small bearing piece to fit on top of the cell, with a 10 - 32 x 1/8" deep threaded mounting hole in the bottom and a conical depression in the top. At attempt was made to position the conical hole on top of the bearing piece accurately so that the plate and cone would be properly aligned.

Proper alignment is a difficult thing to achieve. Alignment was finally made by placing the Farol equipment in position, aligning the system, then pulling out the Farol normal force bar and placing the new system in position. The place and cone were then
Figure 32. Modified Normal Force Apparatus.
aligned (eyeball accuracy) and a mark was made on the stainless steel bearing piece which sits on top of the cell. Then this piece was removed and a small conical hole was drilled in at that point. When the system was replaced the alignment was off a little. The amount was noted and the conical hole was moved by drilling it a little deeper and slightly to one side. After a few tries the alignment was close enough that it was judged satisfactory.

The important item to note in this arrangement is the ball and cone bearing at the bottom. The ball on the end of the rod fits into the cone such that no lateral movement of the rod is allowed at the bearing point.

At this point, still without material between the plates, the effect of variable diaphragm strength was tested. The beryllium-copper diaphragms provided with the rheogoniometer are fairly flimsy, and response suffers when only one of them is used while taking measurements on a highly viscous fluid. Response can be improved almost linearly by using a number of these diaphragms. Two heavier diaphragms were also made, one of 0.025 inch thick copper and one of 0.040 inch thick stainless steel, in hopes that a wide range of response could be obtained. When using these diaphragms it is necessary to calibrate each combination of scales of the charge amplifier and recorder for each diaphragm. Fortunately, signal was almost linear to load in every case and showed only minor variations with changes in diaphragms. Consequently, calibration was a simple procedure.
Our first trial was with the stainless steel diaphragm. Much to our surprise a periodic signal with an amplitude of several hundred gm wt which reoccurred at each rotation of the plate was received from the crystal. When the stainless steel diaphragm was replaced with one of the regular thin diaphragms, a periodic signal was obtained which had an amplitude of only two to three gm wt. After much more testing the conclusion is that the bearing in the driving train of the rheogoniometer has a vertical thrust and withdrawal of appreciable magnitude in comparison with the amount of compression of the load cell. Apparently, if the diaphragm does not have considerable play, it transmits vertical thrust from the bearing through the diaphragm to the load cell. The stiffer the diaphragm the greater the variation is in the signal from the load cell. Thus, if measurements are to be made by mounting the load cell at the bottom of the machine, it is necessary to compromise between fast response and uniform signal. By experimentation we found that reasonable response and a fairly good signal could be obtained by using at once all four of the thin diaphragms originally provided with the rheogoniometer. To put numbers on this, mechanical tangential response was 98% of full signal in about 0.5 seconds at $10^5$ poise fluid viscosity, which indicates a response time of 0.005 seconds to reach 98% of full signal when the viscosity is $10^3$ poise. With no sample in place there was a normal force signal variation of 2 to 5 gm wt. In view of
the liquid response problem, this probably allows sufficient freedom for most practical purposes.

Having examined the potential of the measuring system, we felt ready to test it with a sample in place and chose to use a solution of polymethyl methacrylate in diethylphthalate prepared by H.T. Kim (5). This solution fulfilled the requirements of a fairly viscous material which is easy to load and unload at room temperature, which can give normal forces in the range of measuring capability, and which was available. The requirements were a result of the fact that the normal force system supplied with the rheogoniometer is adequate for low viscosity fluids which give high normal forces and when short transients are not being considered. To greatly improve upon these capabilities it is necessary to handle short normal force transients in more viscous fluids. The loading, unloading, and temperature requirements were to lessen the time required for a given experiment. The sample was loaded, tested, and once more a large periodic noise occurred.

At this point, upon considering the mechanics of the system, we reasoned that noise in the piezoelectric measuring system resulted from extraneous lateral and, or, vertical movements of the plate brought about by an inability to obtain perfect alignment in all directions. A thorough analysis of the mechanical system is given in the discussion later in this section. Two methods for overcoming these difficulties appeared promising. The first was
to align the system well enough that noise would be eliminated as a result of eliminating extraneous motion. The second was to redesign the system such that any necessary movements might take place without greatly affecting the readings.

Many attempts were made to align the system, keeping the ball and cone bearing, so perfectly that noise would be eliminated. The results can best be described as various degrees of failure. A few times noise levels as low as 20 to 40 gm wt were obtained, which were about 10 times the amount considered tolerable. Response was excellent and appeared to be on the same order as the tangential response in all cases. Other attempts were less successful. The really discouraging thing about this set-up was that the degree of success seemed to be random. An alignment to within 0.0002 inches on occasion would give better results than an alignment to within 0.0001 inch. Apparently, some combination of vertical and horizontal alignments is the deciding factor in determining noise level. If this is so, the optimum combination will change each time the system is altered, which would happen frequently in practice. Close alignment, in general, is difficult and time consuming to achieve. Furthermore, there is no present capacity to align the system much better than 0.0001 inch. Consequently, the idea of trying to cure the noise problem by close alignment was dismissed.

In an attempt to circumvent the need for exceptionally good alignment, changes were made in the mechanical arrangement of the
system. There appear to be several possible approaches for preventing force components arising from lateral movements from being transmitted to the load cell. One way is to allow horizontal motion to take place freely so that no horizontal force arises. Another possibility is to resist the horizontal force at some point other than the load cell while allowing transmission of the normal force. Some advantages might also result from placing the load cell measuring system above the place and cone rather than below. Numerous variations and combinations of all of these approaches were tried. A description and results from some of the more sensible of these is given in the following paragraphs.

In Figure 32, A represents the driving member of the instrument, in which there is a 1/2 inch diameter hole. The rod through which normal force is transmitted slides freely up and down through this hole with considerable clearance on the sides. An attempt was made to place a sleeve in this hole which would fit the rod tightly enough so that, while vertical movement was allowed, horizontal movement would be reduced to a negligible amount. This was an easy thing to attempt to do because with A and the rod rotating at the same speed, there was no problem of the rod binding in the hole and ruining the diaphragms. With the bottom of the rod restricted in its motion, the piece with the conical bearing surface in it can be replaced by a "flat" plate. In our case a small piece of window pane was used for the flat bearing surface.
In the first attempt to use this procedure a piece of Tygon tubing of the proper size was placed in the hole and the rod was slipped down through it. The end of the rod rested on the glass plate which rested on the load cell. The rod would slide up and down, but not easily. When the plate was rotated, the noise level was very high, even with no sample in place. Apparently, the tight fitting Tygon sleeve acted like a stiff diaphragm, and forces from vertical thrust and withdrawal due to irregularities in the drive bearing were again transmitted to the load cell.

To avoid this problem a copper sleeve was machined just large enough to allow complete freedom of vertical movement. This required a clearance of about 0.001 inch between the vertical rod and the sleeve. The sleeve was small enough to slide freely in and out of the hole in the driving member, and was held in place by thick silicone grease. The rod was lubricated with a thin film of extremely light silicone oil. With no sample in place, the noise level was once again as low as that obtained with the thin diaphragm.

We were then faced with the problem of aligning the plate with the lower end of the rod free to move somewhat. Since lateral movement at the plate with this arrangement was 0.005 inch, this was as well as the plate could be aligned. The cone was aligned as well as ever by aligning it with the conical bearing piece in place. When this arrangement was tested with a sample in place, there was still periodic noise but the amplitude was smaller.
Later it was discovered that the ball point on the end of the rod was sliding across the glass with a lateral movement of 0.005 inch or more. By judicious alignment techniques, including rotating the sleeve in the hole and placing shims under some of the bolts connecting the normal force apparatus to the driving member, the lateral movement was reduced to approximately 0.0015 inch. The noise amplitude was dramatically lower for lower lateral movements. Unfortunately, in order to reduce lateral movement much further, it would be necessary to design and machine precision adaptor pieces instead of using the relatively crude approach outlined here.

With the lateral movement of the ball across the plate limited to 0.0015 inch, a number of other things were tried, some of which provided more insight into the overall problem. In attempting to cut the noise level further without better alignment, we tried to lessen the amount of horizontal force which might be transmitted to the crystal while the rod end was sliding across the flat plate. To do this, one glass plate was set on the load cell, four ball bearings were placed on top of this, and another glass plate was placed on top of those. The appearance of the plate arrangement was somewhat as shown in Figure 33. It was hoped that allowing the balls to roll when the ball end of the rod moved sideways instead of having the ball sliding on the glass would lower the noise level. Readings taken with this arrangement did have smaller noise levels. A minor variation of this and other arrangements was
Figure 33. Glass Plate and Ball Bearing Arrangement.
made by placing a thin piece of nylon tape, dental dam, paper, etc., on the upper glass plate to act as a bearing surface with a little more flexibility than the glass itself. These did affect the noise level, invariably reducing it until the material wore out. Of the materials used, dental dam was by far the best.

In Figures 34, 35, and 36 some normal force data are given for the arrangement shown in Figure 10 with some dental dam on the glass plate as a bearing surface, and with the copper sleeve in place, along with tangential stress data for the same rotational speeds. The figures are not entirely self-explanatory. The Offner recorder handles two channels and advantage was taken of this feature in obtaining these data by recording normal force and tangential stress data simultaneously. The recorder was set such that 40 mm or 8 large divisions was a full scale reading. The upper of the two channels gives the tangential shear stress as normally recorded and the lower channel gives the total normal force.

Each of the Figures 34, 35, and 36 has a series of explanatory statements written on the chart. These will be explained using Figure 34 as an example. G.B. = 2.2 refers to the rotational speed of the rheogoniometer, the first 2 referring to 2.0 on one gear setting and the second referring to 0.2 on the other gear setting. Chart speed = 5 mm/sec refers to the chart speed of the Offner recorder. Thus, 5 mm equals one second. 2 x 2 N.F. scale refers to the normal force scale. The first two is the setting on the
Figure 34. Normal Forces and Tangential Stresses.
Figure 35. Normal Forces and Tangential Stresses.
Figure 36. Normal Forces and Tangential Stresses.

Temperature: 27.5°C
Chart Speed: 5 mm/sec

\[ \gamma = 19,300 \text{ dyne/cm}^2 \]
\[ \dot{\gamma} = 2.62 \text{ sec}^{-1} \]
\[ \mu = 73.8 \text{ poise} \]
\[ NF = 685 \text{ gms} \]

Transducer Core Displacement

Crystal Signal

Time
charge amplifier, the second is the setting on the Offner recorder. Both have a large capacity for signal amplification, smaller scales representing greater amplification. The choice of scales therefore is somewhat arbitrary, since the signal can be amplified by either device. However, there is less electrical noise with certain combinations, and the scales were generally chosen to minimize the noise. Tangential range refers to the range used on the rheogoniometer for tangential stress readings. With a tangential range of 0.25, a full scale deflection (40 mm or 8 large units) represents a movement of the transducer core of 0.25 thousands of an inch or 250 micro-inches. The temperature was recorded and did not change during these measurements. The size of the torsion bar is used in determining stress. The largest torsion bar available was used in order to maximize instrument response. The 5 cm, 1° cone and plate combination is a convenient set to use with the rheogoniometer, being easy to handle both physically and from a calculational standpoint.

Each normal force scale was calibrated separately as shown in Figure 37 by placing laboratory weights on the plate. It can be noted that the readings are almost linear with weight.

Each of the Figures 34, 35, and 36 has interesting aspects. In Figure 34 the normal force is quite low. The noise level is almost half as large as the reading itself. Consequently, the normal force value chosen is not very precise. For our purposes
Figure 37. Load Cell Calibration.
the tangential stress response is almost instantaneous in Figure 34, as it is in all three of these figures. On the other hand, the normal force response is on the order of two seconds in all three figures. In our opinion, this additional length of time for normal force response is not a material property but is mechanical and is due to the flexing of the glass plate used as a bearing surface. In some of our other attempts to measure normal forces, using a more rigid system, a much higher noise level was observed in the normal force but the response was much faster, perhaps as fast as the tangential response. This will be discussed later. Also, in Figure 34, a typical drift in the normal force signal can be observed. In approximately 30 seconds, the base moved 5 mm or the equivalent of about 7 gm wt of force. From experience we know that the drift is almost linear with time over a short interval. Therefore, normal force can be determined by laying a straight edge from the base point on one end of the chart to the base point at the other end and determining the average reading above the sloping base line during the duration of the test. This illustrates the difficulty of using this normal force system for sensitive measurements over long time periods. While it is no problem to account for the amount of drift over a 30 second interval, it would be another matter to do so over a period of 30 minutes. The drift shown here is probably due to a very small temperature change. Another difficulty that would be encountered in a long test would be the natural decay of
the signal due to inevitable charge leakage over long time periods. This is more pronounced when the more sensitive scales of the charge amplifier are used.

In Figure 35, the noise level is higher but is a smaller percentage of the whole. Each peak represents one complete revolution of the plate, as it does in Figures 34 and 36 also. The reproducibility of the noise becomes readily apparent at faster speeds, but is not at all obvious at low speeds. At high rpms it is not difficult to obtain an acceptable average value for normal force and a fairly high level of noise can be tolerated. As rpms are lowered, the duration of the test must be extended so that an acceptable average can be obtained. Unfortunately, the drift and signal decay problems are then accentuated until finally no acceptable readings can be obtained. Since it is impossible to avoid drift and signal decay, the only way to improve the system is to lower the noise level. Most of our efforts in working with the normal force system were aimed in this direction. In Figure 35, the drift is too small to be observed. Unlike noise, drift is independent of signal magnitude and a drift of 7 gm wt is negligible compared to a signal of 282 gm wt.

Figure 36 shows an experiment giving unacceptable data. However, this is not due to a malfunction of the equipment. The noise level once again is higher but is a smaller percentage of the whole. The important thing to note in this figure is the drop
in both tangential stress and normal force during the test period. This drop can be mistaken for thixotropy but is due to sample deterioration. Upon separating the plate and cone at the end of this experiment, the sample was observed to be balled up at the outer edges of the plate and cone such that some of the surface area of the plate and cone was not contacted by sample. This is a common occurrence when working with viscous polymers.

Table 17 contains the results of these and other experiments with the same equipment and sample. The Table 17, GB is the gear box speed as explained previously, NF (total) is total normal force, and \( P_{22} - P_{11} \) is the normal force difference calculated by the equation

\[
P_{11} - P_{22} = \frac{2 \text{(NF total)}}{\pi R^2}
\]

as derived by Lodge (42). In Equation 65, \( R \) is radius of the plate in cm. The units of \( P_{11} - P_{22} \) are therefore gm wt/cm².

It was apparent from the beginning that some of the problems encountered in the attempts to use the piezoelectric system arose from trying to place it below the plate in association with rotating members of the machine. It was convenient to do this because ample space had been provided there for the Farol normal force gear. If the normal force gear is installed above the plate and cone, the problems of rotation are minimized, but at the same time others are introduced, these being associated with retaining the tangential
TABLE 17
NORMAL FORCE AND TANGENTIAL STRESS VALUES

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<tr>
<th>GB&lt;sup&gt;a&lt;/sup&gt;</th>
<th>S (sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>( \tau ) (dynes/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
<th>NF (total) (gm wt)</th>
<th>( \mu ) (poise)</th>
<th>NF/S</th>
<th>( P_{11} - P_{22} ) (gm wt/cm&lt;sup&gt;2&lt;/sup&gt;)</th>
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<td>1.0&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>2.5</td>
<td>8.25</td>
<td>1,470</td>
<td>6.6</td>
<td>178.5</td>
<td>0.80</td>
<td>0.67</td>
</tr>
</tbody>
</table>

<sup>a</sup>GB refers to operating gear ratio.

<sup>b</sup>Sample deterioration was evident in these two experiments.

Stress measuring capability while introducing the normal force device. Working with W. E. Lewis, we produced several possible alternative designs for placing the load cell above the plate and cone. One of these is shown in Figure 38. We built and tested a crude model of this design. Part A was made from a 2½ inch pipe cap. Holes were drilled in the lip so that the diaphragm could be bolted to it. A diaphragm holder for the Farol normal force equipment was used to fasten the diaphragm to the adaptor, to which the cone was attached. The cell sat on a ball bearing,
Figure 38. Placement of the Load Cell Above the Plate and Cone.
(the recess in the cell is ideally made for this) and steel washers were used at the top to produce the proper spacing. The diaphragm was made of 0.040 inch thick copper plate. With the cell in place, the spacing was made such that a positive pressure of the diaphragm on the ball held the load cell in position. The overall idea of the design was to transmit any vertical force from the cone through the ball to the load cell. We hoped that the ball would allow any necessary rotation and that all the tangential force would bypass the load cell through the diaphragm.

With this crude apparatus, we were unable to obtain good alignment of the load cell with the rest of the system. The only way the cone could be aligned horizontally was by drilling the holes in the diaphragm oversize so that the diaphragm would slide from side to side with the bolts slightly loosened. The load cell had to be positioned by eye prior to bolting the diaphragm in place. Then the whole thing was bolted to the air bearing. Therefore the cell alignment was at best crude from the beginning. Then after the cell, cap, and cone assembly were bolted on the air bearing, it was necessary to loosen the diaphragm bolts and slide the diaphragm in order to obtain alignment of the plate and cone. Thus, by the time measurements were taken, the load cell was probably considerably off center as far as vertical load was concerned.

Some measurements were taken with this apparatus. In the first try, without the Farol normal force gear in place, the noise
level was greater than the signal by orders of magnitude. This probably was once again from thrust in the rotational bearing which was transmitted to the crystal since no diaphragm was in place below the plate. Some auxiliary Farol normal force equipment was obtained and this gear was placed below the plate in order to avoid noise from the bearing. The results obtained this time were quite similar to those from some of the poorer experiments with the load cell below the plate.

Discussion

In describing the experiments we have deliberately refrained from giving a complete interpretation of the meaning of each set of results. Even after having the advantage of observing all of them, on a number of points we are still left with questions which must be answered before a final design can be recommended. To be sure, the results of certain experiments indicate possible or probable answers to these questions, but these speculations can only be verified by more experimentation. In this section our analysis of the interactions between the various components of the piezoelectric system with and without a sample in place is presented and the results are discussed on the basis of this analysis.

The essential elements of the measuring system, with the crystal below the plate and using the ball and cone bearing at the bottom, can be illustrated as shown in Figure 39.
Figure 39. Essential Elements of the Measuring System.
material between the plate and cone, there are two pinning points below the plate, 1 and 2 in Figure 39, and two above, 3 and 4. If diaphragm A is stiff, upon rotation, thrust from the bearing is transmitted to the crystal as explained before. If A is flexible, the plate and rod can be rotated with little effect upon the crystal since the load is essentially constant, being only the weight of the plate, connectors, and rods. The situation is not altered particularly when a low viscosity material is loaded between the plate and cone. In such a case, lateral movement of the plate takes place without affecting the crystal at the bottom. If the material has a normal force component, this can be measured with no particular difficulty. Unfortunately, all is changed if the fluid between the plates has a high viscosity. The problem is twofold in this case. First, any lateral movement of the plate due to misalignment is resisted by the fluid. Second, any slight vertical movement of the plate causes a large normal force. This is an obvious situation after it is pointed out. However, the magnitude of the force created by a few micro-inches of vertical thrust will surprise almost anyone. Williams (43) observed the same phenomenon under somewhat different circumstances and reported it in his work. Lodge (42) also comments on this subject.

In our system as shown in Figure 39, the diaphragm acts as a pivot and forces caused by fluid resistance to sideways movements of the plate are resisted in the bearing at the bottom. Vertical
forces are also transmitted through the rod to the bottom with the diaphragm offering little or no vertical resistance. Therefore, any movements of the plate in the horizontal or vertical directions due to less than perfect alignment create forces which are picked up in the measuring system as noise. This noise is reproducible and periodic in nature, one cycle corresponding with one revolution of the plate.

Figure 40 shows a much simplified version of the forces arising from lateral motion of the plate when the ball and cone bearing is in place at the bottom. In this figure, the force from the rod, $F_h$, is considered to be acting in a horizontal direction. The ball attempts to ride up out of the cone and in so doing is resisted by the fluid between the plates. The result can be a vertical force, $F_v$, in addition to the weight of the plate, fluid, and rod.

There is also a possibility that some noise occurs as a result of rotating irregularities in the plate. To illustrate this, let us presume that the cone has a flaw, this being a ridge, 0.001 inch high running from the center to one edge. Then presume the plate has a similar flaw. When the flaw in the plate crosses the one in the cone, it should cause some abnormal fluid flow, including a normal force due to squeezing the fluid. Multiply this by numerous flaws and it may be possible to account for the type of noise readings observed. The probability of this is discounted as a major noise
Figure 40. Forces Arising from a Ball and Cone Bearing.
causing factor on the basis that much of the noise was eliminated by lessening horizontal motion of the ball when it was free to slide on the glass plate.

If much of the noise is caused by misalignment, the type of bearing used at the bottom becomes the most important factor in attempting to eliminate noise. As noted previously, if a bearing can be obtained which will provide little resistance to small lateral movements but still hold the rod in the general position required, then forces due to lateral motion are minimized. Another possibility mentioned before is to resist lateral motion without allowing the transmission of vertical force components arising from resistance to the lateral motion. Also mentioned was the possibility of advantages arising from placement of the measuring system above the plate and cone. These considerations were the basis of all of our attempts to improve the measuring system.

Of the various arrangements of the components used, the copper sleeve and glass bearing plate combination was best. This arrangement was a combination of a bearing allowing lateral motion and one resisting lateral motion without transmitting this resistive force to the load cell. The clearance required between the sleeve and rod for vertical motion obviously allowed some lateral motion of the rod within the sleeve but prevented this motion from becoming excessive.

The noise level was found to be almost proportional to the amount of lateral motion of the ball across the glass plate. This
suggests several things. First, if the lateral movement could be reduced to zero, the noise level would be much lower. Second, the importance of rotating irregularities of the plate appears to be secondary. Third, it seems probable that a truly superior normal force measurement system can be obtained using a piezoelectric load cell if enough care is taken in the system design and manufacture. Our machined parts can best be described as crude compared with the precision work that can be provided by skilled craftsmen with good machines. It seems improbable that poorly machined components can be used to obtain precise measurements. Fourth, a major amount of the noise is probably due to vertical movement of the plate as the ball slides across the glass. We used ordinary window pane glass for the bearing plate. This is not extremely uniform in thickness and a small amount of vertical movement undoubtedly occurs due to the ball sliding over a non-uniform surface. Also, with a lateral movement of several thousands of an inch, trigonometry dictates that there will be some vertical movement due to the change in angle.

The decrease in noise due to using two glass plates with ball bearings between them is puzzling. Our original thought was to use the ball bearings to assure that no horizontal force components were being resisted in the crystal. However, ball bearings are notoriously non-round, and furthermore, little movement of them was observed. In retrospect, our opinion is that the
reduction in noise was due more to allowing increased vertical motion than to any transverse loading effect. Rough calculations indicate that the glass would bend 10 to 20 micro-inches under the normal force loads we were observing. With this much movement possible the signal noise could be attenuated to a large degree. An experimental observation supporting this notion is that the response was considerably worse with this arrangement, being on the order of 2 seconds. Without the ball bearings and second plate in place, the response appeared to be 0.5 seconds or less, as nearly as could be determined with the amount of noise present.

It is not known why placing dental dam on the glass plate helped, but two theories can be advanced. One is that under load the dental dam compressed and expanded slightly, thereby attenuating the signal. This seems to be denied by the fact that no marked decrease in response was observed. The other is that the dental dam cut down extraneous lateral motion at the bearing point. This would support the theory that an exceptionally well aligned system with little lateral motion would operate much better.

We believe the steady state values reported in Table 17 for both normal force and tangential stress on our sample are adequate. We also believe that normal force response for our materials is not measurably different than tangential response when the measuring system is rigid enough.

The attempts to take measurements with the crystal placed above the plate and cone were too crude to allow any reasonable con-
elusions regarding the advantages or disadvantages of this location. These were undertaken on a short term basis, more to become acquainted with the possibilities of placing the load cell in that location than anything else.

Possible alterations in the equipment

If a viscometer of the same general characteristics as the rheogoniometer were to be built from scratch, including a normal force measuring system, it appears more convenient to place the normal force apparatus above the plate and cone. The advantage arises from having the measuring system out of contact with any rotating parts of the machine, thus allowing easier and more permanent alignment of the system. This does not mean that noise due to rotation is eliminated, but, with the measuring system out of the way, it would be easier to find and eliminate the sources of noise. It is still necessary to provide a bearing arrangement below the plate which will eliminate vertical force components due to horizontal motion of the plate and, or, of the ball on the rod at the bearing surface.

When working with the machine, we were not free to arrange the components at will. Nonetheless, it appears to be feasible to produce adaptors which would permit the normal force system to be placed satisfactorily above the plate and cone. One possible design was presented earlier. Another possible design for this case is
given in Figure 41. With this design it is necessary to build a firm support at the top (A). The support might be welded or bolted to the lathe bed which is the vertical support for the measuring head of the rheogoniometer. We prefer the design of Figure 41 for several reasons. First, it has the major advantage over that of Figure 38 of requiring less precise machining. Second, the measuring system is above the air bearing which will eliminate most horizontal stresses. Third, alignment of the cone is much simpler with the load cell in this position. Fourth, although the arrangement shown has a diaphragm in place, it is doubtful that one is necessary. If a diaphragm is necessary, it can be made very stiff, since the bearing is no longer associated with it, and since the load cell is very rigid. It is necessary for the diaphragm to be stiff in order to allow cone alignment. The load cell is designed to stand 5,000 lbs pressure. A constant pressure on the cell does not affect its measuring capabilities since the charge produced by this force can be shorted out. Thus, with a large constant force on the crystal, a small differential force can still be measured. Therefore, the clamp on the top of the torsion bar can be loosened and the torsion bar held firmly in place by an applied pressure on the load cell from above as shown in b. Tangential forces can still be measured in the same way as before and normal forces can be measured with the load cell.

Under the plate, there are numerous possible arrangements,
Figure 41. Suggested Mountings of the Load Cell.
both with the load cell above or below the plate and cone. The ball and cone bearing, sleeves of various types combined with various bearing plates at the bottom, variations in diaphragm rigidity, and allowable variations in vertical play have been discussed. We will mention one more possible improvement. If a superior bearing instead of a sleeve could be mounted which would hold the rod in place within very close tolerances and yet allow complete freedom of vertical motion, it seems likely that the noise level would be much improved. An air bearing would be best suited for this purpose.

Discussion of Farol equipment

Based on our experience, a few comments on the normal force measuring equipment provided with the basic rheogoniometer can be made.

The Farol equipment has a normal force spring, locked at one end and supported at the other by the combination of a spring and positioning servo mechanism. Under the center, where the rod down from the plate is supported, there is a sensitive transducer. The function of this is to act as a centering device by detecting vertical movement and signaling the servo to push up or down on its end of the bar in such a way as to reposition the rod to the same vertical position. The normal force is determined by measuring the vertical movement of the end of the bar. This movement is calibrated
with normal force at the middle. In the limit, if the transducer responds to differential sized movements, and if the fluid provides no resistance to movement, response is limited only by the electronics and the servo mechanism. The response, therefore, is at best on the order of a few seconds, which is about as good as can be expected from a servo. This is not too bad if fast response is not needed. However when a thick (viscous) liquid sample is in place, their servo mechanism goes into oscillation. This occurs because the fluid resists movement and consequently the servo first overshoots and then over compensates in the other direction.

In a prospectus on a new machine, they propose to avoid this problem by fixing both ends, using a heavy normal force bar, and allowing it to move up to a hundred micro-inches or more at the center. This movement is calibrated and a measure of it gives the normal force. It is true that they will avoid the problem of oscillation by using this procedure but they do so at the expense of instrument response. With a viscous fluid in place, they will have a response of minutes to hours, depending on the viscosity of the fluid. We have seen that a vertical movement on the order of ten to fifteen micro-inches takes about two seconds to accomplish at a fluid viscosity of one hundred poise. Response should decrease linearly with an increase in vertical movement, and should also decrease linearly with an increase in viscosity. Thus, in their proposed arrangement it is unreasonable to expect that they will obtain fast normal force response.
Conclusions and Recommendations

The piezoelectric load cell is basically a superior device for measuring short term transient forces as compared to the normal force measuring methods now in use. Even in its fairly crude developmental stage our system should be adequate for studying normal force transients in fluids with viscosities up to several hundred poises. Furthermore, the low cost of the measuring system, (load cell, charge amplifier, and leads cost less than $1,000 total) is a major advantage compared to the Farol equipment, which costs nearly $5,000.

It appears encouraging to us that the problems left to be conquered are not in the measuring device itself, but in the mechanical placement of the load cell and in the mechanical problem of rotating a plate without allowing or causing extraneous vertical and, or, lateral motion. These types of problems can usually be solved by expenditure of time and money.

For future work with this apparatus, we first recommend that adaptors be made to allow placing the measuring system above the plate, cone, and air bearing, perhaps as is shown in Figure 41. After this is accomplished, the problems of alignment and of finding and placing a better bearing at the bottom of the rod through the driving system can be isolated and solved one at a time.
APPENDIX B

MECHANICAL EQUIPMENT RESPONSE

Denny (2) has treated this problem in some detail and the reader is referred to his work for a thorough discussion. Neglecting inertial effects, when the angle between the plate and cone is small the equation relating angular displacement of the cone, $\varphi$, to time is

$$\varphi = \varphi_{\text{max}} \left(1 - e^{-\frac{K_m}{V}t}\right)$$

where $t$ is time in seconds, $K_m$ is a constant in $\text{dyne-cm/radian}$ and equals $k_\tau \times 10^4/2.54$, $V$ is constant or variable depending upon whether viscosity is constant or variable, and equals $\frac{2\pi R^3 \mu}{3\theta}$. In these equations, $\varphi_{\text{max}}$ is maximum rotational displacement in radians of the cone at the given set of conditions, $R$ is the cone radius in cm, $\mu$ is viscosity of the liquid in poises, $\theta$ is the angle between the plate and cone, and $k_\tau$ is the torsion bar constant. If two per cent is chosen as a practical limit for our ability to read the difference between any $\varphi$ and $\varphi_{\text{max}}$, the time required to reach this value, $t_R$, can be calculated by setting $-\frac{K_m}{V}t_R$ equal to 0.98 or $-\frac{K_m}{V}t_R$ equal to 0.02. Therefore

$$t_R = \frac{V}{K_m} \ln(50) \approx 3.9 \frac{V}{K_m}$$
For a shear thinning non-Newtonian liquid, the response is faster. Since there is more viscous resistance while \( \phi \) is rising than after steady state is reached, consequently \( \phi \) increases more rapidly during this period than it would if the liquid were Newtonian with a viscosity equal to that calculated at steady state. For a viscoelastic liquid, the response can be much slower if the rigidity of the liquid in its elastic range is low compared to the rigidity of the torsion bar.

In working with the normal force equipment and in analyzing Denny's data, an experimental method was needed in order to verify that the equipment response was indeed that which is calculated using Equation 67. Since there were no Newtonian viscosity standards available with viscosities greater than \( 10^3 \) poise, it was necessary to find a suitable liquid before we could proceed with our work. The problem was solved by cooling glycerine to approximately \(-40^\circ C\) by surrounding the plate and cone with dry ice. Since viscosity is measured during the determination of response, fine temperature control was not needed. In Figure 42, the results of a typical experiment using cold glycerine, a \( \frac{1}{4} \), 2.5 cm cone, and the 0.25 inch torsion bar are shown. In this case \( V = 7.8 \times 10^2 \mu \), \( K = 2.08 \times 10^9 \), and \( \mu = 4.06 \times 10^5 \). Therefore, the theoretical amount of time required to reach 98% of the maximum displacement is

\[
\tau_R = \frac{3.9 \times 7.8 \times 10^2 \times 4.06 \times 10^5}{2.08 \times 10^9} = 0.59 \text{ seconds}
\]
Figure 42. Response with Cold Glycerine.
The actual response time was approximately 1.5 seconds. The discrepancy can be due to either a viscoelastic component in the glycerine or to flexibility in parts of the rheogoniometer other than the torsion bar. The latter appears to be a more likely possibility. In any case, the mechanical response is fast enough when using cold glycerine so that this method can be used to test the effects when individual mechanical components are switched. This procedure was used in testing the effect on response of using various diaphragms with the normal force equipment in place.

Using Equation 67 and a plate and cone radius which would give the area of both the plate and cone and the couette portion of the Mooney cup, the response time required to reach 98% of the maximum reading was calculated as approximately one second at a viscosity of one thousand poise and one thousandth of a second at one poise. However, inertial effects become important at low viscosities and a minimum response time of approximately six hundredths of a second is apparent from an analysis of the experimental results.

In analyzing Denny's results, a solid stainless steel lower platen holder was substituted for the thin walled one originally supplied with the rheogoniometer. Using a very viscous polymethylmethacrylate melt sample (\( \mu = 2 \times 10^6 \) poise), the response of the lower platen was checked by monitoring its movement with one of the Farol transducers. It was found that the lower platen
reached its calculated rotational speed in less than half a second. Consequently, viscoelasticity in the fluid is the only possibility for accounting for the slow response seen in Denny's data.
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212


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