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VISCO-ELASTIC PROPERTIES  
OF  
ALUMINUM SOAP - HYDROCARBON GELS  
by  
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A THESIS SUBMITTED IN PARTIAL FULFILMENT OF  
THE REQUIREMENTS FOR THE DEGREE OF  
MASTER OF Applied Science  
in the Department  
of  
Physics

We accept this thesis as conforming to the  
standard required from candidates for the  
degree of MASTER OF Applied Science

Members of the Department of  
Physics  
THE UNIVERSITY OF BRITISH COLUMBIA  
September, 1951

## ABSTRACT

Measurements of velocity of propagation and damping of transverse sonic waves have been made for aluminum soap-hydrocarbon gels. The frequency range covered is 100 to 1000 cycles per second. The experimental results have been fitted to theoretical mechanical models. The mechanical behavior of the gels investigated can be approximated by a Retarded Maxwell Element with a ratio of parallel to series viscosity of about 0.01. The rigidity of the model is of the order of  $10^3$  dynes per square centimeter and the series viscous component of the order of 1 to 10 poise, giving a relaxation time of the order of  $10^{-3}$  seconds.

### ACKNOWLEDGEMENTS

The author wishes to express his appreciation:

To the Defence Research Board for granting leave of absence and financial assistance.

To Dr. E.J. Wiggins, under whose direction this work was started at the Suffield Experimental Station, for his continued advice and encouragement.

To Dr. A.M. Crooker, of the University of British Columbia, for the loan of optical components and for much helpful advice.

To Dr. F.A. Kaempffer, of the University of British Columbia, who acted as supervisor for this work at the University.

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## I. INTRODUCTION

### a) General

Dispersions of aluminum soaps in hydrocarbons such as benzene, gasoline, etc. can exist in a number of different forms ranging from mixtures of discrete swollen lumps of soap in the solvent through visco-elastic gels( or jellies ) to completely mobile solutions. The gel state is of particular interest because of the rather special visco-elastic properties. The physical properties of these gels differ markedly from those of ordinary liquids and render them useful for a number of applications, eg. lubricating greases, pharmaceutical preparations, etc.. During the last war aluminum soap-gasoline gels were used for incendiary bomb charging and flame thrower fuels<sup>1</sup>. A flame thrower fuel should have a high viscosity during flight to prevent shattering and a low viscosity during handling and operation of the flame thrower to prevent frictional losses, permit low firing pressures etc.. Elasticity is also believed to be important in preventing shattering during flight. However, the precise effect of the properties on the firing performance of a fuel is not completely understood at the present time and will not be discussed here.

### b) Material

The physical and chemical properties of aluminum soap - hydrocarbon gels have been discussed by Rideal<sup>2</sup> and others . They are quite stable and are characterized by a relatively high viscosity and rigidity. The actual physical properties

obtained depend on the chain length of the soap, the solvent, the presence of peptizing agents, temperature, etc.. The structure is thought to be two phase. One phase consists of a network of solvated material, the second is a solution of the soap in the solvent and fills the interstices of the network. The network may consist either of relatively rigid crystals or of elastic long chain molecules. Junctions in the network are formed by mechanical interlocking, by hydrogen bonding, true chemical links, etc..

Sheffer<sup>3</sup> has carried out viscosity and osmotic pressure measurements on dilute benzene solutions of aluminum dicaprylate, dilaurate, dimyristate, dipalmitate, distearate, and monostearate. He concludes that the soaps are polymers of high molecular weight ( 60,000 to 900,000 ) which are formed by weak intermolecular links, probably hydrogen bonds.

When preparing a gel it is usual to add a peptizing agent to promote swelling and to increase the solubility of the soap. Peptizers are compounds with strong co-ordinating properties eg. amines, alcohols, phenols, fatty acids etc., and their action is a breaking of links in the soap chains by a preferential linking with the peptizer. After solution is complete the addition of more peptizer will of course lower the viscosity by reducing the chain length.

It is very difficult to exactly duplicate conditions of manufacture of the soap, so the molecular weight of the soap varies considerably from batch to batch. Water is a strong peptizer so that it and other impurities have a very marked

effect on the gelling properties of the soap and on the aging of the resulting gel. For these reasons it is extremely difficult to get consistent experimental results even when gels are prepared with the greatest care in the choice of materials and in mixing and storage.

### c) The Mechanical Properties of High Polymers

#### The Use of Mechanical Models.

The use of mechanical (or electrical) models to represent the mechanical behavior of visco-elastic materials has been considered in detail by Alfrey<sup>4</sup>, Burgers<sup>5</sup> and others.

The behavior of perfectly elastic materials is described by a set of elastic constants. If the material is isotropic the number of constants required reduces to two, Lamé's constants, Young's modulus and the Bulk modulus, etc.. In the ideal case the energy of deformation is completely recoverable. All the work done in producing a strain is recovered when the stresses are removed.

The response of a Newtonian liquid to shearing stress is pure flow, the velocity gradient depending on the viscosity and the applied shearing stress. In this case the deformation is not recoverable and all the work done by the applied forces is dissipated as Joule heat. Where the rate of flow is not a linear function of the applied stress, the fluid is said to be non-Newtonian. Also in some cases the mechanical properties depend upon the previous mechanical treatment of the sample; if flow is accompanied by structural changes it takes a finite time for the material to return to its rested



state after mechanical working. This phenomenon is called thixotropy.

Many materials, including hydrocarbon gels, exhibit neither pure elastic or Newtonian behavior. Their mechanical behavior can only be described by considering elastic and viscous effects at the same time. Alfrey and Doty<sup>6</sup> have discussed the common methods of describing visco-elastic behavior. We wish to consider briefly the use of mechanical (or electrical) models.

A Maxwell element<sup>7</sup> consisting of a Hookean spring in



series with a "Newtonian" dashpot describes the behavior of a material which undergoes an instantaneous elastic deformation and at the same time flows upon the application of a stress. Such an element is illustrated in figure (1). Since the flow deformation depends on both the magnitude and duration of the stress it is necessary to consider the rate of change of deformation of the whole element.

Maxwell Element

Figure 1

If shearing stress =  $S$  (dynes/cm.<sup>2</sup>)

modulus of rigidity =  $G$  (dynes/cm<sup>2</sup>)

elastic displacement =  $\gamma_1 = S/G$

flow displacement =  $\gamma_2$

total displacement =  $\gamma = \gamma_1 + \gamma_2$

then

$$\frac{d\gamma_1}{dt} = \frac{1}{G} \frac{dS}{dt}$$

$$\frac{d\gamma}{dt} = \frac{1}{\eta} S$$

$$\frac{d\gamma}{dt} = \frac{1}{\eta} S + \frac{1}{G} \frac{dS}{dt}$$

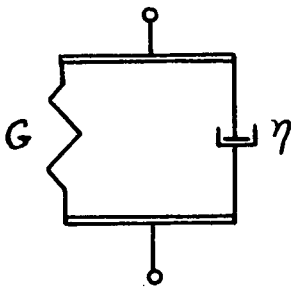
For the case where the sample is forced to suddenly undergo a given deformation and is then held at this constant strain

$$\frac{d\gamma}{dt} = \frac{1}{\eta} S + \frac{1}{G} \frac{dS}{dt} = 0$$

$$S = S_0 e^{-\frac{G}{\eta} t}$$

The stress decays exponentially with time and the ratio  $\eta/G$  is called the relaxation time of the material.

The Voigt or retarded elastic element, figure 2., is



Voigt Element

Figure 2

used to represent the behavior of those materials which undergo an elastic deformation upon the application of stress but requires a certain time in which to take up the new equilibrium position.

Such a damped or retarded elastic response is like that of a spring surrounded by a viscous medium. The displacement of the two components must be the same and the

differential equation describing the displacement is

$$\eta \frac{d\gamma}{dt} + G\gamma = S$$

For a given stress,  $S$ , the deformation time relation is given by the equation

$$\gamma = \frac{S}{G} (1 - e^{-\frac{G}{\eta} t})$$

The quantity  $\tau = \eta/G$  is called the retardation time of the element. Upon the removal of stress the sample will return to its original shape according to the equation

$$\gamma = \gamma_0 e^{-t/\tau}$$

The response to a constant stress applied for a time interval  $t_1$  to  $t_2$  is illustrated in figure 3. for the four types of material discussed above.

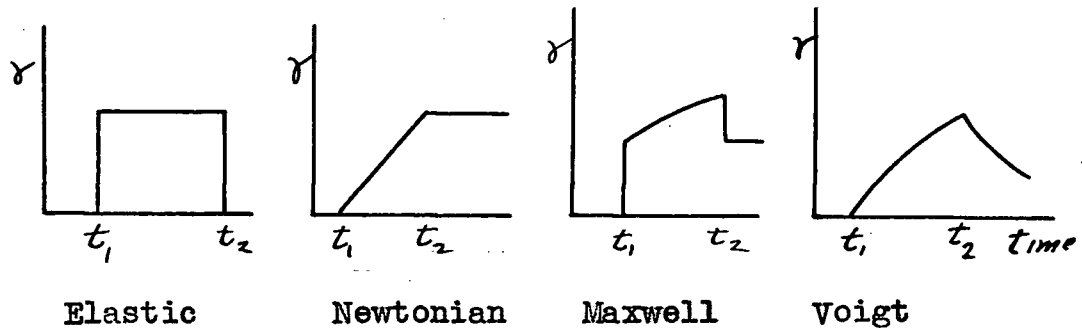


Figure 3.

The effect of the mass of the material has been neglected so far. This may only be so for the static case, for elastic response, and for steady state conditions in considering flow. Where forces vary with respect to time the inertial forces of the material must be considered. Essentially the mass of the elements of a body delays the response of parts remote from the points of application of the stresses. Disturbances produced by the application of forces at points of the body are propagated throughout the body by elastic waves. To construct a model to represent the dynamic behavior of a material it is necessary to include <sup>point</sup> masses at appropriate places in the system of springs and dashpots.

The use of mechanical (or electrical) models to represent the mechanical properties of visco-elastic systems serves two main purposes. The first, and most obvious, is that they provide a convenient and relatively simple means of recording and using data obtained experimentally,

especially in those cases where there is no adequate theoretical basis for reference. Secondly, it is sometimes possible to associate the various components of the model with more or less elementary processes of the material itself.<sup>4</sup>

There is obviously no reason to expect only one Maxwell element or Voigt model to represent the entire mechanical behavior of a material. Many different internal mechanisms determine the mechanical response, each with its own distribution of parameters. However, it is usually possible to use a discrete number of parameters, Maxwell elements in parallel, or Voigt elements in series.

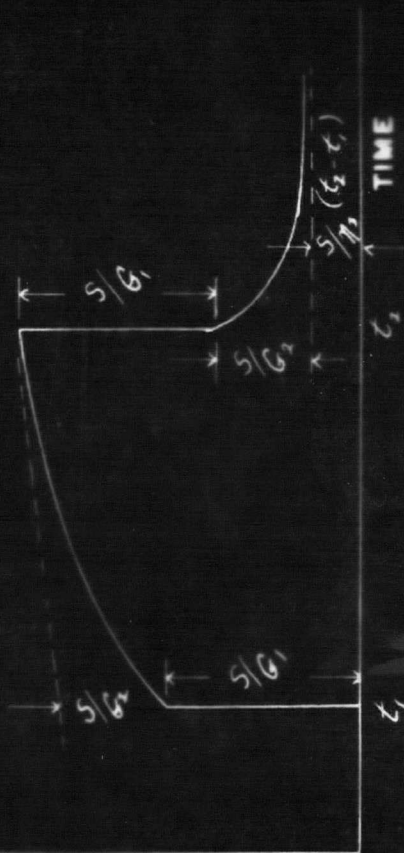
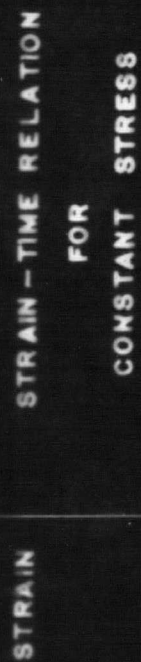
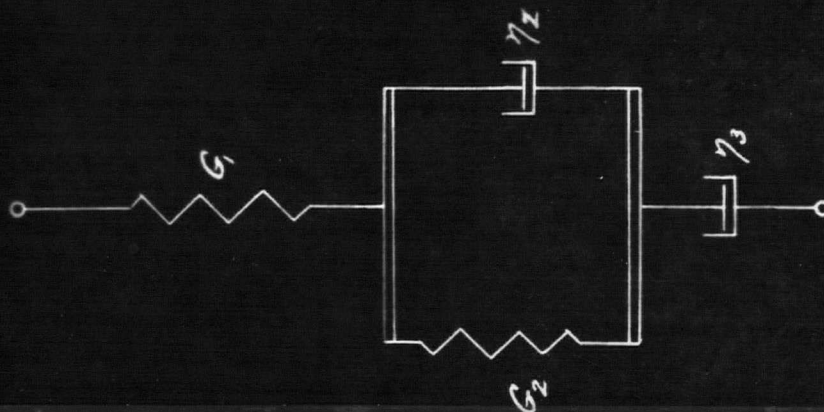
The time scale of an experiment is important in determining a suitable model. By time scale is meant the effective length of time taken to make a measurement of response to stress. Consider a system made up of Maxwell elements in parallel, with the corresponding relaxation times decreasing in going from element 1 to element 2 etc.,  $\tau_1 \ll \tau_2, \tau_2 \ll \tau_3$ . Upon the application of a stress all elements will undergo expansion from both elastic deformation and flow. If the duration of the stress is long in comparison with  $\tau_1$  but short in comparison with  $\tau_3$ , the effect of the applied stress will be essentially different on the corresponding elements though their total displacements are the same. The response of element 1 will be mostly due to flow while that of element 3 will be mostly elastic deformation. In other words, if this were the only observation made, the elastic part of element 1 and the viscous part of element 3 would

practically not be observed. In order to separate the effects of all six parameters in this model it would be necessary to perform at least three experiments with time scales corresponding to the three relaxation times. The expansion to any number of elements is obvious.

In dealing with molecular mechanisms there will not be a discrete distribution of relaxation times for each individual mechanism but a continuous distribution about some value. However, it is usually possible to lump them into a single element, at least as a first approximation. Alfrey<sup>4</sup> takes the four parameter model shown in figure 4 as the simplest representation of the behavior of a polymer in shear.  $G_1$  provides the instantaneous elastic response,  $G_2$  and  $\eta_2$  the retarded elastic response and  $\eta_3$  true flow. The strain time relationship for such a system is illustrated in figure 4.

The instantaneous elastic response represented by  $G_1$  corresponds to the instantaneous deformation of the whole structure upon the application of stress. Such a deformation would involve changes of distance between neighboring molecules, small shape changes of molecules, etc..

The modulus  $G_2$  is taken to represent the so-called configurational elasticity. In the unstressed state the macromolecules are constantly changing in shape but obey a definite distribution law. Upon the application of stress their shapes, on the average, will be changed from the equilibrium position. The effect is completely reversible



since the molecules will revert to their original equilibrium position upon the removal of stress. Since it is reversible it may be considered as an elastic effect.

The true flow represented by  $\eta_3$  and the viscous component connected with the configurational elasticity,  $\eta_2$ , are governed by the same mechanisms. The biased thermal diffusion of molecular segments .

## II Purpose and Theory of the Experiment

The investigation d~~e~~scribed here is part of a broader program of experiments planned by the Defence Research Board Suffield Experimental Station. As explained in Part I, it is not expected that the measurements over the relatively narrow frequency range used here will describe the behavior of the material adequately. Other investigators are working of the measurement of properties over time intervals of the order of several seconds down to intervals of the order of  $1/50$  th of a second. The measurements to be described here extend the time interval down to about 0.001 seconds.

Except for the work of Van Wazer, Goldberg and Sandvik measurements of the physical properties of hydrocarbon gels has been confined to relatively long time intervals. The resonance elastometer developed by Van Wazer et al<sup>8</sup> permits measurements to about  $1/50$ th of a second. A few investigations have been made by suitable techniques on other materials, but so far as is known this is a new region of investigation for flame fuels. It is of interest not only because it will extend the data available for consideration of molecular effects but also the time periods involved here are of the same order of magni~~t~~ude as those involved in firing. Thus the measurements are possibly of direct emperical use in assessing fuels.

The behavior of visco-elastic systems over short time intervals is much easier to study by means of periodically varying stresses rather than attempting to study very rapid



transient phenomena. Ferry<sup>9</sup> has described a method of measuring the physical properties of concentrated polymer solutions by means of transverse sonic waves. This method depends upon the material being optically clear and strain birefringent. It was known that hydrocarbon gels are strain birefringent<sup>14</sup> and since it was thought that slip at polymer-instrument interfaces was a possible source of error in direct measurements of stress and strain this method was chosen to begin the investigation of physical properties in the higher frequency range. It is hoped that it will be possible to make measurements in the same frequency range by other methods and investigate the effect of slip at some later date. It is known that very pronounced slip can be obtained in rotating cylinder viscometers with rapidly increasing rate of shear. However, it is not known whether this effect can be produced or observed at higher frequencies.

When the mass of the material can be neglected the response to a shearing stress can be completely described either by a complex viscosity<sup>10</sup>,

$$\bar{\eta} = \eta' - i \eta'' \quad (1)$$

or a complex rigidity<sup>11</sup>

$$\bar{G} = G' + i G'' \quad (2)$$

With high polymers Poisson's Ratio is usually very nearly one half and so  $E = 3G$ , where  $E$  is Young's Modulus and  $G$  is the shear modulus as before. Since behavior in shear is generally easier to study experimentally we consider only behavior in shear. The real part of the complex rigidity  $G'$  is equal to the component of the stress in phase with the

strain divided by the strain. The real part of the complex viscosity  $\eta'$  is the component of stress in phase with the rate of strain divided by the rate of strain. If  $\omega$  is  $2\pi$  times the frequency then

$$G'' = \omega \eta' \quad , \quad \eta'' = G' / \omega \quad \text{etc.}$$

The values of  $G'$  and  $G''$  obtained experimentally generally vary with frequency and mechanical models are made up by combining springs and dashpots to duplicate the experimental results.<sup>12</sup>

For a Maxwell element with a spring of rigidity  $G$  and dashpot of viscosity  $\eta$  and relaxation time  $\tau = \eta / G$

$$G' = G \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} \quad (3a)$$

$$\eta' = \eta \frac{1}{1 + \omega^2 \tau^2} \quad (3b)$$

For a Voigt element

$$G' = G \quad (4a)$$

$$\eta' = \eta \quad (4b)$$

the values being independent of frequency in this case.

For a retarded Maxwell element, that is a spring with rigidity  $G$  in series with a dashpot of viscosity  $\eta_s$  and in parallel with a dashpot of viscosity  $\eta_p$  :

$$\tau_s = \eta_s / G \quad (5a)$$

$$\tau_p = \eta_p / G \quad (5b)$$

$$G' = G \frac{\omega^2 \tau_s^2}{[1 + \omega^2 (\tau_s + \tau_p)^2]} \quad (5c)$$

$$\eta' = \eta_s \frac{[1 + \omega^2 \tau_p (\tau_s + \tau_p)]}{[1 + \omega^2 (\tau_s + \tau_p)^2]} \quad (5d)$$

In our case we wish to determine the mechanical behavior by studying the propagation of transverse sound waves. We assume that the elastic wave may be described by the following:

$$u = u_0 e^{i\omega t} e^{-[i\frac{2\pi}{\lambda} + \frac{1}{X_0}]\chi} \quad (6)$$

where  $u$  is the displacement.

By analogy with the theory for a perfectly elastic solid one can define a new rigidity  $\tilde{G}$  for a visco-elastic material such that the differential equation describing the motion is

$$\rho \frac{\partial^2 u}{\partial t^2} = \tilde{G} \frac{\partial^2 u}{\partial \chi^2} \quad (7)$$

and

$$\tilde{G} = \frac{\omega^2 \lambda^2 \rho}{4\pi^2} = v^2 \rho \quad (8)$$

where  $v$  is the measured velocity of propagation of the wave. The two quantities  $\tilde{G}$  and  $\lambda/X_0$  may then be used to describe the physical properties of the material at the frequency at which they were measured.

The relation between  $\tilde{G}$  and  $\lambda/X_0$ , and  $G'$  and  $\eta'$ , may be found by substituting from (2) into the differential equation

$$\rho \frac{\partial^2 u}{\partial t^2} = (G' + i\omega\eta') \frac{\partial^2 u}{\partial \chi^2}$$

then putting

$$\omega^2 \rho = \frac{4\pi^2 \tilde{G}}{\lambda^2}$$

from equation (8), giving

$$-\frac{4\pi^2}{\lambda^2} \tilde{G} = (G' + i\omega\eta') \left( i\frac{2\pi}{\lambda} + \frac{1}{x_0} \right)^2$$

Equating real and imaginary parts

$$\frac{4\pi^2}{\lambda^2} \tilde{G} = \left( \frac{4\pi^2}{\lambda^2} - \frac{1}{x_0^2} \right) G' - \frac{4\pi\omega\eta'}{\lambda x_0}$$

$$\frac{4\pi}{\lambda x_0} G' + \omega\eta' \left( \frac{4\pi^2}{\lambda^2} - \frac{1}{x_0^2} \right)^2 = 0$$

and

$$G' = \tilde{G} \frac{4\pi^2 \left[ 4\pi^2 - (\lambda/x_0)^2 \right]}{\left[ 4\pi^2 + (\lambda/x_0)^2 \right]} \quad (9a)$$

$$\eta' = \frac{\tilde{G}}{\omega} \frac{16\pi^3 (\lambda/x_0)}{\left[ 4\pi^2 + (\lambda/x_0)^2 \right]} \quad (9b)$$

The measured values may then be compared with those for theoretical models by substituting from relations such as (3), (4) or (5) into equations (9a) and (b).

For the three models considered this gives:

Maxwell Element

$$\tilde{G} = G \frac{2\omega\tau}{\omega\tau + \sqrt{1 + \omega^2\tau^2}} \quad (10a)$$

$$\lambda/x_0 = \frac{2\pi}{\omega\tau + \sqrt{1 + \omega^2\tau^2}} \quad (10b)$$

Voigt Element

$$\tilde{G} = G \frac{2(1 + \omega^2\tau^2)}{1 + \sqrt{1 + \omega^2\tau^2}} \quad (11a)$$

$$\lambda/x_0 = \frac{2\pi\omega\tau}{1 + \sqrt{1 + \omega^2\tau^2}} \quad (11b)$$

## Retarded Maxwell Element

$$\tilde{G} = G \frac{2 \omega \tau_s}{1 + \omega^2 (\tau_p + \tau_s)^2} \frac{\omega^2 \tau_s^2 + [1 + \omega^2 \tau_p (\tau_p + \tau_s)]^2}{\omega \tau_s + \sqrt{\omega^2 \tau_s^2 + [1 + \omega^2 \tau_p (\tau_p + \tau_s)]^2}} \quad (12a)$$

$$\frac{\lambda}{x_0} = \frac{2 \pi [1 + \omega^2 \tau_p (\tau_p + \tau_s)]}{\omega \tau_s + \sqrt{\omega^2 \tau_s^2 + [1 + \omega^2 \tau_p (\tau_p + \tau_s)]^2}} \quad (12b)$$

The above relations are shown graphically in figure 5.

It is perhaps easier to visualize the quantities  $G'$  and  $\eta'$  also, it is necessary to convert to these to make comparisons with other types of measurements. For the retarded Maxwell element we define  $\tau_s = \eta_s / G$  and  $\tau_p = \eta_p / G$  and the relations are:

$$G' = G \frac{\omega^2 \tau_s^2}{[1 + \omega^2 (\tau_s + \tau_p)^2]} \quad (13a)$$

$$\eta' = \eta_s \frac{[1 + \omega^2 \tau_p (\tau_s + \tau_p)]}{[1 + \omega^2 (\tau_s + \tau_p)^2]} \quad (13b)$$

These are illustrated graphically in figure 6..

For the Maxwell element the value of  $\tilde{G}$  approaches a limiting value at high frequencies and the damping is severe at low frequencies and falls to zero as the frequency is increased. For the Voigt element both  $\tilde{G}$  and the damping increase indefinitely with frequency. For the retarded Maxwell element the behavior is like that of a Maxwell element at low frequencies and of a Voigt element at high frequencies.

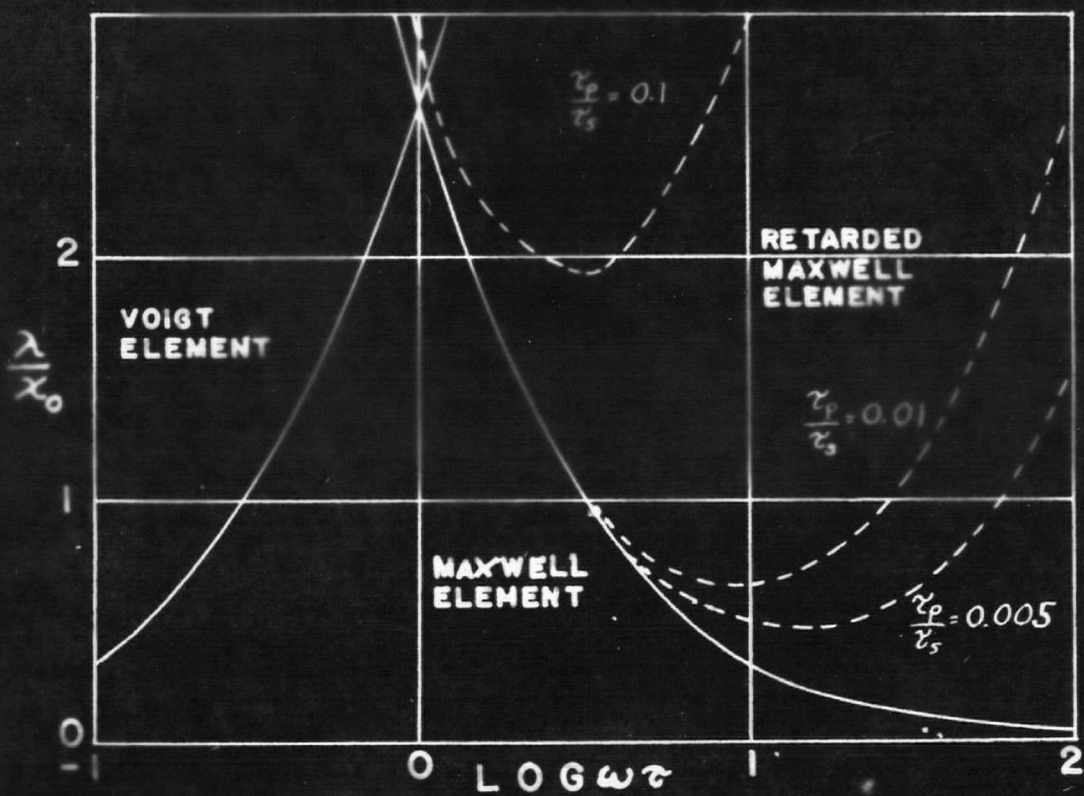
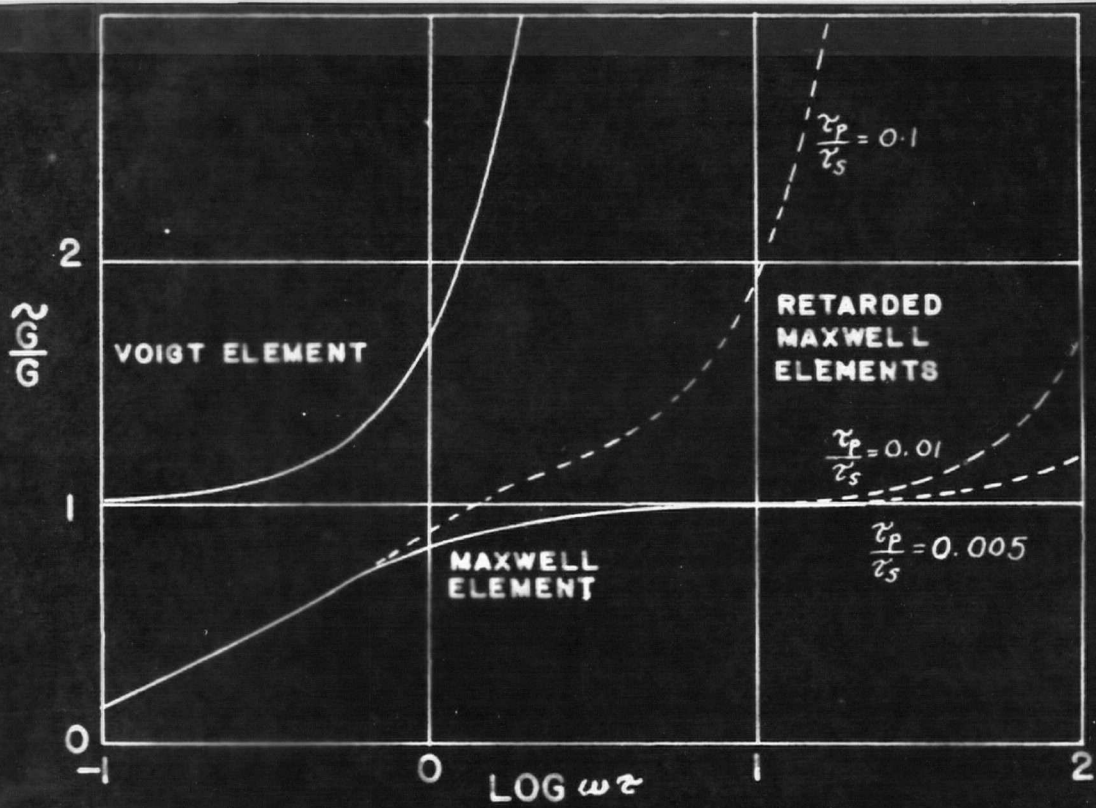
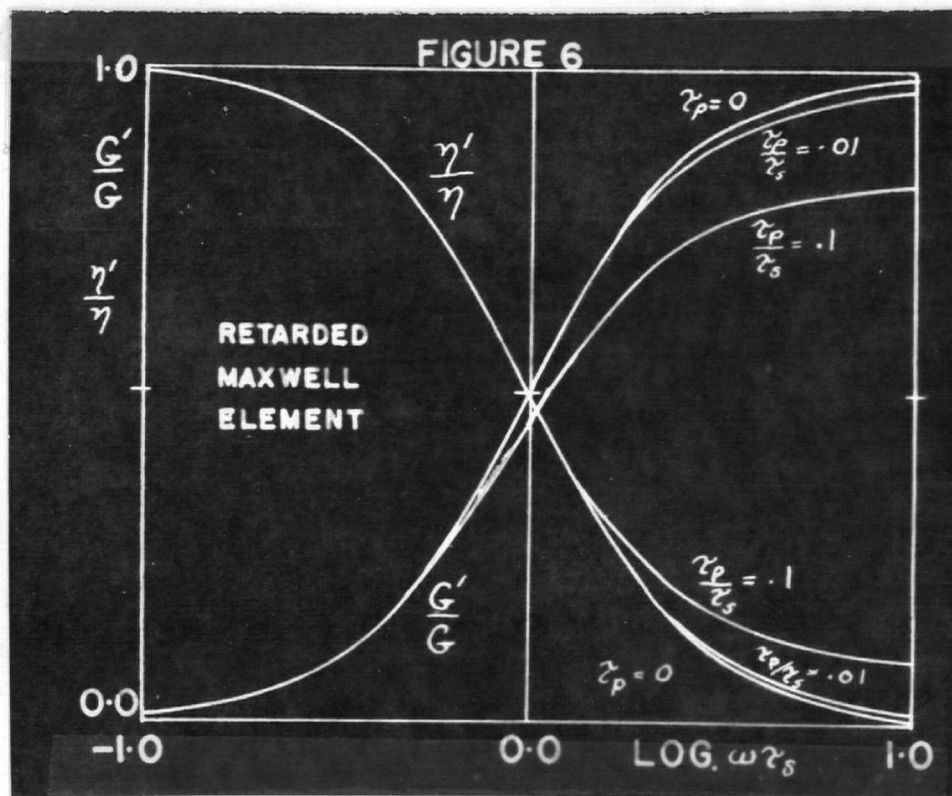


FIGURE 5



### III APPARATUS AND EXPERIMENTAL PROCEDURE

#### a) General

To obtain the values of  $\tilde{G}$  and  $\lambda/x_0$  for a given sample it is necessary to measure the velocity of propagation of a plane shear wave and also, to measure the damping of the wave. If this can be done over a wide enough frequency range then it is possible to fit the experimental data to theoretical curves and so find a model to represent the mechanical behavior of the material under the conditions of the experiment.

The experimental method used was essentially as described by Ferry<sup>9</sup>. Transverse sound waves were produced in a sample of gel by a thin vane vibrating sinusoidally in its own plane. The direction of propagation was horizontal and at right angles to the direction of observation. Under the action of the stresses produced by the shear waves the gel becomes birefringent with axes at forty five degrees to the direction of propagation of the sound wave. If the gel is observed between crossed Polaroids, with the axis of the polarizer vertical and that of the analyzer horizontal, the field will be dark in the absence of signal and will be crossed by alternate light and dark bands in the presence of a shear wave. In order to observe these light and dark bands it is necessary to, either produce standing waves in the gel, or, to use travelling waves and synchronize the source of light with the source of the sound waves. The latter is much simpler and is the method used here. The



spacing between adjacent light and dark bands corresponds to one half wavelength and thus measuring this spacing will give the wavelength of sound in the gel. However, since the intensity of light varies according to  $\sin^2 \delta$  where  $\delta$  is the relative optical retardation in the gel, it is difficult to locate the mid point of the bands accurately. An alternate method of observing the birefringence is to insert a compensator between the gel and the analyzer. If a Babinet compensator is used in the usual way with its optic axis at forty five degrees to the axes of the polarizer and analyzer, the field is crossed by light and dark bands perpendicular to its optic axis. In this case the retardation produced by the compensator is equal to the amount of double refraction introduced before it. However, if the compensator is used with its optic axis at a small angle,  $\alpha$ , from the vertical then the field is faintly illuminated all over and alternately crossed by light and dark bands as before. But the displacement produced by a small amount of double refraction introduced before it is magnified according to the relation

$$\tan \delta = - \frac{\tan \Delta}{\sin 2\alpha}$$

where  $\delta$  is the amount of strain double refraction and  $\Delta$  is the equivalent relative retardation introduced by the compensator. The effect of stroboscopically illuminating the shear wave is then to produce wavy lines crossing the field of view. The distance between successive peaks corresponds to the wavelength of sound in the gel. This method has the further advantage that if it can be assumed

that the amount of strain double refraction is proportional to the amount of strain, then measuring the decay of displacement of the lines crossing the compensator will give the damping factor for shear waves in the gel. Photographs of a 10% gelatine gel at 500 cycles per second with no compensator and at 1000 cycles per second with the compensator axis at  $5^{\circ}$  to the vertical are shown in figure 7..

#### b) Apparatus

Plate I shows the apparatus as used with the compensator. The support stand consisted of three 1 inch diameter brass rods screwed into a 1x12x12 inch brass plate. Mounted on the rods were two 3/8 inch thick aluminum plates which could be clamped at any desired point on the rods. The top plate carried the electromagnetic driver and vane. The bottom plate carried the material to be tested in a rectangular glass cell which in turn was inside a temperature control bath. Also mounted on the bottom plate was a piece of steel channel on which the optical components could be mounted. The whole assembly rested on a thick piece of foam rubber to damp out extraneous vibrations.

The principle parts of the optical system are shown in Plate I and are sketched in figure 8. The light source was a 631-P strobotron synchronized with the oscillations of the vane. Next was a three inch diameter condensing lens to direct the light through the gel. The light was polarized in the vertical direction before entering the gel by the Polaroid P. The portion of the gel in the plane

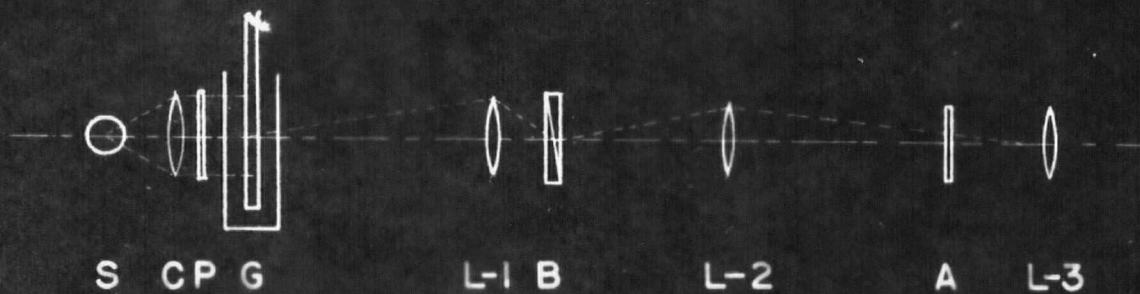
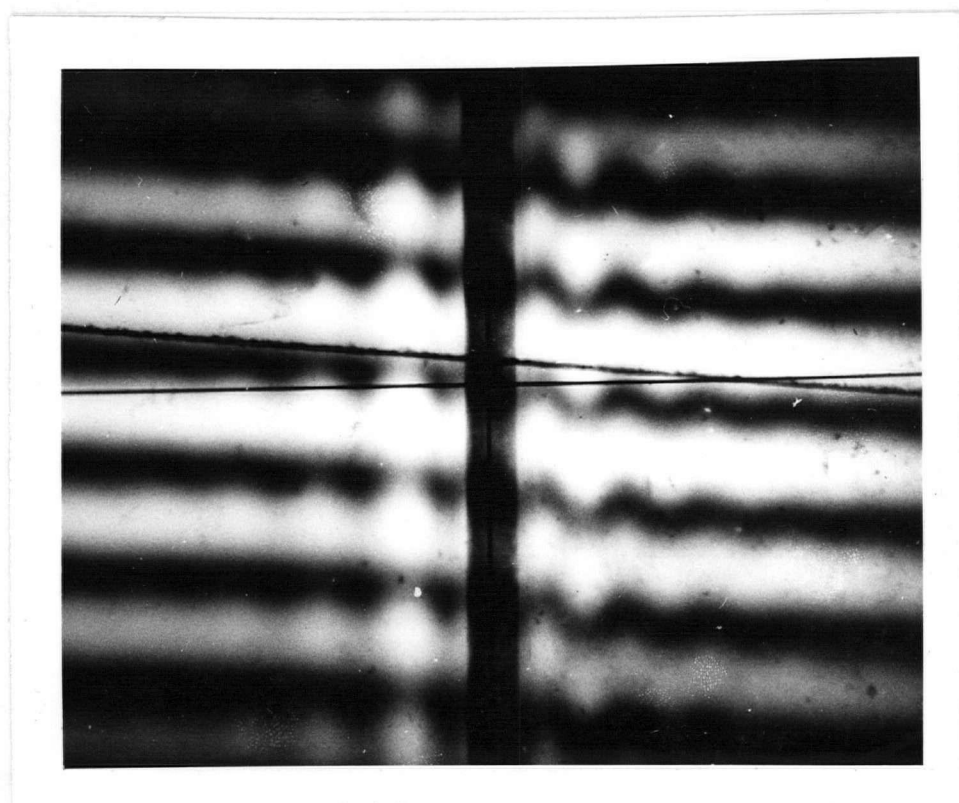
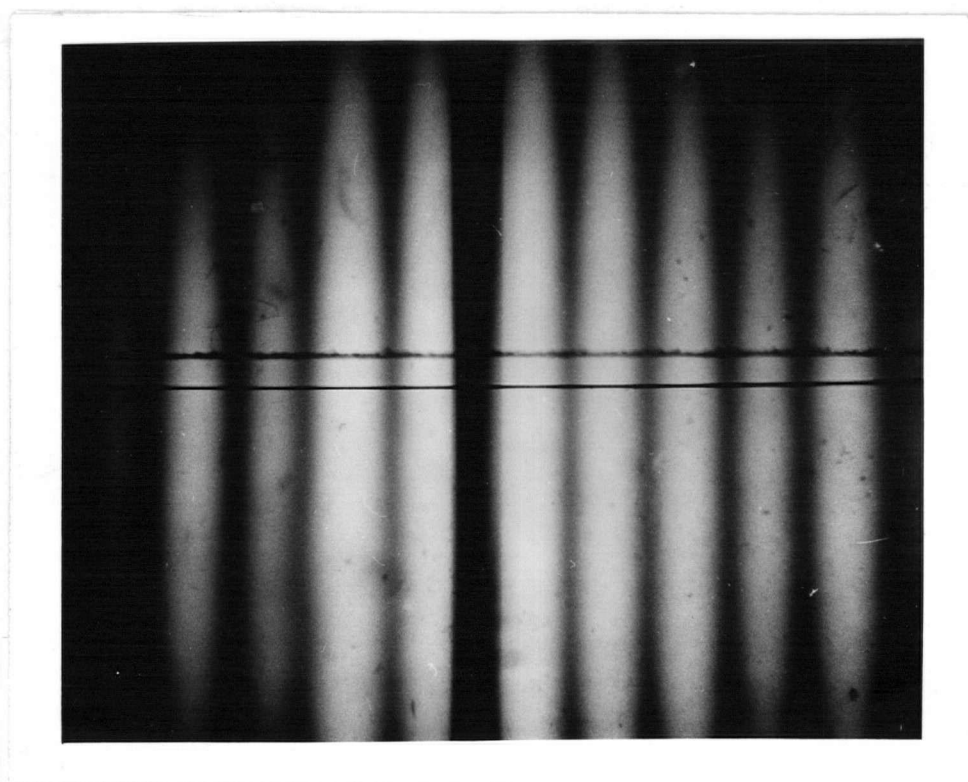


FIGURE 8



containing the glass vane and at right angles to the direction of observation was focussed onto the compensator by a two inch ( $f$  1.5) camera lens. Then the image of the strained gel and Babinet Compensator was projected through the Polaroid analyzer A onto the focal plane of a filar micrometer eyepiece by a small telescope lens. With this optical arrangement it was possible to make observations either with or without the compensator and to make wavelength measurements either directly with the crosshair and micrometer movement or with a photograph. The polarizer, analyzer and compensator could be rotated independently.

All the components except the light source, condensing lens and polarizer were mounted on a  $1\frac{1}{4}$  inch steel channel. This channel had a  $\frac{1}{4}$  inch slot milled out for most of its length and was fastened to the bottom of the lower aluminum plate by means of two  $\frac{1}{4}$  inch screws. The eyepiece, analyzer and second lens were mounted permanently onto the end of the channel. A brass carriage which slid along the top of the channel carried the compensator mounting and the objective lens. Thus it was possible to focus on the plane of the Babinet by sliding the carriage along the channel. Focussing of the plane in the gel onto the compensator was accomplished by moving the objective lens in its mount, either by means of a coarse sliding adjustment or, by means of the regular screw focussing adjustment. Adjustment of the over-all magnification was made by moving the channel on its supporting screws.

The gel sample was held in a rectangular glass cell. Two sizes were used, the first was a small absorption cell 2x3 centimeters in cross section and 5 centimeters high. The second was 2x10 centimeters in cross section and 5 centimeters high and the direction of propagation was in the lengthwise direction in both cases. The use of cells of finite size has been investigated<sup>13</sup> and it has been shown that with reasonable care the error introduced by assuming plane waves in a medium of infinite extent is small compared with the experimental errors. This is particularly so with measurements of wavelength. Measurements of damping were not made with the short cells. The large cells were constructed of ordinary window glass, cut and ground to size and cemented together with DeKohtinsky Cement. No difficulty has been encountered with these cells, either from mechanical failure or from spurious double refraction.

The temperature of the sample was controlled by holding the glass cell inside a Lucite box 8x15x5 centimeters, inside dimensions, through which water of the desired temperature was circulated. The Lucite box was held securely to the lower aluminum plate and since the glass cell was clamped between the bottom and top cover of the box the sample was held securely in place.

Vibrations were set up in the sample by means of a glass vane which was oscillated vertically in its own plane by a horn loudspeaker driver (Atlas Sound Corp.). The vane was approximately 0.1x0.6x8 centimeters made by cutting a microscope slide lengthwise and polishing down the edges.

It in turn was cemented into a slot in a duralumin adapter which was threaded on its opposite end. The adapter screwed into a small Lucite cylinder which was cemented directly to the thin bakelight diaphragm of the driver. The Lucite cylinder was cemented centrally and parallel to the axis of the driver by first mounting on a cap which threaded onto the mounting thread of the driver. It was made to match the spherical contour of the diaphragm by softening the end with glacial acetic acid and then applying sufficient force during the cementing to make the material flow.

The temperature was maintained by a circulating water system. The temperature of a bath of water was held to  $\pm 0.5$  degrees centigrade by means of a bimetallic thermo-regulator (American Instrument Co.) and a 250 watt knife heater (Cenco). Temperatures below room temperature were obtained by circulating cold tap water or by surrounding the bath with ice. Water from the bath was pumped through the Lucite bath past the cell by a small centrifugal pump (Eastern Industries Model B-1) at a bout 5 liters per minute.

Alignment of the apparatus was checked by first lining up the vertical crosshair of the micrometer eyepiece with a hanging plumb line. The vertical cross hair was then used as a reference for the rest of the components. The polarizer was set with its axis parallel to this cross hair. The Babinet compensator has a line on the stationary wedge and at right angles to the optic axis thus the angular scale and vernier could be used to measure angles from the vertical.

The analyzing Polaroid was set with its axis horizontal by finding the position for minimum transmission with both the polarizer and compensator axes vertical.

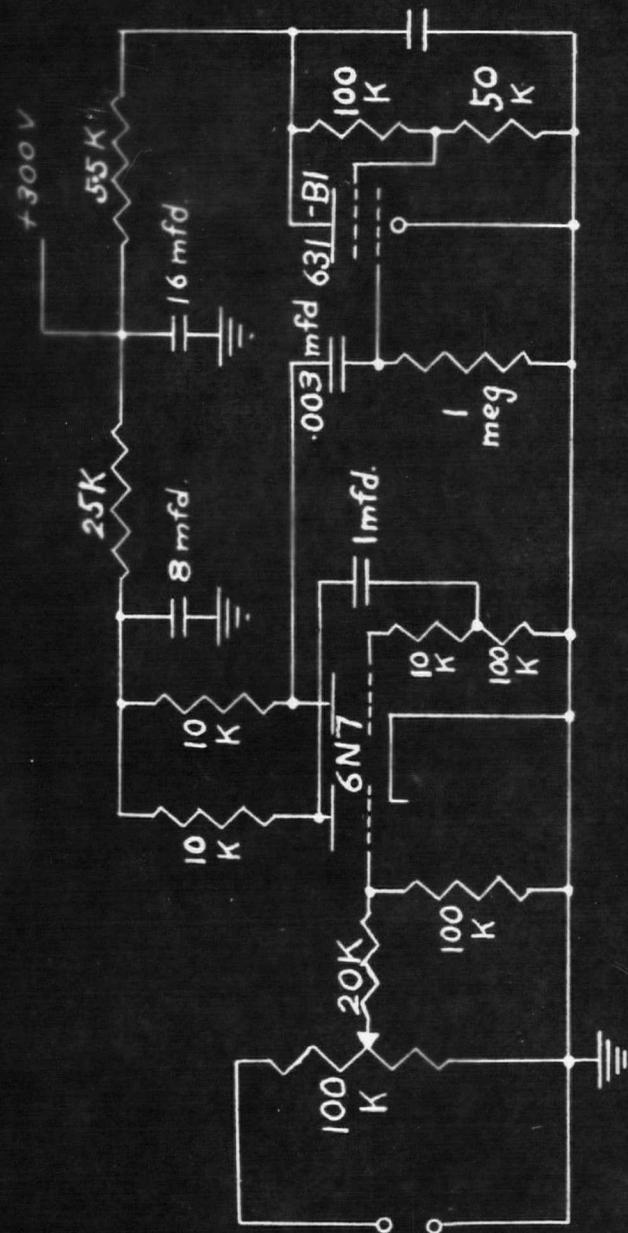
Static alignment of the glass vane was simply compared with the vertical cross hair. Whether or not its motion was truly in its own plane was also checked visually. This could be done by replacing the regular synchronized driving circuit of the strobotron with a General Radio Co. Strobotac Type 631-B. If the frequency of the light source was adjusted manually until it differed from that of the vibrating vane by a fraction of a cycle a second the vane could be seen to move slowly throughout its complete cycle. The over-all magnification was about forty times and under these conditions no appreciable lateral motion of the vane was observed.

The electro-magnetic transducer used to drive the vane was a commercial horn loudspeaker driver, rated at 25 watts, 16 ohms. The driving signal was supplied by an ordinary audio oscillator calibrated for frequency against the 60 cycle house supply. The signal was amplified and fed to the loudspeaker by a three tube audio oscillator. The amplifier was of conventional design. It consisted of a resistance capacitance coupled phase inverter and driver and a pair of push-pull output tubes transformer coupled to the load. The tubes were one 6SL7GT and two 6L6Gs. The output transformer was a Hammond type 1637. The output was also used to supply the triggering impulses for the synchronized light source.

The circuit for the strobotron light source is shown



in figure 9.. It has two main sections, the strobotron and its associated discharge circuit, and, the pulse shaping and triggering circuit. The length of the discharge is determined by the 1 microfarad condenser and the tube internal and lead resistance. With a similar circuit and a 4 microfarad condenser a duration of less than 5 microseconds is claimed for the light flash . The discharge is initiated by causing a glow discharge between the two grids. This is done by a voltage pulse to either one of the grids; the magnitude and sign being determined by the static potentials of both grids. To obtain good synchronization the triggering pulses should have a sharp front and should be of short duration compared to the interval between pulses. Sharp pips were obtained with a pulse shaping circuit. A 6N7 double triode was used as a square wave generator by applying a very large input signal and thus over-driving in both grid and plate circuits. The resulting approximately square wave was then changed to a series of sharp pips by an RC differentiating circuit. The triggering pips were applied to the inner grid and, since the second grid was normally 100 volts positive, only negative pulses produced a glow discharge. Thus the tube was triggered once every cycle, provided plate and second grid voltages were near normal. The 631-P is rated at a maximum of 250 flashes per second so the circuit constants are such that at around 300 cycles per second the recharge time of the discharge condenser is of the same order as one period of the signal. From this point a discharge occurs only when the



STROBOTRON TRIGGER CIRCUIT

FIGURE 9

second grid reaches some limiting value; synchronization is maintained but the flashing rate does not exceed the rated maximum. This method of synchronizing was found to be superior to that of applying a synchronizing signal to the multivibrator circuit in the General Radio Strobotac as used by Ferry et al .

### c) Methods of Measuring Wavelength and Damping

Two methods of making measurements were used, one permitted measurement of wavelength only, the second permitted measurement of wavelength and damping. We will refer to them as Method A and Method B respectively;

#### Method A

A compensator was not available when these experiments were started so it was necessary to find some other method of measuring the wavelength of sound in the gel. As mentioned before, the intensity of light transmitted by a doubly refracting medium (in this case a strained gel) between crossed Polaroids, optic axes of medium at forty five degrees to those of the Polaroids, is proportional to  $\sin^2 \delta$ , where

$\delta$  is the relative retardation. It has been shown<sup>9</sup> that if a second doubly refracting medium, with relative retardation  $\Delta$ , is placed before the analyzer with its optic axis at an angle  $\alpha$  to that of the polarizer, the intensity is governed by the following:

$$I \propto \sin^2 \frac{\delta}{2} + \frac{1}{2} \sin \Delta \sin 2\alpha \sin \delta + \sin^2 \frac{\Delta}{2} \sin 2\alpha \cos \delta$$

Suppose  $\Delta = \lambda/4$  and that  $\alpha$  is a small angle. Then since  $\delta$  is always small in the present case ( $\ll \pi$ ),  $\cos \delta$  will always

be positive and its effect will be to increase the over all illumination. However,  $\sin \delta$  will be positive for positive  $\delta$  and negative for negative  $\delta$ . Thus its sign will reverse every half wavelength in the gel. The transmitted light will be increased for positive retardation  $\delta$  and decreased for negative  $\delta$ .

A mica plate was used to produce the desired  $\Delta$ . It was obtained by splitting mica sheet and selecting by trial for the desired effect, the thickness was about 0.027 mm.. By adjusting the angle of the plate for optimum effect it was possible to practically eliminate every other line and at the same time greatly increase the apparent sharpness of the remaining lines.

Measurements of wavelength were made with the micrometer eyepiece. The position of points of equal intensity on either side of a line of minimum or maximum intensity were measured and the average taken as the position of the mid-point referred to some arbitrary datum line. This was done for all the lines visible on each side of the vane, usually about three or four. Differences between adjacent lines gave the wavelength. Measurements were not made closer than a half wavelength from the vane in order to avoid possible errors due to structural changes etc. at the vane surface. No systematic variation in wavelength was observed at varying distances from the vane.

The lowest measureable frequency was determined by the difficulty of setting the cross hair accurately on the relatively broad lines. The upper end of the frequency range was determined by the disappearance of double refraction.

### Method B

This method used the Babinet compensator set up as described above. A few measurements, only, were taken with the micrometer eyepiece. Measurements of wavelength could be made relatively easily but it was not possible to measure the decay of line displacement by this method. The latter measurement was attempted by rotating the eyepiece 90 degrees so that the motion of the cross hair was vertical. The variation of intensity is sinusoidal, for monochromatic light, and with the compensator at a small angle ( $5^\circ$ ) small so that it is impossible to make accurate settings of the cross hair. This difficulty was overcome by photographing the image in the eyepiece and printing on high contrast paper. High speed panchromatic film was used (Kodak Super XX roll film). By suitable exposure and development on high contrast enlarging paper it was possible to get quite sharp variation between the light and dark lines and it was then possible to make measurements of decay of amplitude. Measurements of wavelength were also made on the photographs, the image of the vane being used as a calibration. As in Method A, readings were not taken closer than a half wavelength from the vane. Measurements of wavelength could be made over the same frequency range as with Method A, but measurements of decay of line displacement could only be made over a much smaller range due to the rapid decay of birefringence with increasing frequency.

The loudspeaker driver was driven at maximum rated input for all measurements. Measurements were made on a 6% Digel-3%Octoic Acid in Gasoline gel to determine the variation in amplitude of motion of the vane with frequency and the effect of input power on measured wavelength. The results are shown in Table 1. for amplitude frequency measurements.

Table 1.

Amplitude of vane, speaker input 20 watts

<u>Frequency</u> cycles/sec.	<u>Amplitude</u> millimeters
100	0.5
200	0.8
300	0.4
400	0.15
500	0.05

The maximum around 200 cycles/second was caused by a mechanical resonance in the system. The variation in wavelength was less than 2.5% for driving powers between 10% and 140% of the rated power for the same gel at 340 cycles/second, 50°C. Because of these results no attempt has been made to limit the vane amplitude to any particular value, to attempt to have a constant strain etc.. Strains and rates of strain are apparently small enough to avoid thixotropic effects, etc.. No systematic variation of wavelength with distance from the vane was ever noted.

The measurement of damping is difficult to do accurately, particularly in the case of the experiments reported here. The method of measurement was as follows. The positions of peaks and troughs of the wavy lines were

measured relative to an arbitrary base line, in this case the line on the Babinet. Differences were taken between successive measurements and ratios taken of the successive differences. If the decay of double refraction  $\delta$  is exponential these ratios will be constant and equal to  $e^{-\lambda/2x_0}$  since readings were taken every half wavelength. The quantity  $\lambda/x_0$  was then found by taking the  $\log_e$  of the average ratio.

The ratios found in these experiments were between 1.1 and 1.5 and were generally measured with a variation of  $\pm 0.1$ . From this it was assumed that the decay of strain double refraction and therefore the decay of strain was exponential. Unfortunately with ratios of this magnitude the variation in the calculated  $\lambda/x_0$  is of the order of 100% for a variation of 0.1 in the argument, so the values of  $\lambda/x_0$  are subject to considerable error.

#### d) Material

The aluminum soaps used in the two series of measurements reported here are supposedly of the same type. However since the behavior appears to be quite different in the two cases, we label the first soap used by the original Canadian name Digel and the second by the later name Octal. The origin of the Digel powder is not known at present and an attempt is being made to trace it. The origin and particulars of manufacture etc. are known for the Octal powder used.

The gasoline used is ordinary commercial grade but

requires some comment. An attempt was made to make gels in Vancouver with locally obtained gasoline and considerable difficulty was encountered in making observations due to the small amount of strain double refraction. This could possibly have been due to a different mixing procedure or to different soaps. However, it was learned that other difficulties have been experienced with gels during the past year and that much of the difficulty was caused by the quality of the gasolines used. Samples of gasoline have been checked by Defence Research Chemical Laboratories, Ottawa, and the only acceptable gasoline at the present time appears to be straight run from Alberta crude.. For this reason all the gels used were obtained from the Defence Research Board Suffield Experimental Station and were prepared with "acceptable" gasoline.

The benzene used was reagent grade.

Mixing was done at  $25^{\circ}\text{C} \pm 1^{\circ}\text{C}$ , in a large "field mixer" for the first series and in a small scale laboratory mixer for the Octal series. The small mixer is designed to give results similar to those obtained with operational mixers but this is not necessarily so with the properties investigated here.



#### IV EXPERIMENTAL RESULTS

Measurements have been made on two groups of gels. A series of mixes of Digel (soap) with octoic acid in gasoline have been investigated using Method A. Method B has been used on a series of Octal (soap) with octoic acid in gasoline and in benzene. The results of these two groups of measurements are quite different. It was possible to approximate the behavior of the first group with a simple Maxwell element but this could not be done for the Octal mixes in either solvent.

##### a) Digel and Octoic Acid in Gasoline

###### Method A

It was found possible to fit the results of these measurements to Maxwell models. The procedure was as follows. Values of  $\tilde{G}$  were calculated from the measured wavelengths according to the equation  $\tilde{G} = f^2 \lambda^2 \rho$ . The density  $\rho$  was taken to be 0.75 gm/cm<sup>3</sup> in all cases; errors introduced by assuming  $\rho$  constant are negligible compared to experimental errors. The limiting value of  $\tilde{G}$  was found by plotting  $\tilde{G}$  vs  $\tilde{G}/f^2$ , the intercept on  $\tilde{G}/f^2 = 0$  being taken as  $G$ , the rigidity of the equivalent Maxwell Model. With this result values of  $\tilde{G}/G$  were calculated and plotted against  $\log f$ . The plotted points were superimposed on a standard plot for a Maxwell element for best fit. The value of  $f$  for  $\omega\tau = 1$  was taken from this curve giving the relaxation time of the model. Table 2. summarizes the results of these measurements. Typical curves are illustrated in figure 10.

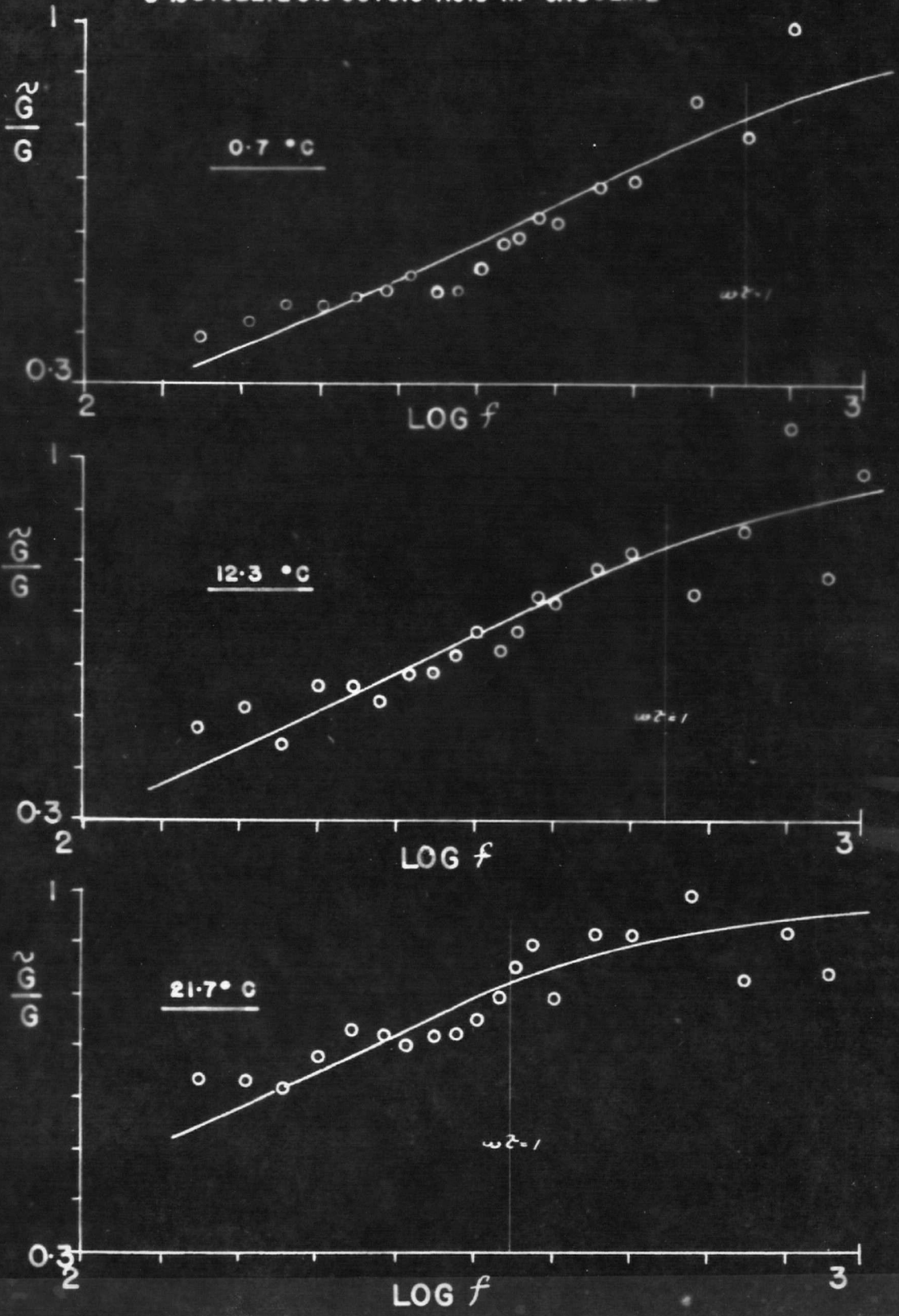
Table 2  
 Constants for Maxwell Model

Digel and Octoic Acid in Gasoline

<u>Concentration</u>		<u>Temperature</u>	<u>Rigidity</u>	<u>Relaxation Time</u>	<u>Viscosity</u>
<u>%Digel</u>	<u>%Octoic</u>	<u>°C</u>	<u>dynes/cm<sup>2</sup></u>	<u>10<sup>-3</sup>sec.</u>	<u>poise</u>
3	3/4	2.5	1200	0.6	0.7
		11.2	750	0.7	0.4
		20.5	650	>1.6	>1.
		31.2	700	>1.6	>1.1
4	1	1.5	1600	0.5	0.8
		11.2	1600	0.5	0.8
		21.5	1500	0.7	1.
		30.7	1300	0.8	1.
		41.2	1270	1.0	1.3.
		50.5	1160	>2.0	>2.
5	1 1/4	0.7	3900	0.2	0.8
		12.3	3400	0.3	1.
		21.7	2800	0.4	1.1
		32.2	2200	>1.1	>2.
		42.0	1900	---	---
		51.3	1700	---	---
3	1 1/2	1.2	780	0.5	0.4
		7.0	640	0.8	0.5
		14.5	600	0.9	0.5
		25.3	520	1.3	0.7
		36.7	500	1.1	0.6
		49.0	470	1.8	0.8
4	2	0.5	1220	0.6	0.7
		11.7	1120	0.6	0.7
		21.0	1020	0.8	0.8
		31.3	940	0.9	0.8
		41.3	940	0.9	0.8
		51.3	900	1.2	1.1
5	2 1/2	1.0	4600	0.3	1.4
		11.7	4100	0.3	1.2
		20.0	3400	0.5	1.7
		31.3	3100	0.6	1.9
		41.7	2900	0.6	1.7
		51.3	2600	0.9	2.3
6	3	1.1	3900	0.4	1.6
		10.5	4900	0.3	1.5
		20.5	4100	0.4	1.6
		30.6	3500	0.5	1.8
		40.7	2800	>1	>2.8
		50.7	2800	>1	---

**FIGURE 10**

**5 % DIGEL-25% OCTOIC ACID IN GASOLINE**



The rigidity,  $G$ , increases with concentration. Results for both soap to peptizer ratios are shown in figure 10, where  $\log. G$  is plotted against  $\log. (\text{soap concentration, weight\%})$ . The relation is approximately linear with a slope of about three in both cases. Thus the rigidity is approximately proportional to the cube of the soap concentration.

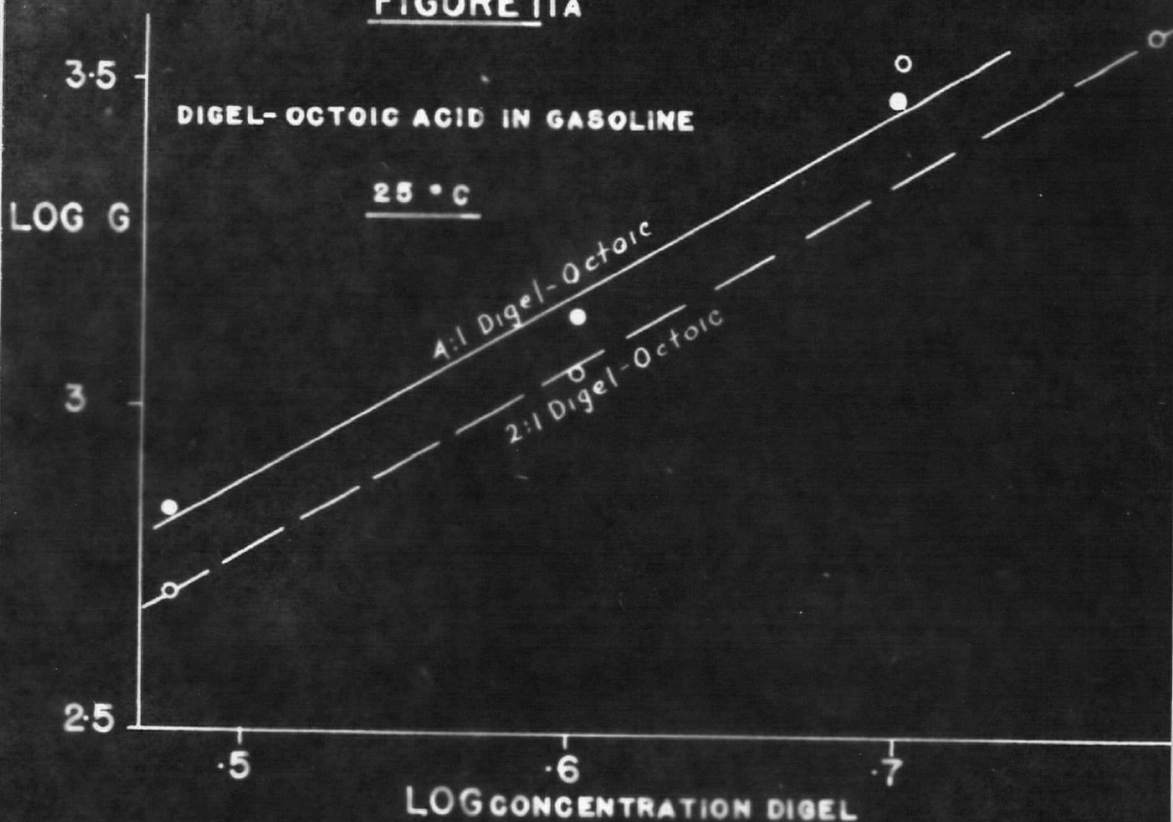
Rigidity decreases with increasing temperature.  $\log. G$  vs  $1/T$ , where  $T$  is the absolute temperature, gives a straight line for any one mix but the slope varies somewhat with soap concentration and with soap to peptizer ratio. These curves for the 2:1 soap to peptizer series are shown in figure 11. and those for the 4:1 series were similar but with slightly higher slope. If we assume that the rigidity-temperature dependence can be described by an equation such as

$$G = G_0 e^{-\frac{Q_g}{RT}}$$

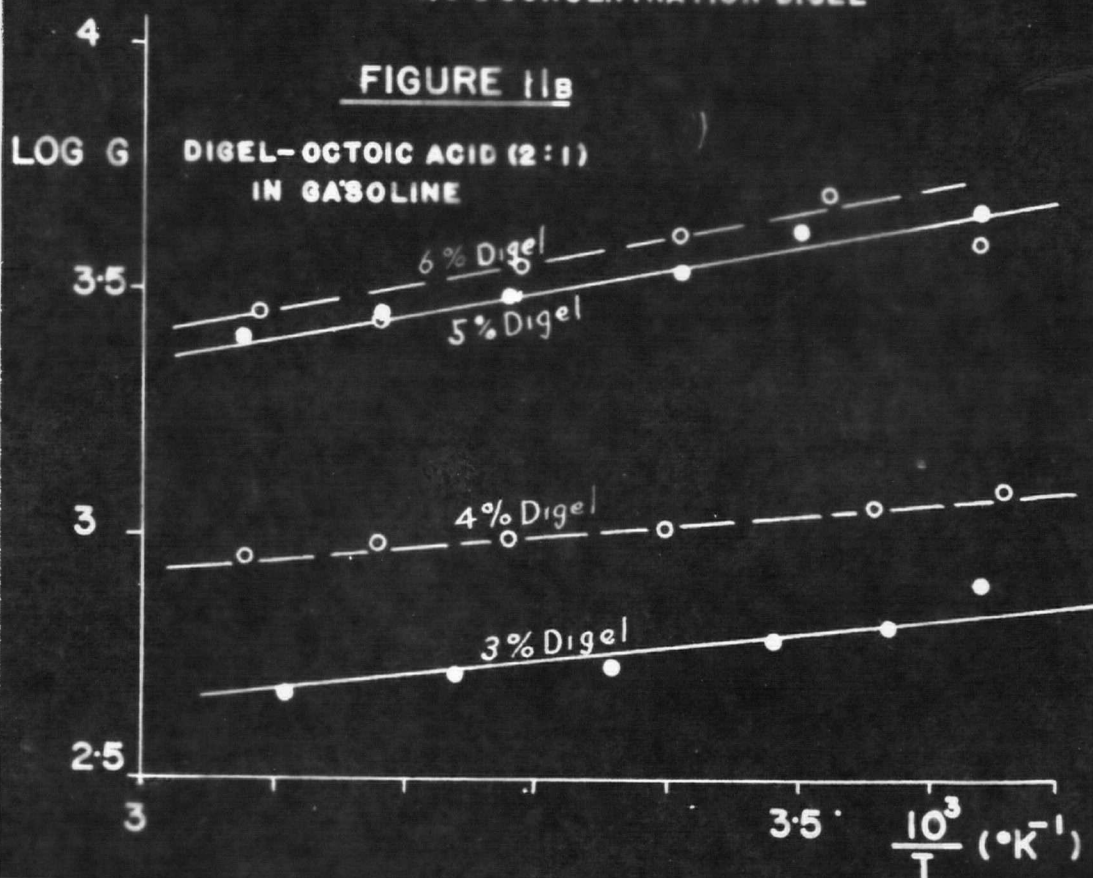
then the activation energy  $Q_g$  for the rigidity is between 1 and 2 Kcal. per mole.

Since the values for the relaxation times are found by a rather indirect procedure here, they can only be considered as very approximate. However, in all cases it has been found that the relaxation time tended to decrease with increasing soap concentration and to increase with increasing temperature. The magnitude of the viscous component of the Maxwell model was calculated from the values of  $G$  and  $\tau$  ( $\eta = G\tau$ ), and found to increase with increasing soap concentration and with increasing temperature and to decrease with increasing peptizer. Viscosities were of the order of 1 poise and the variation was about

**FIGURE 11A**



**FIGURE 11B**



100 % in the temperature interval  $0^{\circ}$  to  $50^{\circ}\text{C}$ .

b) Octal-Octoic Acid in Benzene

Two mixes were investigated, 5% Octal 1.25% Octoic Acid and 5% Octal 1.7% Octoic Acid.

Both were measured at  $25^{\circ}\text{C}$ , the resulting values for  $\tilde{G}$  are shown in Table 3. below.

Table 3.

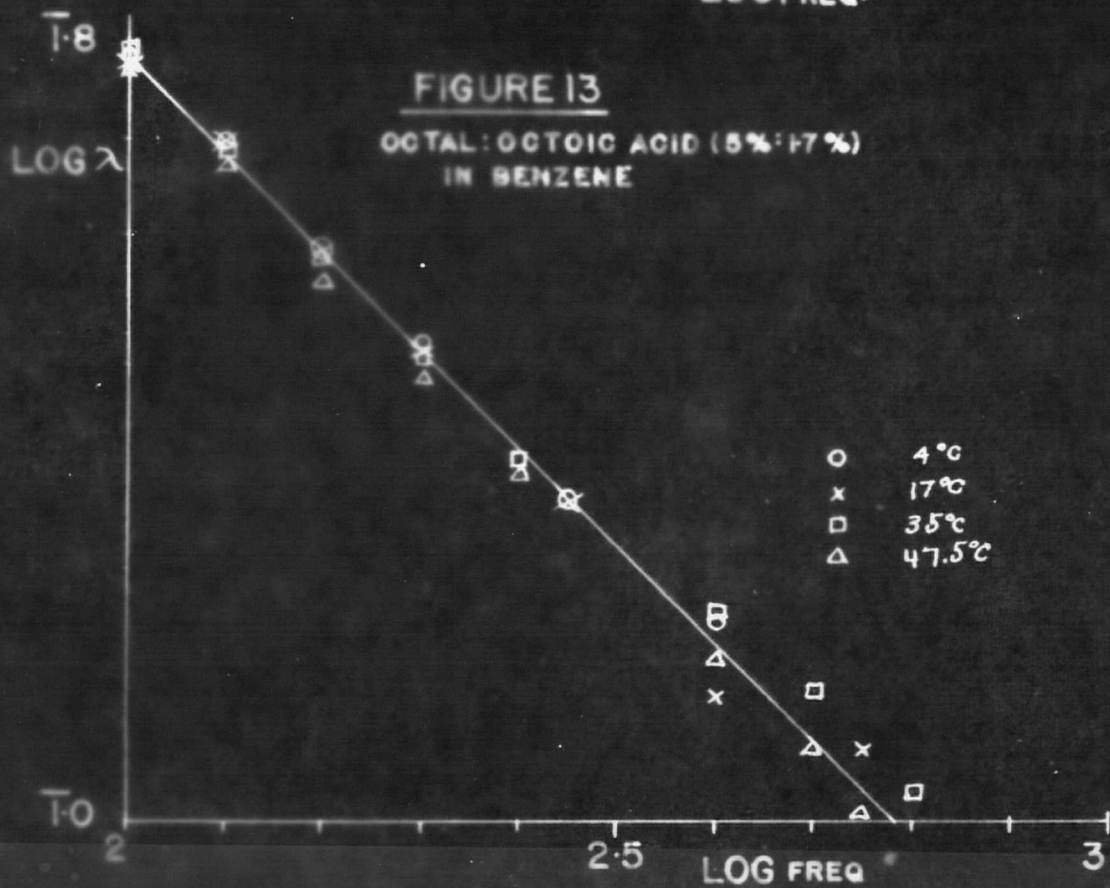
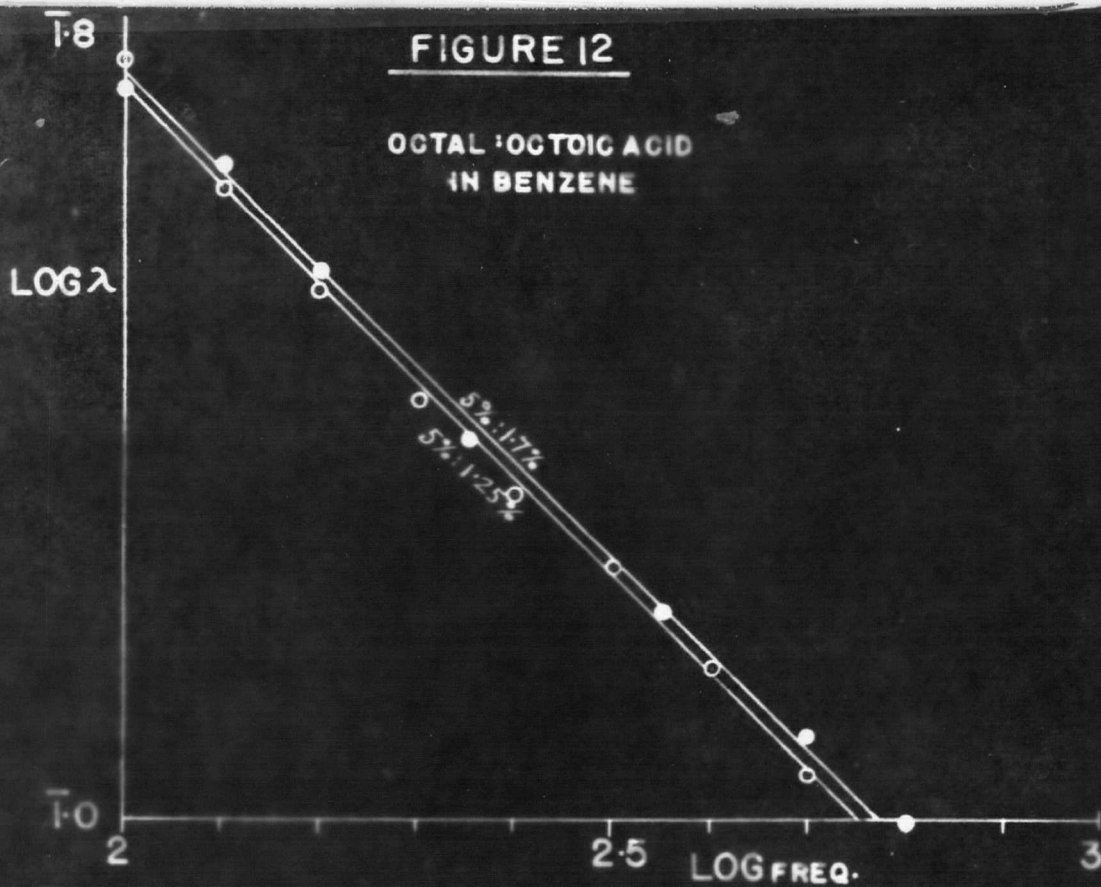
Rigidity, $\tilde{G}$ , for Octal-Octoic Acid in Benzene at $25^{\circ}\text{C}$								
5% 4:1								
Frequency, c/s	126	158	199	251	316	397	500	
$\tilde{G}$ , dynes/cm <sup>2</sup>	2350	2320	2170	2240	2460	2400	2320	
5% 3:1								
Frequency, c/s	100	126	158	224	355	500	630	792
$\tilde{G}$ , dynes/cm <sup>2</sup>	2340	2620	2520	2280	2500	2730	2900	3010

The 4:1 gel gave values of rigidity approximately independent of frequency, the values for the 3:1 gel show a slight increase at the high frequency end of the measurements. Figure 12. shows  $\log.\lambda$  plotted against  $\log.$  freq., the curves are straight lines drawn at forty five degrees indicating that in both cases  $\log.\lambda + \log.f$  may be approximated by a constant over the frequency range covered. The values of  $f\lambda$  calculated from the intercepts of these lines with either axis are taken as the average velocity of propagation and used to calculate the average value of the rigidity,  $G_{av}$ .

The average values found were:

5%Octal 1.25%Octoic Acid	$G_{av} = 2700$ dynes/cm <sup>2</sup>
5%Octal 1.7 %Octoic Acid	$G_{av} = 2400$ dynes/cm <sup>2</sup>





The effect of temperature was also determined for the 3:1 mix. The results are shown in figure 14, below.

Table 4..

Rigidity,  $\tilde{G}$ , for 5%Octal 1.7%Octoic Acid in Benzene.

Log. f	2.0	2.1	2.2	2.3	2.4	2.45	2.6	2.7	2.75	2.8
Temp °C										
4	2800	2900	2850	2850		2750	3050			
17	2750	2900	2800	2750		2750	3400	3270		
35	2800	2800	2800	2650	2600		3200	3500		3400
47.3	2600	2650	2400	2400	2500		2550	2650	2600	

As found in the measurements at 25°C, the rigidity  $\tilde{G}$  is independent of frequency at low frequencies and tends to higher values at the high frequency end of the range measured. This is illustrated graphically in figure 14..

$$\log \lambda + \log f \approx 2.78 \quad \text{and} \quad G_{av} \approx 2850 \text{ dynes/cm}^2.$$

Unlike the mixes of Digel in gasoline investigated by Method A the rigidity of this mix appears to be almost independent of temperature over the range covered.

In favorable cases, it is possible to make measurements of the decay of birefringence. The temperature and frequency dependence of  $\lambda/x_0$  is illustrated in Table 5. below. It is not possible to make accurate measurements of damping with this method and in many cases it was not possible to make any measurement at all. However, the values shown in Table 5. indicate a minimum in the value of  $\lambda/x_0$  as a function of frequency and that this minimum tends to move to higher frequencies as the temperature is increased.



Table 5. $\lambda/x_0$  for 5%Octal 1.7%Octoic Acid in Benzene

Temp. °C Log. f	<u>4</u>	<u>17</u>	<u>35</u>	<u>47.5</u>
2.0	.5	.6	.8	--
2.1	.4	.4	.7	--
2.22	.3	.4	.5	.4
2.3	.3	.3	.5	--
2.45	.5	.4	.3	.3
2.6	--	.5	--	--
2.7	--	.7	--	--

Comparison with the theoretical curves of figure 5. shows that the behavior cannot be approximated by a simple Maxwell element in this case. Not only because of the fact that the rigidity remains independent of frequency and then tends to rise at high frequencies, but also because of the minimum for  $\lambda/x_0$  vs frequency. The variation of both rigidity and damping may be approximated by a <sup>Retarded</sup> Maxwell element with the ratio  $\tau_p/\tau_s = 0.005$ . It is not possible to determine the position of the minimum precisely so a determination of relaxation time has not been attempted. The order of magnitude for relaxation time is about  $10 \times 10^{-8}$  seconds.

c) Octal-Octoic Acid in Gasoline

Method B

The results of this series of measurements are essentially the same as for the Octal-Octoic-Benzene

measured by the same method and, therefore, differ considerably from those of the Digel mixes in gasoline.

Measurements have been made near room temperature on gels ranging in soap concentration from 3% to 6% and with soap to peptizer ratios of 2:1, 3:1 and 4:1. Some difficulty has been obtained in obtaining consistent relationships between gels of differing concentrations. This is possibly due to differences in aging rates, presence of impurities, etc.. In certain cases it has been found that the rigidity of a particular gel is less than gels of lower soap concentration.

The variation of rigidity,  $\tilde{G}$ , with frequency is illustrated in Table 6 for some of the samples tested.

Table 6

Rigidity  $\tilde{G}$  of Octal-Octoic Acid in Gasoline at 25°C  
(age 2 weeks)

<u>Concentration</u>		<u>Frequency</u>							
		cycles/second							
<u>%Octal</u>	<u>%Octoic</u>	<u>100</u>	<u>126</u>	<u>158</u>	<u>199</u>	<u>251</u>	<u>316</u>	<u>397</u>	<u>500</u>
4	1	850	950	950	1000	950	950	1150	---
5	1.25	1500	1550	1500	1450	1600	1650	1680	---
3	1	1050	1000	1000	1250	1150	1200	1250	---
4	1.33	900	900	900	900	850	850	1200	1300
5	1.7		700	700	750	800	800	950	---
4	2	400	500	450	450	550	650	750	---
5	2.5		1400	1300	1400	1350	1400	1400	1600

As with the benzene mixes, the rigidity tends to be independent of frequency at low frequencies and to begin to increase rather sharply at the high frequency end of the spectrum investigated.

The behavior of the quantity  $\lambda/x_0$  is also similar to that for the benzene mixes. The minimum in the case of the gasoline gels was not quite as low as for the benzene gels, in the majority of cases it was around .5. This together with the frequency characteristic for the rigidity suggests that the mechanical behavior may be approximated by a retarded Maxwell element with a ratio of parallel to series viscosity of the order of 0.01.

The dependence of rigidity on temperature was determined for the 5%Octal 1.7%Octoic Acid mix. Measurements were made at 2.5, 21.2 and 42.5 °C. The rigidity, G, was found to be substantially independent of temperature over this small range and as before was approximately independent of frequency from 100 to 500 cycles per second. The average value of the rigidity was approximately 750 dynes/cm<sup>2</sup>. This is the same mix as in Table 6. and this value compares well with the values shown there for 25°C.

As a check on the fall of rigidity with increasing concentration a second measurement was made on the 4% Octal mix with the same peptizer ratio. An average rigidity of approximately 900 dynes/cm<sup>2</sup> was found. This confirmed the readings of Table 6. and again indicated a decrease of rigidity with concentration.

The above two groups of tests were made at ages of two and three weeks respectively. The two gels rechecked appear to be quite stable and this would seem to eliminate differing aging rates as a possible explanation of the anomaly.

The effects of aging present a difficult problem in experiments of this type with gels. It is very difficult to determine the effect of soap concentration, soap to peptizer ratio, etc., unless the gels are relatively stable or a very detailed knowledge of their aging characteristics is known. The practice has been to make all measurements on a particular series at the same age, if possible. This is possibly not the best procedure, since, in general, deterioration with age is likely to be more rapid for low soap concentrations or for low soap to peptizer ratios. Very marked differences may be caused by impurities, eg. minute traces of acid on the walls of containers can cause very rapid break down of the gel.

The different aging rates of two gels of the same soap concentration but different peptizer concentration are illustrated in Table 7 below.

Table 7.

Effect of Aging on Octal-Octoic Acid in Gasoline  
(at 21°C)

<u>Concentration</u>		<u>Age</u>	<u>Average Rigidity, G.</u>
<u>%Octal</u>	<u>%Octoic Acid</u>	<u>Days</u>	<u>dynes/cm<sup>2</sup></u>
5	2.5	13	1500
		42	750
5	1.25	8	1850
		48	1500

It is not possible to make an accurate determination of the values of  $\lambda/x_0$  and so locate the position of the minimum and find a value of  $\tau_s$ . Also measurements do not extend far enough into the dispersion regions to fix the value of  $\tau_s$  from rigidity measurements alone. It is possible to make an estimate of order. Since the minimum always occurs in the frequency range 100 to 500 cycles/second,  $\omega\tau_s = 10$  in this frequency range. Therefore  $\tau_s$  is of the order of  $10 \times 10^{-3}$  seconds and the corresponding value of  $\eta_s$  of the order of 10 poise.

## V DISCUSSION

Measurements have been carried out on aluminum soap hydrocarbon systems at low sonic frequencies. The primary aim of the present investigation has been to determine the practicability of using the transmission of transverse sonic waves as a method of determining the mechanical properties. With certain limitations this has been found to be a useful method, particularly for the measurement of rigidity. The frequency range over which measurements can be made is rather limited. Also the measurement of damping or viscous forces is difficult because measurements must be made in a frequency range where damping, in space, is small; at least for the cases investigated.

An attempt has been made to approximate the mechanical behavior with mechanical models. This is one way of comparing results of experiments using different techniques, in different frequency ranges etc.. It has been found that this may be done with relatively simple models. In certain cases Maxwell elements are sufficient, in others, Retarded Maxwell elements are necessary. The data available, in most cases, is not sufficient to make a really accurate fit to a model. When more data from other experiments at different frequencies are available it will be possible to choose much more useful models. By using electrical analogs, and adjusting experimentally for the correct impedance characteristic, it is possible (in principle) to find models to match behavior of any complexity.

The results for mixes made with two supposedly identical soaps give different results, though only in degree. In one case a simple Maxwell element is sufficient of describe the behavior, in the second a more complicated model is necessary. Within the accuracy of the measurements and frequency range covered a retarded Maxwell element with a very small parallel viscous component is needed in the second case. The rigidities,  $G$ , necessary for the respective models are of the same order but the series viscous elements differ by a factor of about ten, being higher in the case with the retarded element. It is probable that a retarded Maxwell element would be necessary in the first case also if measurements could be made at high enough frequencies. Because of the low viscosity and relaxation time measurements have been made in the region where a Maxwell element is sufficient if  $\tau_p/\tau_s$  is small which it certainly is in this case.

A further difference has been observed. This is the difference in the range of frequencies over which observations may be made with the two soaps. In only one case with the Digel mixes was it not possible to make measurements up to 1000 cycles per second, in the majority of cases measurements were made at frequencies over 1000 cycles per second. With Octal mixes, both in gasoline and benzene the rapid decay of strain double refraction with increasing frequency made it impossible to make measurements past 500 cycles per second in most cases. This may be due to differences in strain optical coefficients or to differences in the damping of the sonic

waves. In the Digel mixes measurements have been made in the region where  $\omega\tau \ll 1$  and  $\lambda/\chi_0$  decreases with increasing frequency. A retarded Maxwell element is necessary for the Octal mixes,  $\lambda/\chi_0$  has a minimum and then increases with increasing frequency. At the higher frequencies the damping is more in the second case and therefore limit of observability of the double refraction is lowered.

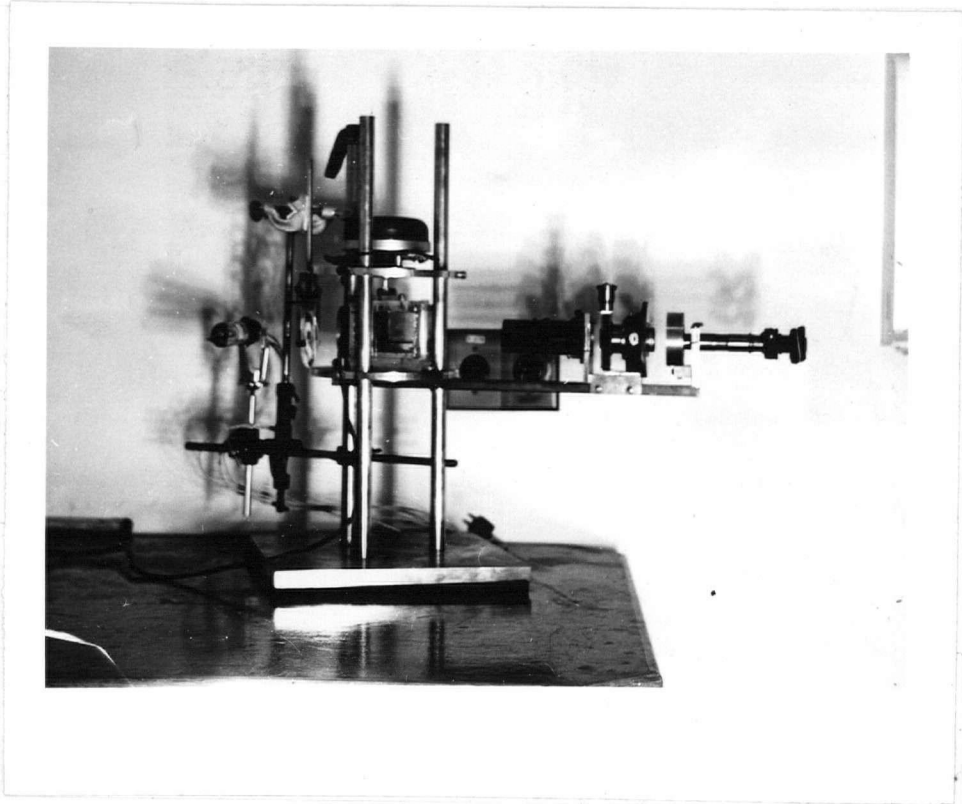
The rigidities found are of the order of  $10^3$  dynes per square centimeter in all cases. These are of the same order as rigidities determined by Gunn<sup>15</sup> for aluminum soaps in benzene at frequencies of a few cycles per second in a concentric cylinder apparatus. It must be stressed here that this rigidity is neither of the rigidities in the model discussed in the Introduction but the cumulative effect of several mechanisms. We find that the rigidity tends to decrease with increasing temperature but that the effect is small. Now, the retarded or configurational elasticity, which arises from the change of entropy due to molecules uncurling from their most probable configurations, is proportional to the absolute temperature<sup>16</sup>. On the other hand, intermolecular forces give rise to a rigidity which decreases with increasing temperature. Also if we consider the system to be two phase there is the additional complication of interchange of soap between the network and the surrounding solution. This would probably tend to reduce the rigidity with increasing temperature by removing material from the network. The observed temperature dependence is the sum of the above effects.



It is not possible to conclude anything about the dependence of rigidity on soap concentration. One would expect that the concentration would have a very marked effect on the rigidity due to the rapid increase in the number of mesh points with increasing concentration.<sup>17</sup> The results are contradictory here, in some cases the rigidity does vary rapidly with concentration and in others it appears to decrease with increasing concentration. It is felt that the presence of impurities is the main cause of these differences.

The viscosity of the series damping element is of the order of 1 to 10 poise. This is  $10^3$  to  $10^5$  times smaller than the viscosity as measured in conventional viscometers.<sup>15</sup> This is to be expected since the mechanisms involved in the two cases are different. In the case of true flow one must consider the breaking and reforming of bonds of the network. In the present case strains are small, the network is deformed but bonds are apparently not broken or thixotropic effects would have been observed. The viscosity observed here is probably entirely due to the movement of segments of macromolecules. Measurements of damping are not extensive enough at present to determine the dependence on temperature or concentration especially since it is also complicated by the two phase structure of the system. From the results available the effect of temperature seems to be small.

PLATE I



## VI BIBLIOGRAPHY

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