ABSTRACT (PART I)

The rotational viscometer which had a uniform stress, designed by Dr. W. Philippoff was used for measuring the viscosities of 6% L-200 in PRIMOL 355 and Lekutherm x-30. Viscosities of 6% L-200 in PRIMOL 355 (polyisobutylene) was measured to check the change of material that was left in the visometer for almost two years. The result showed that the new viscosities are higher than the older results.

The main interest of this thesis is to measure the viscosity of Lekutherm x-30, epoxy resin produced from Germany. No one has ever measured the whole range of temperatures of its viscosity. The measurements were done at different temperatures and different shear stresses.

The viscosity at 29.9° C was used for a reference value in order to calculate the constants C_1 and C_2 from the WLF equations, and their values were used for further calculation of viscosities in a variety of temperatures. The calculated and experimental values of their viscosities were compared. The results are considerably close in their values.

The viscosities of Lekutherm x-30 were rechecked three months later. The results showed high increases in new measurements: 64% at 29.9° C, 66.19% at 31.9° C, 57.10% at 39.9° C and 30.32% at 50° C.

There are three measurements of recoil data. Modulus and relaxation times were calculated.

Lekutherm x-30 resin was used to investigate birefringence in 1-2, 1-3 and 2-3 planes. For the birefringence in the 1-2 plane, the study was done at different temperatures and different shear rates. The highest temperature was 80° C and the lowest temperature was 30° C. It is difficult to measure at lower temperatures. This is due to the inability of the apparatus and the characteristics of the material being used. For low temperatures a correction angle has to be used. A new zero point is changed at 60°C by -2 degrees. The stress-optical coefficients, C_{br}, were calculated and compared to the values of other investigations. At high temperatures the stress-optical coefficient is in agreement with the Kuske and Zech Value but at low temperatures their values are much higher. At low temperatures the 1:4 slit, 1:20 slit and true values of C_{br} which were measured by Dr. W. Philippoff were found to be in the middle range between Kuske and Zech and my values. The 1:4 slit values of C_{br} were used to calculate the $\Delta n_{(1-2)}$ at low temperatures and further these values were used to calculate the percent ratio of $\Delta n_{(1-3)}$ and $\Delta n_{(2-3)}$. The values of birefringence in the 1-2 plane were calculated from the experimental values of C_{br} as a function of viscosity and shear rate.

The temperature effect of a newtonian Lekutherm x-30 resin was found to have a stress-optical coefficient dependent on shear stress and low temperature changes under 70° C. At higher temperatures above 70° C there is very little effect on the stress-optical coeficient C_{br}.

The birefringence in 1-3 plane was observed by using the simple slit arrangement apparatus. The measurements were done at room temperature but the variation of temperatures that occured depended upon room temperature conditions. The values of $\Delta n_{(1-3)}$ were much smaller than $\Delta n_{(1-2)}$ values. Only one experiment could reach equilibrium. The percentage ratio between $n_{(1-3)}$ and $n_{(1-2)}$ are 2.8 and 4.5, where 2.8% ratio calculated from C_{br}- true value.

The birefringence in 2-3 plane is very small, the percentage ratio between $\Delta n_{(2-3)}$ and $\Delta n_{(1-2)}$ are about one percent or less. There is a definite effect of birefringence in 2-3 plane. This conclusion was also proved in the experiment by Biss in 1974.

I. TRANSIENT PHENOMENA OF POLYMER

II. ANILINE-FORMALDEHYDE FIBER AND COPOLYMER ANILINE-PHENOL-FORMALDEHYDE FIBER

by

Ing-On Vibulbhan-Watts

Thesis submitted to the Faculty of the Graduate School
of the New Jersey Institute of Technology in partial
fulfillment of the requirements for the degree
of Master of Science

APPROVAL SHEET

Title of Thesis: I. Transient Phenomena of Polymer

II. Aniline-Formaldehyde Fiber And Copolymer Aniline-Phenol-Formaldehyde Fiber

Name of Candidate: Ing-On Vibulbhan-Watts

Master of Science in Engineering Science, 1980

Thesis and Abstract Approved: 5/12/80
Date

Dr. George Y. Lei
Assistant Professor
Department of Chemical
Engineering and Chemistry

5/12/80
Date

5/12/80
Date

Signatures of other members of the thesis committee.

5/12/80
Date

5/12/80
Date

VITA

Name: Ing-On Vibulbhan-Watts

Permanent Address:

Degree and date to be conferred: May , 1980

Date of birth:

Place of birth:

Secondary education: Pibulvitayalai, Thailand, 1966

Collegiate institutions attended	Dates	Degree	Date of Degree
Saint Peter's College	1969-72	-	-
Rutgers University	1972-75	B.S.	1975
Columbia University	1970-72	-	-
New Jersey Institute of Technology	1976-80	M.S.	1980

Major: Chemistry

ACKNOWLEDGEMENT

I wish to express my appreciation to Dr. W. Philippoff and Dr. George Lei, whose guidance and assistance was very helpful in this research. I would like to thank the National Science Foundation at New Jersey Institute of Technology who sponsored the study of Transient Phenomena of Polymer. Special thanks to my husband for his patience and help in making the final thesis possible.

TABLE OF CONTENTS

TRANSIENT PHENOMENA OF POLYMER RHEOLOGY -------- VISCOSITY

RHEO-OPTICAL INVESTIGATION OF AN EPOXY-RESIN (LEKUTHERM X-30) AT DIFFERENT TEMPERATURES

I. INTRODUCTION

Rheology and The Mechanical Properties of Polymers

Rheology by definition is the science of deformation and flow of matter. The rheological behavior of polymers involves several widely different phenomena. This can be related to some extent to different molecular mechanisms. These phenomena are as follows:

1. Viscous flow is the irreversible bulk deformation of polymeric material. This also is involved with irreversible slippage of molecular chains past one another.
2. Rubber-like elasticity, where the local freedom of motion associated with small-scale movement of chain segments is retained, but large scale movement of flow is prevented by the restraint of a diffuse network structure.
3. Viscoelasticity, where the deformation of the polymer specimen is reversible but time dependent, is associated as in rubber elasticity with the distortion of polymer chains from their equilibrium conformations through activated segment motion involving rotation about chemical bonds.
4. Hookean elasticity, where the motion of chain segments is drastically restricted, probably involves only bond stretching and bond angle deformation, the material behaves like a glass.

1. Viscous Flow

Phenomena of viscous flow state that if a force per unit area (τ) causes a layer of liquid at a distance (x) from a fixed boundary wall to move with a velocity (V) in the y-direction, the viscosity η is defined as the ratio between the shear stress and the velocity gradient or rate of shear $\dot{\gamma}$.

The equation is Newton's law:

$$\tau = \eta \frac{\partial V}{\partial x} = \eta \dot{\gamma}$$

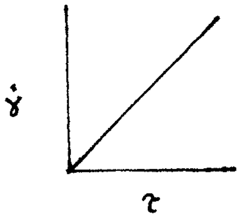
$$\eta = \frac{\tau}{\dot{\gamma}}$$

Unit of viscosity η is 1 poise = dynes . sec/ cm^2

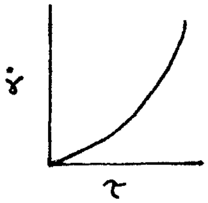
A. Newtonian behavior of liquid viscosity takes place when the viscosity (η) is independent of the rate of shear. This phenomenon is an ideal flow behavior. Two types of deviations from Newtonian flow are commonly observed in polymer solutions and polymer melts.

B. Non-Newtonian behavior is shear thinning, a reversible decrease in viscosity with increasing shear rate. This results from the tendency of the applied force to disturb the long chains from their favored equilibrium conformation. It is causing elongation in the direction of shear. An opposite effect is shear thickening, in which viscosity increases with increasing shear rate. This phenomenon is rarely observed in polymers.

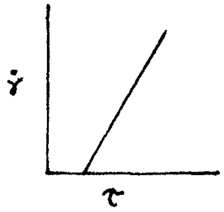
C. Yield Stress followed by Newtonian flow is the exhibition of a yield value. It is a critical stress below which no flow occurs. Above the yield value, flow may be either Newtonian or non-Newtonian.



A. Newtonian Flow



B. non-Newtonian Flow



C. Yield stress followed by Newtonian Flow

For low-molecular-weight liquids, the temperature dependence of viscosity is found sometimes to follow the simple exponential relationship,

$$\eta = A^{-(E/RT)}$$

where E is an activation energy for viscous flow, A is a constant.

Summary of methods for measuring viscosity

Method	Approximate Useful Viscosity Range, Poises
Capillary pipette	$10^{-2} - 10^{3}$
Falling sphere	$1 - 10^{5}$
Capillary extrusion	$1 - 10^{8}$
Parallel plate	$10^{4} - 10^{9}$
Falling coaxial cylinder	$10^{5} - 10^{11}$
Stress relaxation	$10^{3} - 10^{11}$
Rotating cylinder	$1 - 10^{12}$
Tensile creep	$10^{5} - 10^{12}$

Above methods commonly used for measuring the viscosity of polymer solutions and melts. The most important of these methods are rotational and capillary devices.

Rotational viscometry

There are variable types of rotational viscometry. They have several different geometries, for example, concentric cylinders, two cones of different angle, a cone and a plate or combination of these. Measurement with rotational devices become difficult to interpret at very high shear stresses. This is due to the generation of heat in the specimen because of dissipation of energy, and to the tendency of the specimen to migrate out of the region of high shear.

Cappillary viscosity

Capillary rheometers are usually made of metal. They are operated either by dead weight or by gas pressure, or at constant displacement rate. They have advantages of good precision, ruggedness, and ease of operation. They may be built to cover the range of shear stresses and temperatures found in commercial fabrication operations.[1]

2. Rubber-like elasticity

The properties of typical elastomers are defined as follows:

A. They must stretch rapidly and considerably under tension, reaching high elongations (500-1000%) with low damping, for example, little loss of energy as heat.

B. They must exhibit high tensile strength and high modulus (stiffness) when fully stretched.

C. They must retract rapidly, exhibiting the phenomenon of snap or rebound.

D. They must recover their original dimensions fully on the release of stress, exhibiting the phenomena of resilience and low permanent set.[2]

3. Viscoelasticity

Where the deformation of a polymer specimen is reversible but a time dependent one, one refers to the behavior as viscoelasticity. It is associated with the distortion of polymer chains from their equilibrium conformations through activated segment motion involving rotation about chemical bonds, as in rubber elasticity.[3]

Ideally elastic bodies follow Hooke's law, according to which the external stress or stress component, is proportional to the corresponding deformation, or deformation of stress: $P = GS$ where G is the static modulus of elasticity and S is strain.[4]

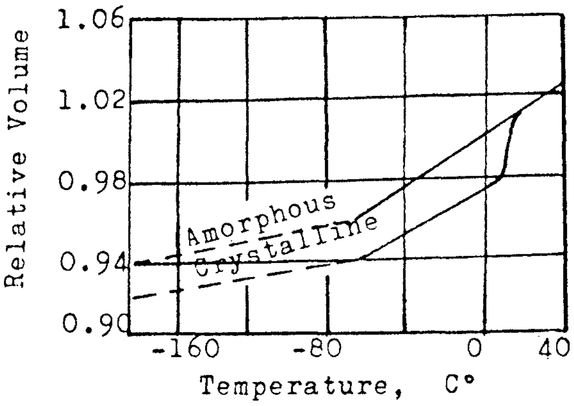
Time-temperature equivalence states that an increase in temperature accelerates molecular and segmental motion, this brings the system more rapidly to equilibrium or apparent equilibrium, and it accelerates all types of visco-elastic processes. A temperature change can be duplicated by a change in time.[5]

Viscoelastic behavior is derived from two models. One is an ideal of elastic element, which is represented by a spring which obeys Hooke's law, with a modulus of elasticity. The elastic deformation is instantaneous and independent of time. Another ideal is pure viscous liquid which obeys Newton's law. Its deformation is linear with time while the stress is applied and is completely irrevocable. A sample mechanical analogy of a Newtonian fluid is dashpot.

The two elements of spring and dashpot can be applied in the Maxwell and Kelvin-Voigt models. Viscoelastic materials differ from purely viscous fluids they have recoil or strain recovery properties when the stress is released. Pure elasticity occurs when the body returns to its original form after release of stress. Pure viscosity occurs when liquid flows under any amount of stress applied and that it does not retake the shape after release of stress. Viscoelastic materials combine both of these effects simultaneously, which is the combination of elastic and viscous deformations. For low stresses and short times of observation, the elastic characteristic is predominant. But viscous flow takes over when high stresses and longer times of observation occur. Therefore, total deformation which occurs in viscoelastic materials is the sum of elastic and viscous deformation. In this case the energy which is stored in a body undergoing stress and partly dissipates as heat.[6]

4. The Glassy State and The Glass Transition

All amorphous polymers at low temperatures have the characteristics of glasses, including hardness, stiffness, and brittleness. One property of the glassy state is a low volume coefficient of expansion. This low coefficient occurs as slope of the curve of volume versus temperature below the point called the glass transition temperature T_g; above it in the rubbery region this slope is longer. This behavior is shown for natural rubber (see below). In the high-temperature region, the slope of the curve which as expansion coefficient is characteristic of a rubber. The region below Tg at about - 70° C is characteristic of a glass.[7]



Historical Development

The historical development of rheology first started in 1540 B.C., an Egyptian Amenemhet used the flow of water in a conical vessel to measure time, considering changes in viscosity and temperature.[8] Rheology was derived from the Greek word, rheos, which means flow. Eugene Bingham was proclaimed the father of rheology, giving the field its name--rheology. K. Weissenberg and M. Reiner had devoted most of their time to this field.

Braunbeck was the first to do serious work on recoverable shear, about 1929 using cable compound. The first to measure elastic properties of viscoelastic materials with an instrument based on coaxial cylinders was A.A. Trapeznikov In 1956, A. A. Trapeznikov and his associate, T. G. Shalopalkina studied recoverable strain as a function of deformation time. They have investigated many types of solutions.

Philippoff, Gaskins and Brodnyan were the first group to investigate the measurement of recoverable shear versus shear rate of polymer solution, 100% polyisobutylene in 1957. The measurement of shear strain was measured by this investigative group.[9] In 1965 G.V. Vinogradov and I. M. Belkin studied polymer melts and solutions and discovered that shear stress growth become non-monotonic with increasing deformation rates. He used a rotational elastoviscometer with a rigid dynamometer. It is basically the combination of cone and plate type of instrument.[10] In 1967, A. A.

Trapeznikov observed stress growth undershoot as well as overshoot. In the same period, J. D. Huppler and associates observed shear growth, normal stress growth as a function of shear rate. The instrument studied was a Weissenberg Rheogoniometer. They found that normal stress growth increased more slowly than shear stress growth and reached its maximum at a later time.[11] In 1970, A. A. Trapeznikov and A. A. Pylaeva discovered that shear stress undershoot exists for very high shear rates.[12] In 1972, I-Jen Chen and D. C. Bogue investigated high and low density polyethylene and polystyrene melts. They had collected some of the experimental values of overshoot and undershoot.[13] In 1974, the rheology properties of SBR polymers was observed by Charles Goldstein. He discovered that there is no overshoot in the shear stress growth, but he obtained low range of shear rate.[14]

Polymer melts of Lekutherm x-30, epoxy resin was investigated for its transient properties. Its viscous flow was studied in various temperatures. The experimental investigation for this thesis was observed by the use of a rotational viscometer.

II. EQUIPMENT AND MATERIALS

A. Rotational Viscometer

The rotational viscometer, a hollow cylinder rotor, has two three degree ends which rotate in a cup. The clearance between rotor and cup measures 0.075 inches. The rotor eliminates end effects by curving the ends of the bob. This maintains a constant shear rate over the whole rotor surface. The sharp edge of the cup on the rotor top creates very low shear rates, thus eliminating the Weissenberg effect. Fastening a weight to a nylon string wound around the drum attached to the rotor shaft creates the viscometer's driving force. An air bearing supports the entire weight of the rotating components, shown in detail on Figure 1. One uses the speed of the angular rotation of the rotor to measure polymer shear rate. The rotor and stationary components are shown in Figure 2. The rotational viscometer components, designed by Dr. Philippoff, are shown in Figurs 3 and 4. The rotational viscometer works as follows: air is forced out against the rotor's bearing plates through the holes of the viscometer's stationary components at a pressure of sixty PSIG. This reduces friction between the moving airplate and the stationary plate to a few thousandths of a dynes /cm^2 in shear stress terms. This measured at approximately 0.006 ± 0.0002 dynes/cm^2. (15)

The use of a cone-and-plate system for measuring viscosity was considered by Mooney and Ewart (1934). It made the same shear stress, hence eliminate the side effect, which similar to rotational viscometer that the sample is stress in uniformly.[16]

The following equation measures shear stress in the rotational viscometer:

$$\tau = \frac{981\ Wr}{2\pi R_1^2 L_o} = K_1 W \quad \text{dynes/cm}^2$$

where: W is the driving load (grams)

r is the radius of the drum where the thread is wound (cm)

R_1 is the radius of the inner cylinder (cm)

L_o is the equivalent length of the conical cylinder (cm)

The rate of shear, $\dot{\gamma}$, is given by:

$$\dot{\gamma} = \frac{2w}{1-C^2} = \frac{K_2}{t_{10^\circ}}$$

where T 10° is the time required to transverse ten degrees.

C is the ratio of the radius of the inner to outer cylinder, C = 0.950

w is the angular velocity in radians/second

Viscosity is then given by:

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{K_1 w t_{10^\circ}}{k_2} = k\ w t_{10^\circ}$$

Calibration with a reference oil (Bureau of Standard Oil 03) determined the constant K. The result -- a value of 11.17 as opposed to the calculated value of 10.92.

Calculation of the equivalent length caused the error of one %. K_1 and K_2 were calculated to give 4.00 and 3.58

$$\tau = 4.00\ W\ t$$

$$\dot{\gamma} = 3.58/t_{10^\circ}$$

Low rates of shear and a mirror over the drum on the shaft together with a simple optical system increased measuring accuracy. Later, this idea was improved. 36 mirrors, ¼" X ¼" X 1 1/6" reflected the lamp light on a curved scale at 229 cm. Each mirror equals about 10 degrees in angular displacement. Only the operator's ability sets the viscometer's limitations.[21]

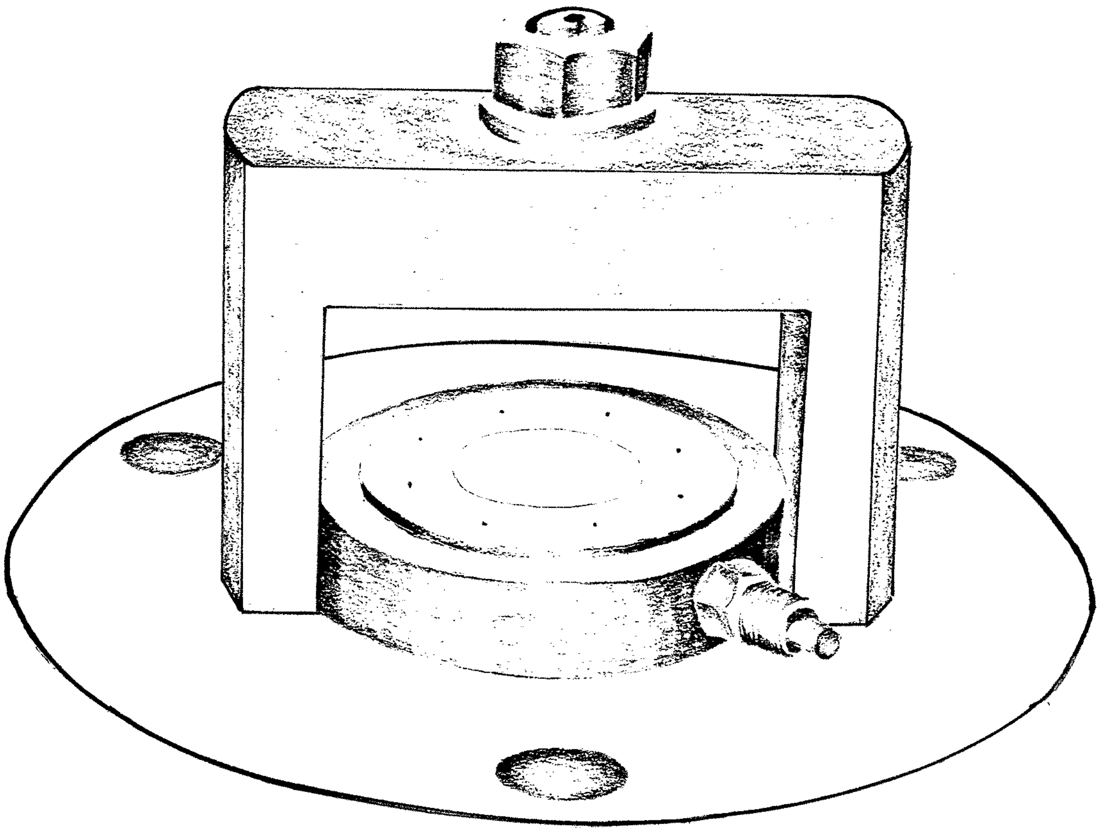


FIGURE 1[17]

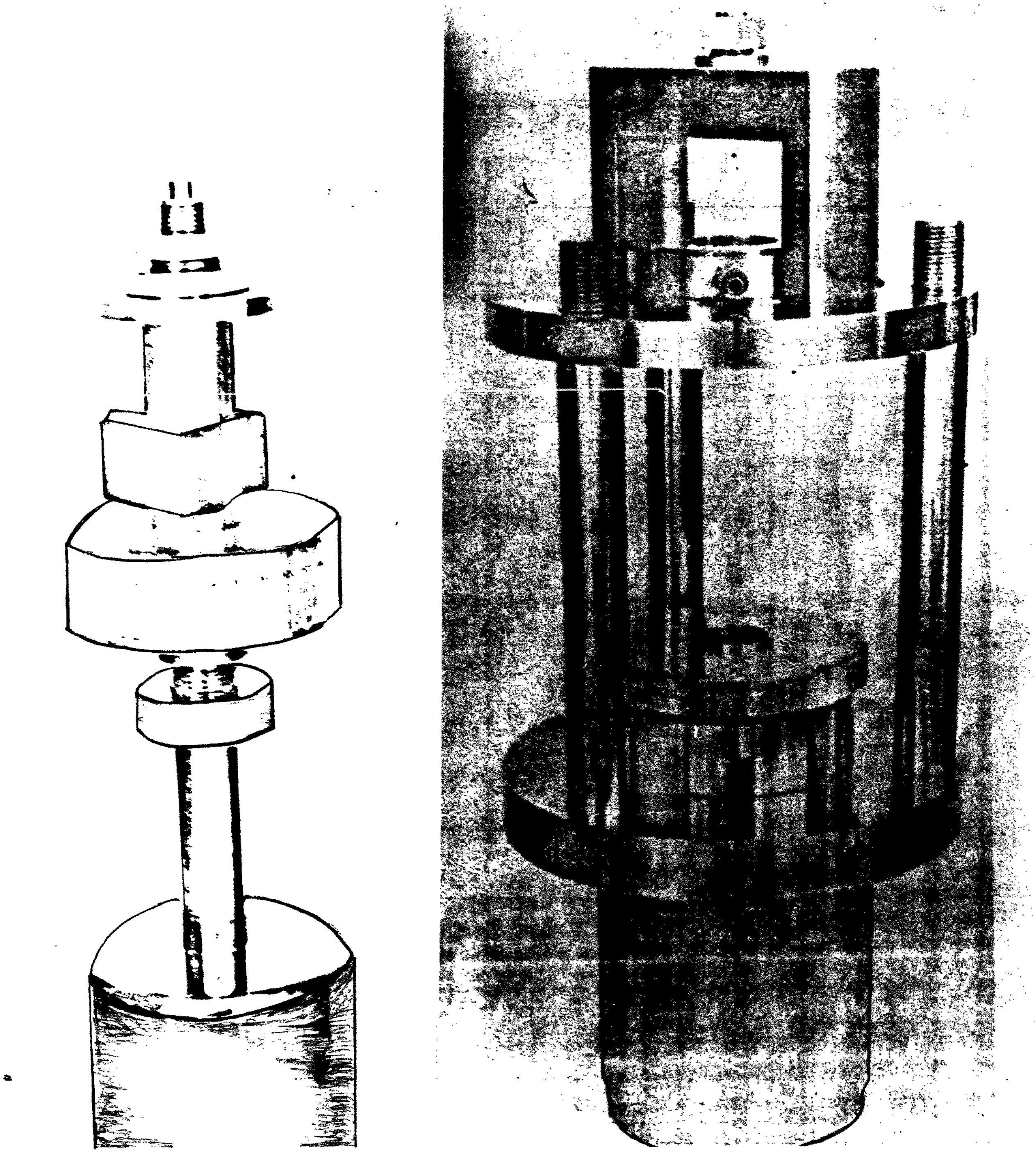


FIGURE 2[18]

ROTATIONAL VISCOMETER

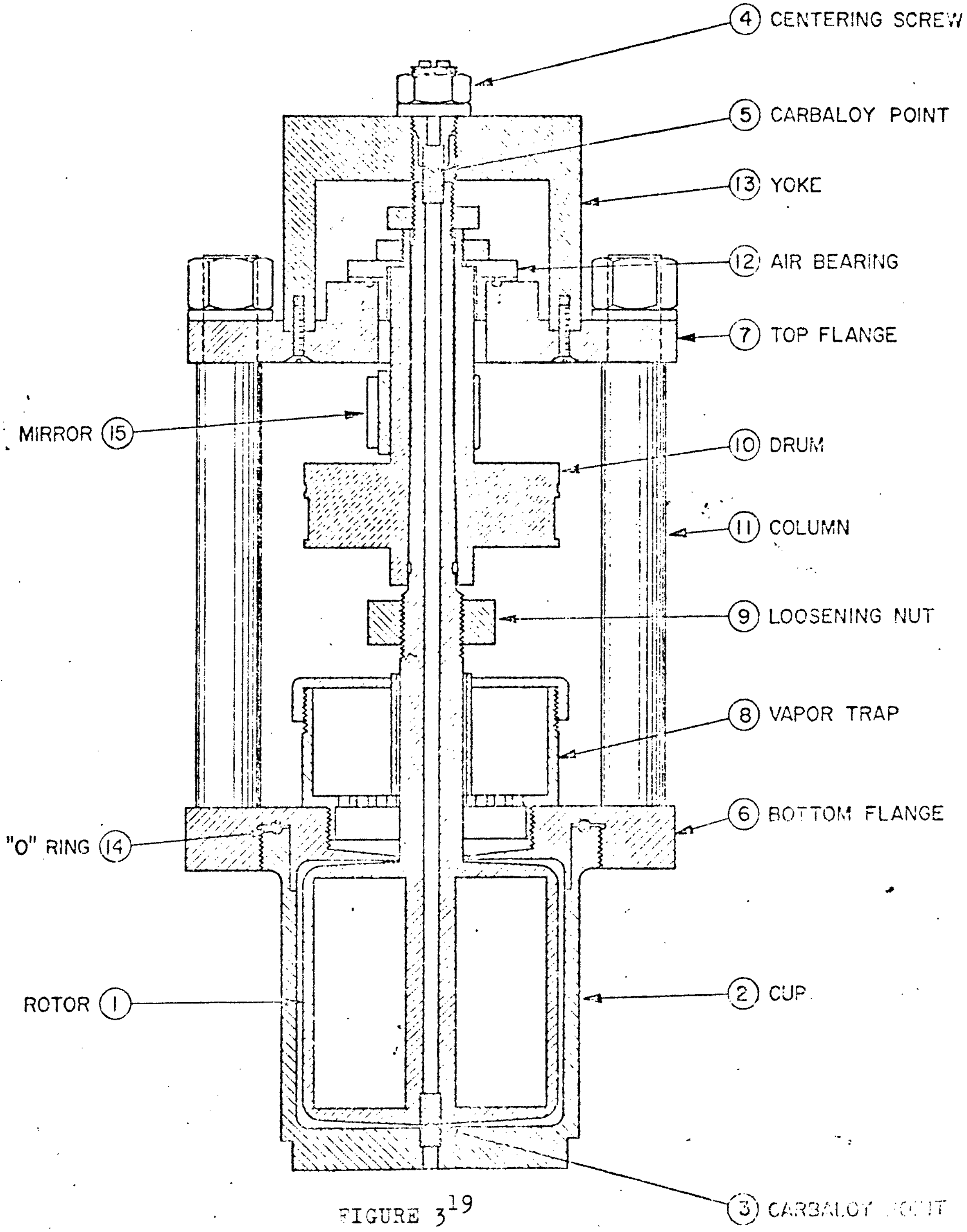


FIGURE 3[19]

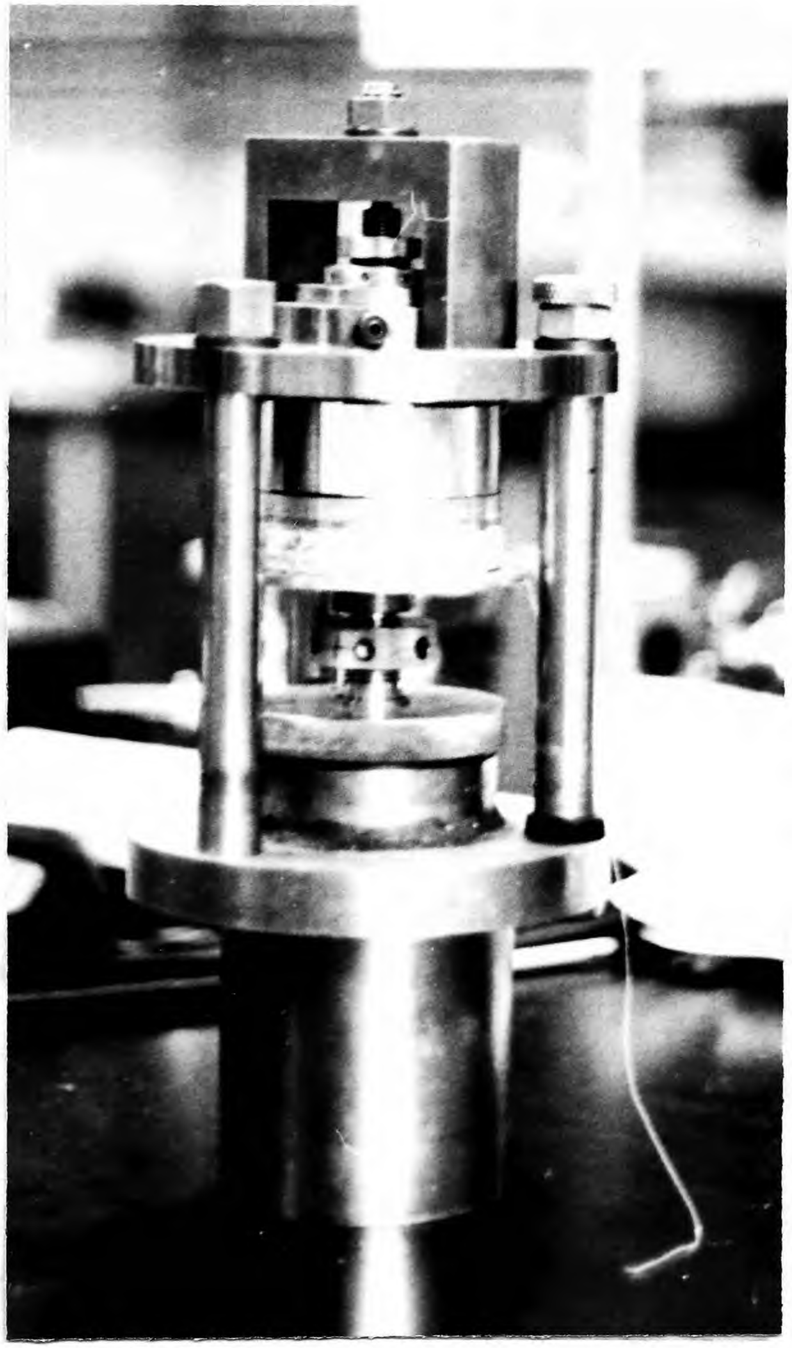


FIGURE 4[20]

B. Optical System

The optical system's component layout is shown in Figure 5. The light source is model 31-33-37, produced by Bausch & Lamb Incorporated of Rochester, New York. The transformer used with the lamp is produced by Jefferson Electronic Co. of Bellwood, Illinois (Cat. No. 969-001-069). The jack, which translates the lamp mounted on it into a vertical plane, is a Leno-Lerner-Lab-Jack (#19089). The beam of light enters an 888 mm. focal converging lens produced by Bausch & Lamb Optical Company of New York (cat. No. L-117, item #DCX-6-011). The half covered lens in front of the lamp produces a vertical semicircular image on a curved scale 299 cm from the viscometer. The converging lens increases image, sharpens to produce scale readings of ± ¼ mm. Then the viscometer's drum's 36 mirrors reflect the beam emerging from the converging lens to a curved scale 299 cm distant. Total resolution is 80 mm per degree. Two photocells, eight degrees apart turn on or off the electronic timing mechanisms, increasing viscosity accuracy and recoil measurements. This optical system is used primarily for low constant stresses when measuring viscosity, and is dependent on how viscous the polymer is. The operator determines the operation's cut-off point. For low constant stresses, use the optical system. For high constant stresses, measure degrees of displacement on the viscometer's drum.

When the image from the lamp hits the photocell at the 0° point. It triggers a stop-load mechanism and constant stress is removed. Then the image reverses itself to some equilibrium value. Thus the optical system increases the accuracy of the readings by measuring mm for recoil measurement.[22]

OPTICAL SYSTEM AND ROTATIONAL VISCOMETER LAYOUT

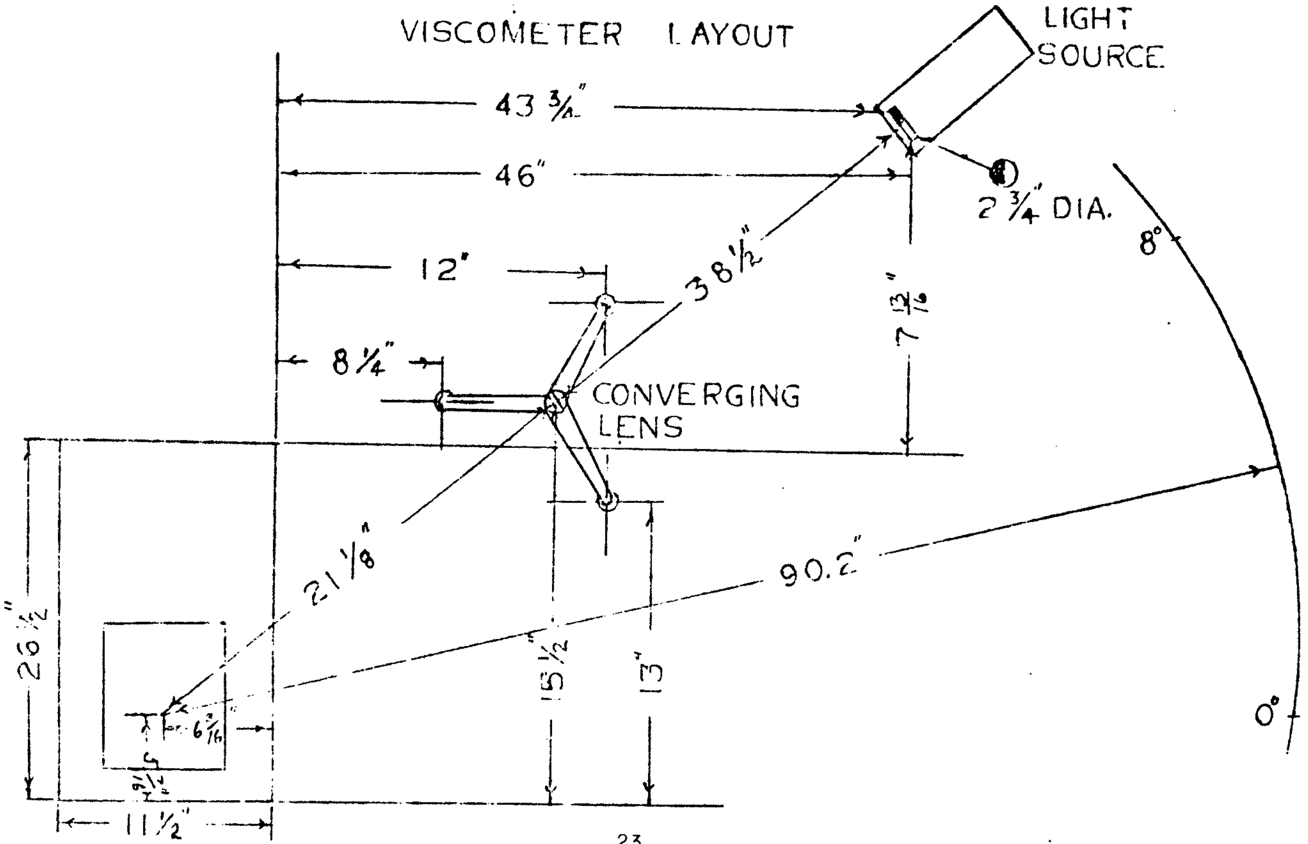


FIGURE 5^{23}

C. Timing and Heating Mechanism

A thermostat (Haake R21) produced by Haake of Berlin, Germany, keeps the temperature of the bath constant. The viscometer is placed in this bath. It is important that the constant water temperature in the bath equals the temperature of the polymer inside the viscometer. Run the experiment several times until the values become constant.

It is also important that water does not soak in through the flanges and contaminate the polymer; otherwise, much experimental time and data will be wasted. Place water resistant putty around the flanges to prevent water seepage.

The viscometer switching mechanism operates as follows:

1. Reflected light hits the first photocell, activating a timer which records the seconds used to travel eight degrees. To measure time for longer distances, cover up the stop time photocell for the amount of displacement desired.
2. When reflected light reaches the second photocell, the first timer stops and the recoil timer starts. At the same time, a stop load mechanism starts which catches the falling weight. Either procedure may be run, or both at once.

The viscometer switching circuit layout is shown in Figure 6 (Drawn by L. Hom of Esso Research).

It works as follows: When light hits the first photocell, relay 7-2-R_1 starts. This in turn opens 5-8-$R_2{}^2$ and closes 3-1-R_1 and 6-8-$R1^2$. When 6-8-$R1_2$ closes, the first clock starts.

When light reaches the second phtocell (also the stop-light) the 7-2-R2 relay starts. This in turn closes 5-8-$R2_2$, opens 6-8-$R1_2$ and closes 1-3-R2 and 4-1-$R1_1$. When 5-8-$R2^2$ opens, the first timer stops. When R_2 starts the first clock stops and the second relay R3 starts. This in turn starts the record clock and activates the solenoid, which removes the clamp from its unlock position.[24]

SWITCHING CIRCUIT FOR VISCOMETER

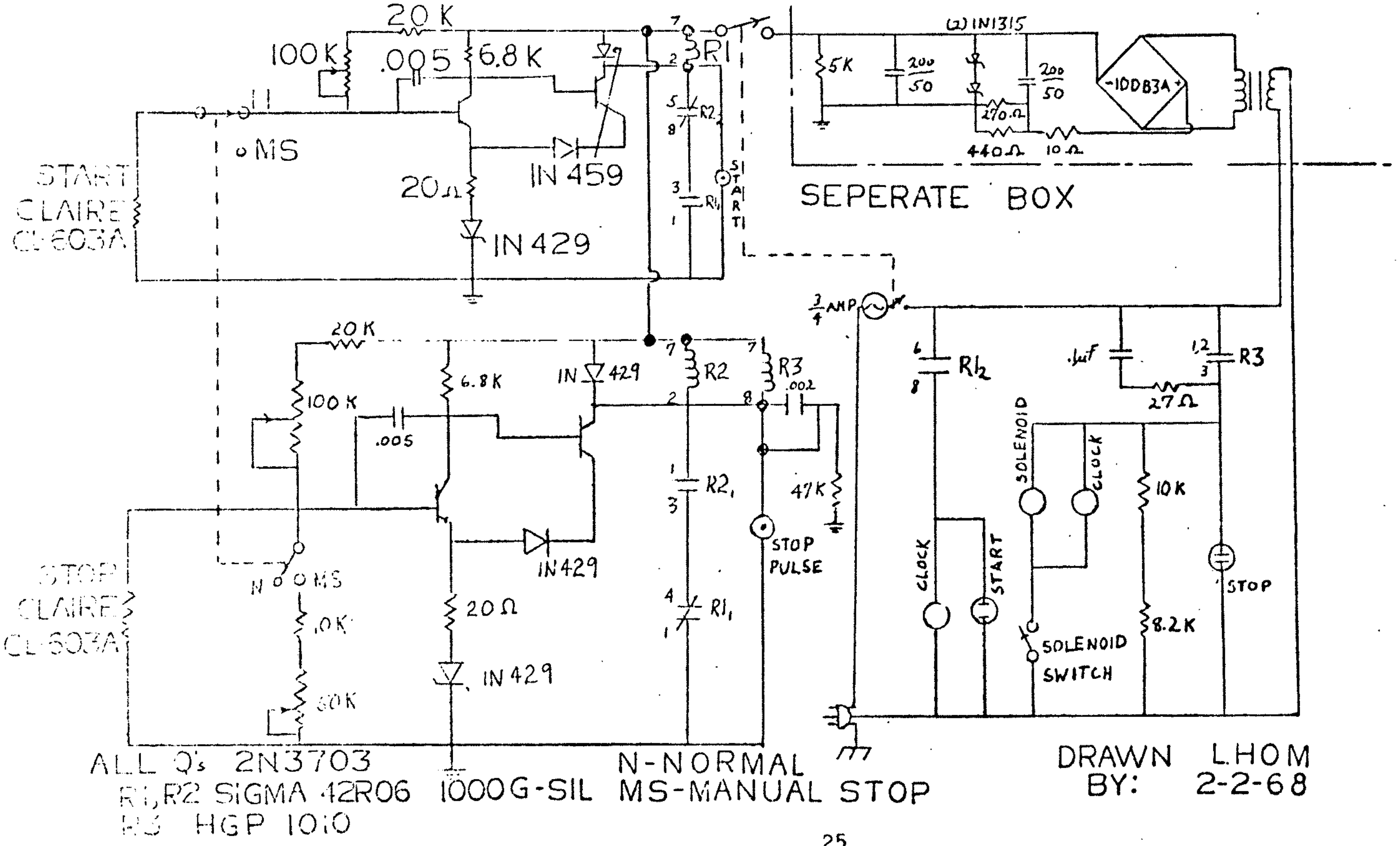


FIGURE 6

D. Apparatus Setup

The apparatus setup is shown in Figure 5. It functions: rays from the light source first pass through the image lens, located directly in front of the lightbulb. The image lens is an ordinary circular glass plate half-covered by non-transparent tape. Thus one may project a semi-circular image on the degree scale. The vertical edge can be used to read measurements. One can start and stop the timing mechanism by placing photocells eight degrees apart.

Next, the light rays pass through a converging lens, which converges rays onto the mirror of the viscometer's drum. The mirror reflects the light rays onto the measuring scale.

The measuring scale units are in degrees and mm. One degree equals 80 mm.

Originally one degree equaled 64 mm (6.4 cm). With these figures one can compute the scale's actual design radius of curvature so the differences result in insignificant error.

When the angle of the drum rotates one degree, the angle made by the viscometer and scale is two degrees: twice the angle made by the drum as shown in Figure 3. The actual radius of curvature determined by this formula is 183.439 cm.

One can now determine the change in α' due to the difference in radius.

Substituting the values in the following equation:

$$229\,\frac{(2)}{180\,\pi} \quad = \quad 80 \quad = \quad 183\,\frac{(\alpha')}{180\,\pi}$$

α' is 2.5°. Therefore, a radius of 229 cm and a corresponding of 2° relates to a 180 cm radius by a 5° increase, or $\alpha' = 2.5°$. The following error equation determines how this effects the radius of the light beam as it travels along the measurement scale.

Using the following error equation:

$$(1-\cos\theta_1) - (1-\cos\theta_1')\,\frac{183}{229} \quad = \quad \frac{|\Delta R_1| \times 100}{299} \quad = \quad \%\ \text{Error}$$

The reading from 0° - 4° will only be considered because the results of 4° - 8° will be symmetrical with the first results.

From 0° - 1°:

$$(1-\cos 2^\circ) - (1-\cos 2\tfrac{1}{2}^\circ)\,\frac{183}{299} \quad = \quad \frac{|\Delta R_1| \times 100}{299} \quad = 0.01987\%$$

From 0° - 2°:

$$(1-\cos 4^\circ) - (1-\cos 5^\circ)\,\frac{183}{299} \quad = \quad \frac{|\Delta R_1| \times 100}{299} \quad = \quad 0.0634\%$$

From 0° - 3°:

$$(1-\cos 6^\circ) - (1-\cos 7\tfrac{1}{2}^\circ)\,\frac{183}{299} \quad = \quad \frac{|\Delta R_1| \times 100}{299} \quad = \quad 0.1375\%$$

From 0° - 4°

$$(1-\cos 8^\circ) - (1-\cos 10^\circ)\,\frac{183}{299} \quad = \quad \frac{|\Delta R_1| \times 100}{299} \quad = \quad 0.2225\%$$

Since the error involved is small, we are justified in using a measurement scale with a design radius specification of 183 cm to one of 229 cm radius. Use of a measurement scale with a design radius specification of 183 cm to one of 229 cm radius is justified since the error is small.[26]

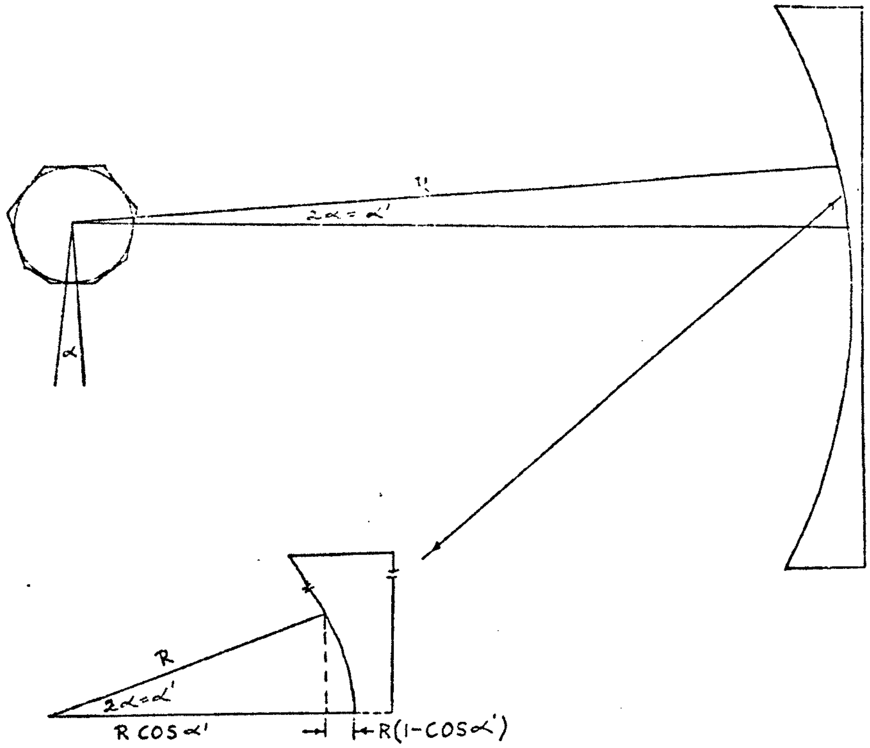


FIGURE (7)[27]

the following relationship is used;

$$L = R \cdot \frac{\pi}{180} \alpha'$$

where: L = Length of Arc
R = Radius of curvature
α' = Angle of rotation of arc

E. Materials

There are two kinds of materials which are used to measure the viscosity.

1. 6% L-200 in PRIMOL 335 (Polyisobutylene)

   This polymer solution was measured in 1975 by Dr. Philippoff. The polymer solution was made just before he had started to do the experiment, and then stored in the apparatus for two years. Therefore one can attempt to remeasure the material to see how it will react over a period of time. It's viscosity will show the change of the material. One can also check the instrument to be sure of accuracy for the next experiment.

2. Lekutherm x-30

   This material is epoxy resin, a product from Germany which no one ever measured the whole range of temperature of its viscosity. Lekutherm x-30 will be used in birefringence to find its stress-optical coefficient for the optic part of the experiment.

III. EXPERIMENTAL PROCEDURE

Viscosity Measurements in Terms of Stress and Shear Rate

The apparatus setup of this experiment has been shown in the previous chapter. Viscosity measuring equipment is composed of a weight which is attached to a string wound around rotational viscometer drum. The weight is pulled down due to the gravity, therefore, causing the drum and bob to rotate. The mirrors on the top of the drum also rotate. At the same moment the rays from a light source passing through a converging lens will reflect off the mirror onto the measuring scale (see Figure 8). Two photocells are placed eight degrees apart on the measurement scale. The photocells are placed eight degrees apart on the measurement scale. The photocells are operated by triggering a timing mechanism on and off. This records time versus displacement The viscosity can be calculated by knowing the weight and displacement time for eight degrees as follows:

$$\eta = \frac{\tau}{\dot{\gamma}}$$

$$\dot{\gamma} = \frac{3.58}{1.25t_{8^\circ}} = \frac{3.58}{t_{10^\circ}}$$

where η is viscosity, measurement in poise or (dynes x sec)/cm^2. τ is shear stress, four times weight and unit is dynes/cm^2. $\dot{\gamma}$ is rate of shear and unit is sec^{-1}. t_{8° is time for displacement of eight degrees, measurement in seconds.

Approximately sixty grams of an epoxy resin is added to the cup. One has to be careful about the resin level, which should be safely below the water trap holes. The error due to this problem, is decreasing in rate of shear, therefore, one will obtain a higher than normal viscosity reading. It is also important that the rotary shaft in the section of the vapor trap compartment is completely free of any resin, for it also tends to give higher than normal viscosity readings.

The viscometer containing the polymer is submerged in a constant temperature water bath. The water level is three fourths of the way up to the vapor trap component. This will keep the temperature of the polymer the same as the water bath temperature.

Eight degree time measurements are taken at regular intervals until constant readings are obtained. At the higher weights measurement of viscosities, one can obtain the degree reading right at the drum of the viscometer. This method is used only when the time measured for eight degrees becomes too small to measure accurately.

The centering screw is adjusted when measurement is obtained. For high weight measurements, the air pressure has to be turned off and the centering screw is turned on (all the way), until contact is made between the carbaloy point and the rotational shaft. Then reserve the centering screw is one quarter of a turn. After the air bearing plate is off the viscometer is now ready to measure. For the low weight measurement the air bearing plate is used. This will make the rotational viscometer virtually frictionless with the air pressure forcing the bob up from its carbaloy point making. In higher weight the air bearing plate nut must be loosened completely. This will allow more play between the carbaloy points, therefore, the centering screw should be adjusted as outlined before. The rotational viscometer is not sensitive to the small friction that may arise from the carbaloy points for high weights. To determine the cutoff point by using the intermediate weights with the air plate on and with the air plate off. When the viscosity deviates between using the air plate on and off, the cutoff point is determined. Leaving the air plate on after the cutoff point will show increased viscosity readings.

Check that the rotational viscometer is leveled, and that the contact surface between the air bearing and the top flange is smooth and clean.

Be careful that the flanges of the rotational viscometer, which is submerged under a constant water bath, is covered with water insoluble putty to prevent water leaking. To prevent slippage use high weights by using a strong stop-load clamp with a high frictional coating. This will help increase the accuracy of the measurement. Also use a device that will stabilize the clamp of the rotational viscometer in place to prevent any movement that will cause the rotational viscometer to slip out of place.

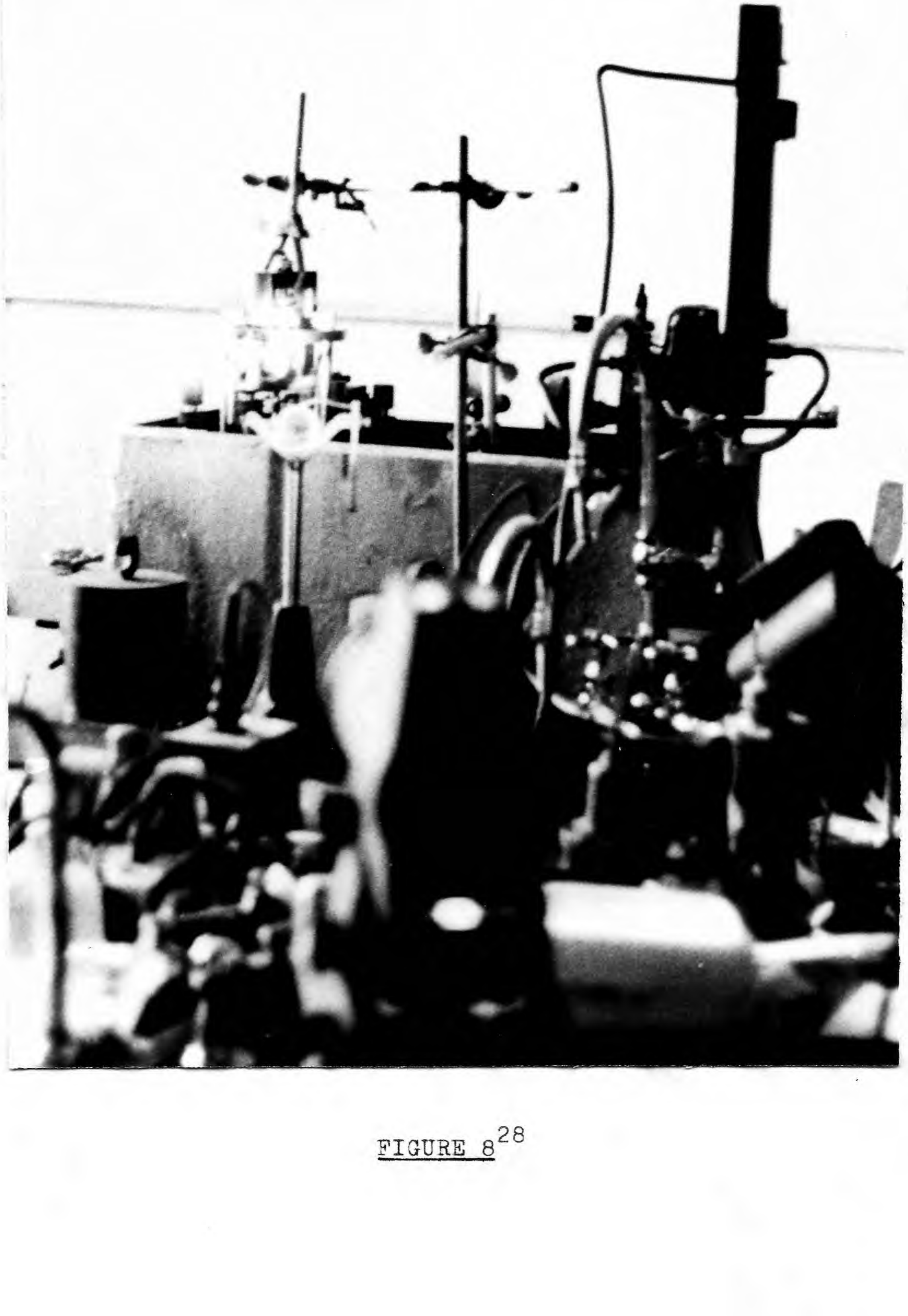


FIGURE 8[28]

6% L-200 in Primol 355 measured temperature at 25° C and the epoxy resin (LEKUTHERM X-30) measured at varying temperatures.

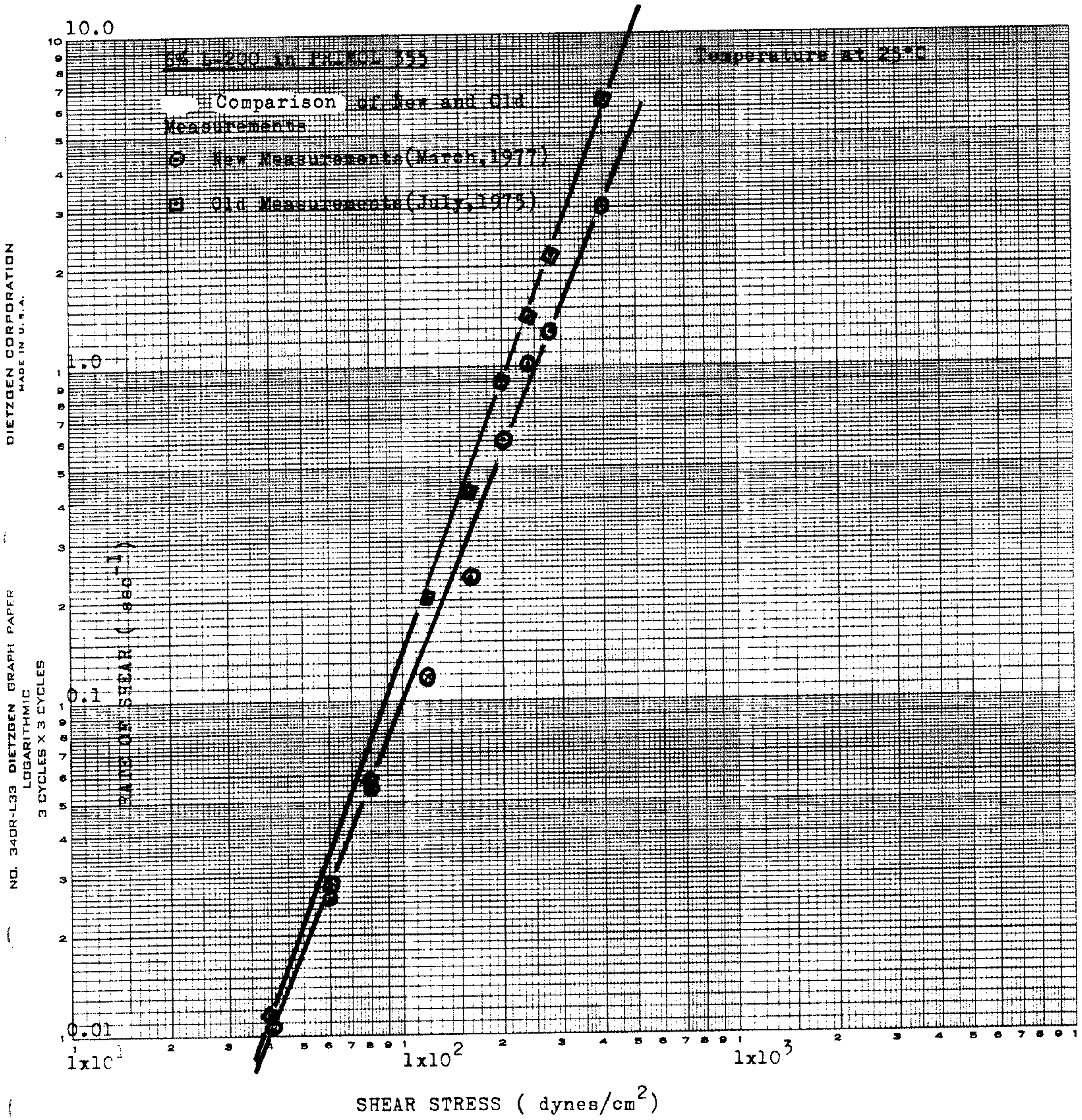
A. Recheck viscosity of 6% L-200 in PRIMOL 355

g	τ $\frac{\text{dynes}}{\text{cm}^2}$	t''_{10°	$\dot{\gamma}$ sec^{-1}	η in P
100	400	339.61	1.054×10^{-2}	37950.664
150	600	139.07	2.574×10^{-2}	23310.023
200	800	68.15	5.253×10^{-2}	15229.393
300	1200	30.00	0.119	10084.034
400	1600	15.14	0.236	6779.661
500	2000	5.92	0.605	3305.785
600	2400	3.43	1.044	2298.851
700	2800	2.80	1.278	2190.923
1000	4000	1.15	3.113	1284.934

Temperature at 25°C, 3/7/1977

6% L-200 in PRIMOL 355, temperature at 25°C July, 1975

g	τ $\frac{\text{dynes}}{\text{cm}^2}$	$t''_{10°}$	$\dot{\gamma}$ sec^{-1}	η in P
1	4	119000	0.301×10^{-4}	133000
2	8	57680	0.620×10^{-4}	129000
3	12	36000	0.994×10^{-4}	120000
5	20	20860	1.720×10^{-4}	117000
7	28	14300	2.500×10^{-4}	112000
10	40	9520	3.760×10^{-4}	106500
15	60	5840	6.120×10^{-4}	98000
20	80	3860	9.270×10^{-4}	86300
30	120	2310	1.550×10^{-3}	77400
50	200	1010	3.550×10^{-3}	56400
70	280	613	5.840×10^{-3}	48000
100	400	312.5	1.145×10^{-2}	35000
150	600	126	2.840×10^{-2}	21100
200	800	61.	5.860×10^{-2}	13650
300	1200	17.15	0.208	5760
400	1600	8.5	0.421	3800
500	2000	3.95	0.906	1960
600	2400	2.55	1.400	1710
700	2800	1.67	2.15	1300
1000	4000	0.58	6.15	650


5% L-200 in PRIMOL 355
Temperature at 25°C
Comparison of New and Old Measurements
⊙ New Measurements(March,1977)
⊡ Old Measurements(July,1975)
RATE OF SHEAR (sec⁻¹)
SHEAR STRESS (dynes/cm²)
10.0
1.0
0.1
0.01
1x10
1x10²
1x10³
DIETZGEN CORPORATION
MADE IN U.S.A.
NO. 340R-L33 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 3 CYCLES

B. Data of LEKUTHERM X-30 March, 1977

T(°C)	Wt(g)	τ $\frac{dynes}{cm^2}$	$t''_{10°}$	$\dot{\gamma}$ (sec^{-1})	η (MP)	η (MP) average	log η average
29.9	2860	11440	42717.71	$8.381x10^{-5}$	136.52	137.53 * ± 1.01 0.73%	2.1384
	4596	18384	26980.8	$1.327x10^{-4}$	138.54		
31.9	1500	6000	26184	$1.367x10^{-4}$	43.89		
	2860	11440	13990	$2.559x10^{-4}$	44.70	44.38 * ±0.36 0.80%	1.6473
	3767	15068	10592	$3.380x10^{-4}$	44.58		
33.9	1000	4000	14875.2	$2.410x10^{-4}$	16.6		
	1500	6000	9675.2	$3.700x10^{-4}$	16.2	16.20 * ± 0.28 1.75%	1.2095
	2860	11440	4934.4	$7.200x10^{-4}$	15.8		
	3767	15068	3840.8	$9.300x10^{-4}$	16.2		
35.9	500	2000	11904.0	$0.301x10^{-3}$	6.64		
	1000	4000	5944.0	$0.602x10^{-3}$	6.64		
	1500	6000	3944.0	$0.908x10^{-3}$	6.61	6.64 * ±0.02 0.29%	0.8222
	2860	11440	2081.2	$1.720x10^{-3}$	6.65		
	3767	15068	1585.0	$2.260x10^{-3}$	6.67		
37.9	200	800	12608.0	$0.284x10^{-3}$	2.82		
	500	2000	5000.0	$0.716x10^{-3}$	2.79		
	1000	4000	2432.0	$1.474x10^{-3}$	2.71	2.75 * ±0.05 1.79%	0.4390
	1500	6000	1640.0	$2.180x10^{-3}$	2.75		
	2860	11440	840.0	$4.260x10^{-3}$	2.67		
	3767	15068	650.0	$5.500x10^{-3}$	2.74		
39.9	100	400	10496.0	$0.341x10^{-3}$	1.173		
	200	800	5392.0	$0.664x10^{-3}$	1.205		
	500	2000	2200.0	$1.630x10^{-3}$	1.227		
	1000	4000	1055.0	$3.390x10^{-3}$	1.180	1.21 * ±0.02 1.76%	0.0828
	1500	6000	735.0	$4.870x10^{-3}$	1.232		
	2860	11440	381.0	$9.400x10^{-3}$	1.217		
	3767	15068	289.0	$12.380x10^{-3}$	1.217		

*Error

Data of LEKUTMERM X-30

T(°C)	Wt(g)	τ $\frac{dyms}{cm^2}$	$t''_{10°}$	$\dot{\gamma}$ (sec^{-1})	η (MP)	η (MP) average	log η average
41.9°	1000	4000	536	6.680×10^{-3}	0.59	0.58 *±0.0087 1.49%	- 0.236
	1500	6000	349	1.030×10^{-2}	0.58		
	2860	11440	180	1.990×10^{-2}	0.57		
	3767	15068	136	2.630×10^{-2}	0.57		
43.9	1000	4000	260	1.380×10^{-2}	0.29	0.29 *±0.00 0.00%	- 0.538
	1500	6000	173	2.000×10^{-2}	0.29		
	2860	11440	90	3.980×10^{-2}	0.29		
	3767	15068	69.5	5.150×10^{-2}	0.29		
45.9	1000	4000	133	2.690×10^{-2}	0.15	0.15 *±0.00 0.00%	- 0.824
	1500	6000	92.5	3.870×10^{-2}	0.15		
	2860	11440	46.3	7.730×10^{-2}	0.15		
	3767	15068	35.0	10.230×10^{-2}	0.15		
47.9	1000	4000	72.7	4.930×10^{-2}	0.081	0.081 *±0.0005 0.62	-1.092
	1500	6000	48.1	7.440×10^{-2}	0.081		
	2860	11440	25.6	14.010×10^{-2}	0.082		
	3767	15068	19.1	18.710×10^{-2}	0.081		
50.0	500	2000	83.6	4.283×10^{-2}	0.0467	0.046 *±0.00047 1.02%	-1.337
	1000	4000	41.5	8.637×10^{-2}	0.0463		
	1500	6000	27.4	13.091×10^{-2}	0.0458		
	2860	11440	14.4	24.861×10^{-2}	0.0460		
	3767	15068	10.8	33.284×10^{-2}	0.0453		
55.0	50	200	229.7	1.559×10^{-2}	0.0128	0.0125 *±0.00017 1.38%	- 1.901
	100	400	112.6	3.179×10^{-2}	0.0126		
	200	800	56.1	6.378×10^{-2}	0.0125		
	500	2000	22.7	15.781×10^{-2}	0.0127		
	1000	4000	11.2	32.044×10^{-2}	0.0125		
	2860	11440	3.9	93.035×10^{-2}	0.0123		

*Error

Data of LEKUTHERM X-30

T(°C)	Wt(g)	τ $\frac{dynes}{cm^2}$	t''_{10°	$\dot{\gamma}$ (sec^{-1})	η (MP)	η (MP) average	log η average
60.0	50	200	78.675	4.550×10^{-2}	0.004396	0.004315 •±.000053 1.23%	-2.365
	100	400	38.890	9.210×10^{-2}	0.004343		
	200	800	19.100	18.740×10^{-2}	0.004268		
	500	2000	7.770	46.075×10^{-2}	0.004341		
	1000	4000	3.874	92.411×10^{-2}	0.004328		
	2860	11440	1.320	2.712	0.004218		
	1500	6000	2.571	1.392	0.004310		
65.0	50	200	30.145	1.188×10^{-1}	0.001684	0.001667 •±.000029 1.72%	- 2.778
	100	400	15.215	2.353×10^{-1}	0.001699		
	200	800	7.570	4.729×10^{-1}	0.001692		
	500	2000	2.986	1.1989	0.001668		
	1000	4000	1.465	2.4437	0.001637		
	1500	6000	0.9675	3.7003	0.001621		
70.0	50	200	13.660	2.621×10^{-2}	0.000763	0.000742 •±.000016 1.54%	- 3.130
	100	400	6.643	5.389×10^{-1}	0.000742		
	200	800	3.267	1.096	0.000739		
	500	2000	1.321	2.710	0.000738		
	1000	4000	0.665	5.383	0.000743		
	1500	6000	0.423	8.287	0.000724		
75.0	50	200	6.666	0.5375	0.000372	0.000362 •±.000008 2.23%	- 3.453
	100	400	3.312	1.089	0.000367		
	200	800	1.637	2.187	0.000366		
	500	2000	0.634	5.647	0.000354		
	1000	4000	0.314	11.401	0.000351		
85.0	5	20	22.282	0.161	0.0001242	0.0001177 •±.000005 4.3%	- 3.957
	10	40	10.734	0.334	0.0001200		
	20	80	5.181	0.691	0.0001160		
	50	200	1.978	1.810	0.0001105		

•Error

Data of LEKUTHERM X-30 **March25, 1977**

T(°C)	Wt(g)	τ $\frac{\text{dynes}}{\text{cm}^2}$	$t''_{10°}$	$\dot{\gamma}$ (sec^{-1})	η (MP)	η (MP) average	log η average
95.0	5	20	8.530	0.4197	0.00004765		
	10	40	4.146	0.8635	0.00004632		
	20	80	1.962	1.8247	0.00004384	0.00004409	- 4.3556
	50	200	0.742	4.8248	0.00004145	•±.0000002	
	100	400	0.372	9.6237	0.00004156	0.56%	

Data of X-30 March 28, 1977

50.0	500	2000	83.88	4.268×10^{-2}	0.04686	0.0466	
	1000	4000	41.59	0.861×10^{-1}	0.04650	•±.0002	
						0.42%	

•Error

Data of LEKUTHERM X-30 Viscosity, Recheck

T(℃)	Wt(g) --	τ $\frac{\text{dynes}}{\text{cm}^2}$	t''_{10°	$\dot{\gamma}$ (sec^{-1})	η (MP)	η (MP) average	log η average
29.9	4596	18384	44244.33	$8.0914\text{x}10^{-5}$	227.204	226.582 •±0.622 0.27%	2.3555
6/13/77	3767	15068	53686.88	$6.6683\text{x}10^{-5}$	225.960		
31.9	1500	6000	43689.26	$8.1940\text{x}10^{-5}$	73.224		
6/7/77	2860	11440	22982.80	$1.5580\text{x}10^{-4}$	73.427	73.753 •±0.612 0.83%	1.8678
w/ air	3767	15068	17726.40	$2.0196\text{x}10^{-4}$	74.609		
39.9	1500	6000	1134.40	$3.1560\text{x}10^{-3}$	1.90114		
6/7/77	2860	11440	599.40	$6.0230\text{x}10^{-3}$	1.8994	1.9009 •±0.0016 0.082%	0.2790
w/ air	3767	15068	451.95	$7.9210\text{x}10^{-3}$	1.9023		
6/10/77	4596	18384	368.10	$9.7260\text{x}10^{-3}$	1.89	with air	
	4596	18384	422.50	$8.47 \text{ x } 10^{-3}$	2.17	with out air	
50.0	200	800	263.00	$1.361\text{x}10^{-2}$	587.8	with air	
6/3/77	500	2000	111.625	$3.207\text{x}10^{-2}$	623.6	with out air	
	1000	4000	56.20	$6.370\text{x}10^{-2}$	627.94	" " "	
	1500	6000	37.10	$9.650\text{x}10^{-2}$	621.76	" " "	
	2860	11440	19.40	$1.845\text{x}10^{-1}$	620.05	" " "	
	3767	15068	14.75	$2.427\text{x}10^{-1}$	620.85	" " "	
50.0	100	400	529.30	$6.764\text{x}10^{-3}$	591.366		
6/6/77	200	800	271.70	$1.318\text{x}10^{-2}$	606.98		
w/ air	500	2000	106.41	$3.360\text{x}10^{-2}$	595.238		
	1000	4000	53.90	$6.640\text{x}10^{-2}$	602.41	599.325 •±5.02 0.84%	- 1.222
	1500	6000	35.54	$1.007\text{x}10^{-1}$	595.65		
	2860	11440	18.81	$1.903\text{x}10^{-1}$	601.16		
	3767	15068	14.31	$2.501\text{x}10^{-1}$	602.47		

•Error

Comparison between new viscosity and old viscosity

T(°C)	η (MP) NEW average	Errors %	η (MP) OLD average	Errors %	% diff.
29.9	226.582	0.27	137.530	0.73	64.76
31.9	73.753	0.83	44.380	0.80	66.19
39.9	1.901	0.08	1.210	1.76	57.10
50.0	0.05993	0.84	0.04602	1.02	30.32

Data of the reversible value (when stop weight suddenly)

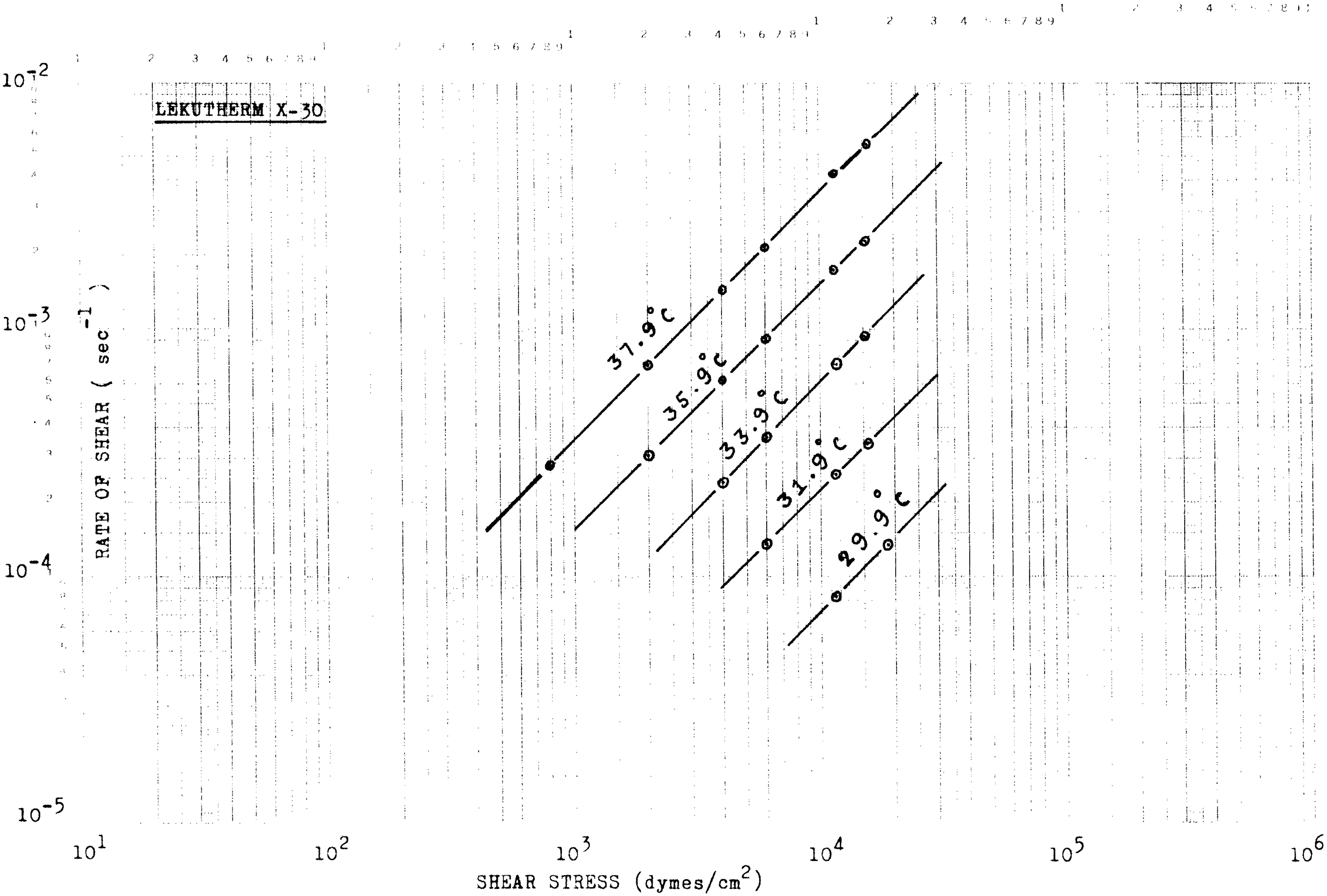
T(°C)	Reversible values (go back) (mm)	Wt (g)
29.9	4	3767
72.0	2	1000

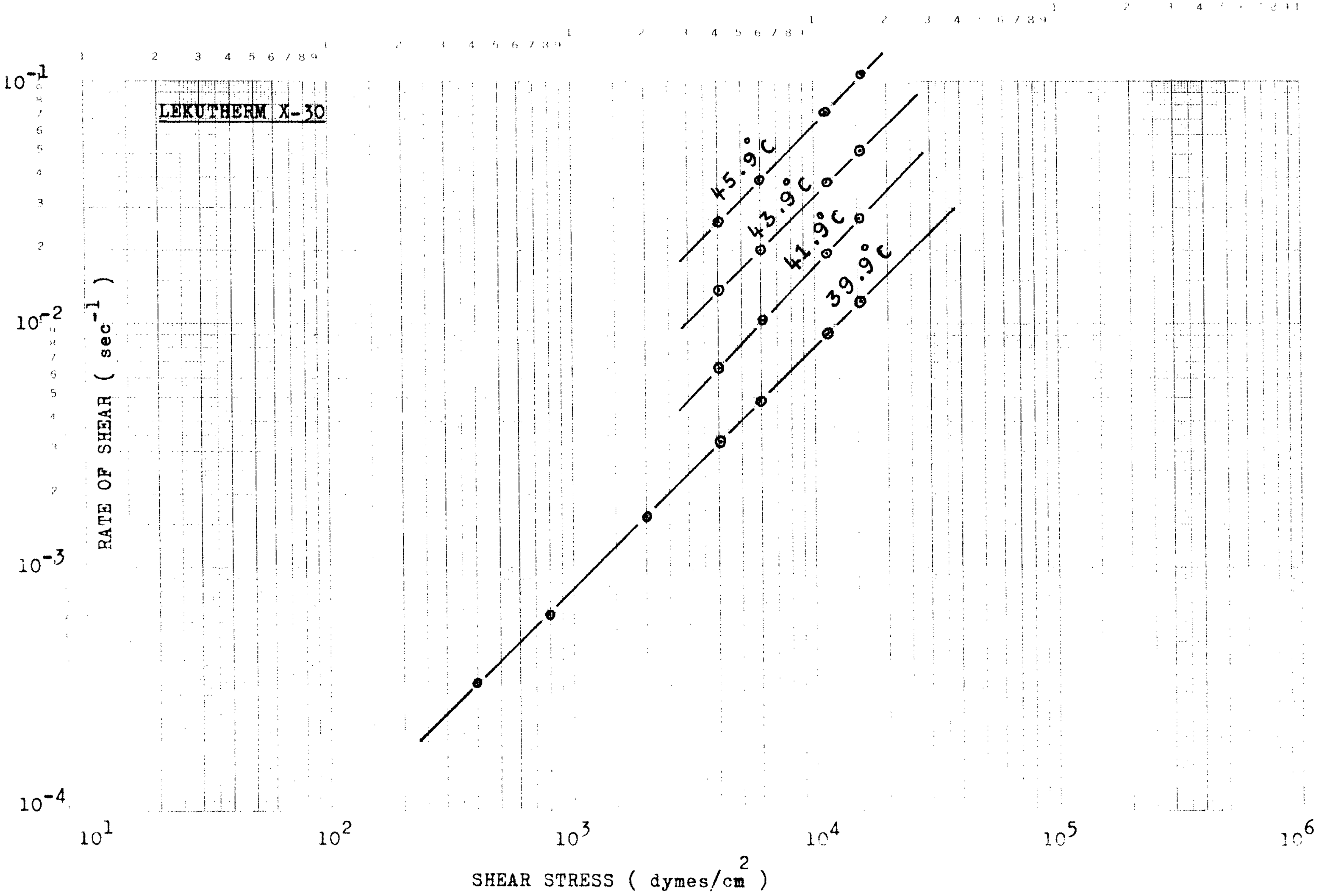
Viscosity of LEKUTHERM X-30 from Extrapolated Valuee

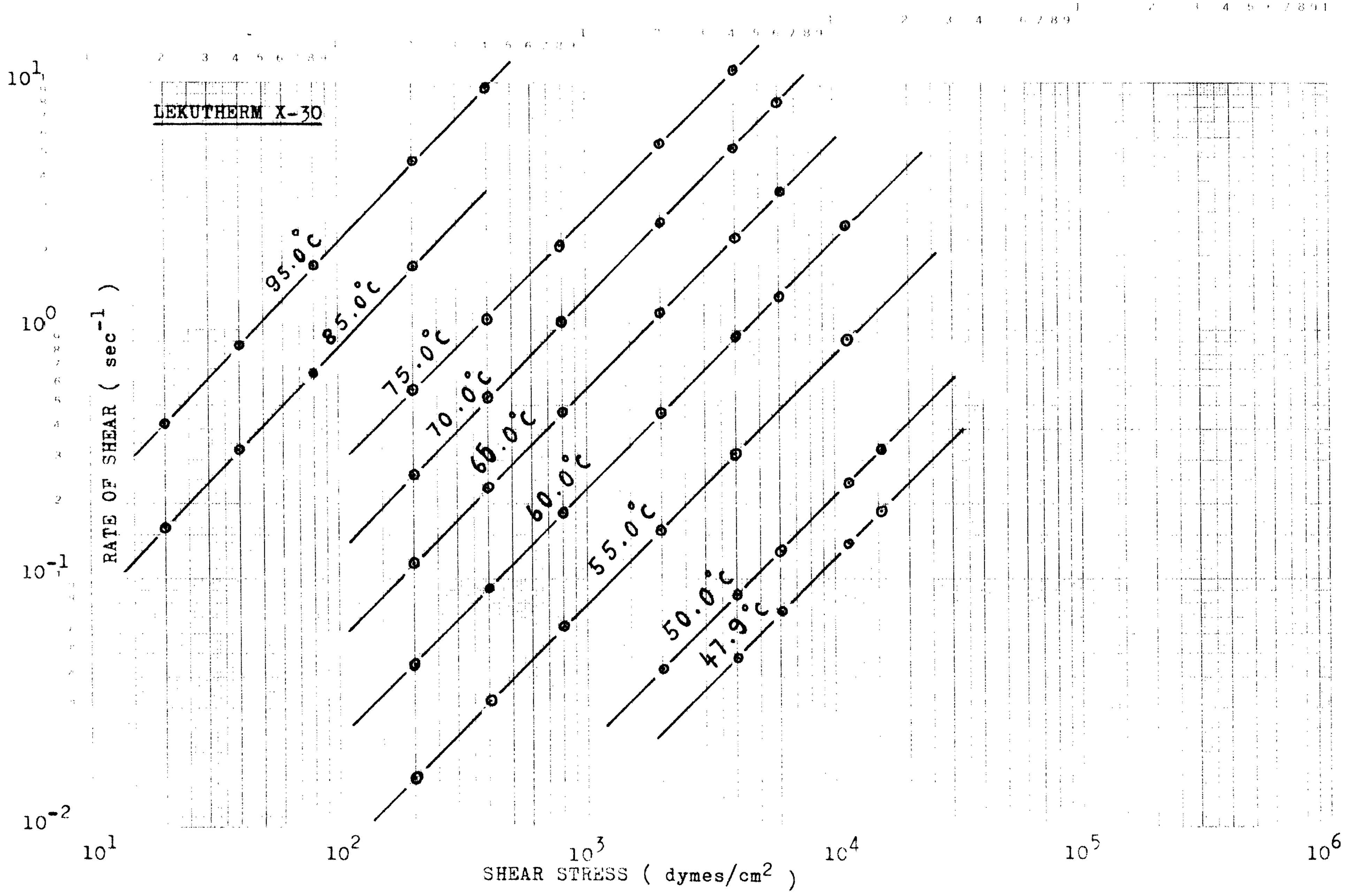
T (°C)	log η	η (MP)
12	6.900	7943282.347
14	6.250	1778279.410
16	5.650	446683.592
18	5.100	125892.541
20	4.575	37583.740
22	4.050	11220.185
25	3.300	1995.262
28	2.575	375.837
29	2.350	223.872
100	- 4.550	2.818×10^{-5}
110	- 4.925	1.189×10^{-5}
120	- 5.300	5.012×10^{-6}
130	- 5.600	2.512×10^{-6}
140	- 5.900	1.259×10^{-6}
150	- 6.275	5.309×10^{-7}
160	- 6.450	3.548×10^{-7}

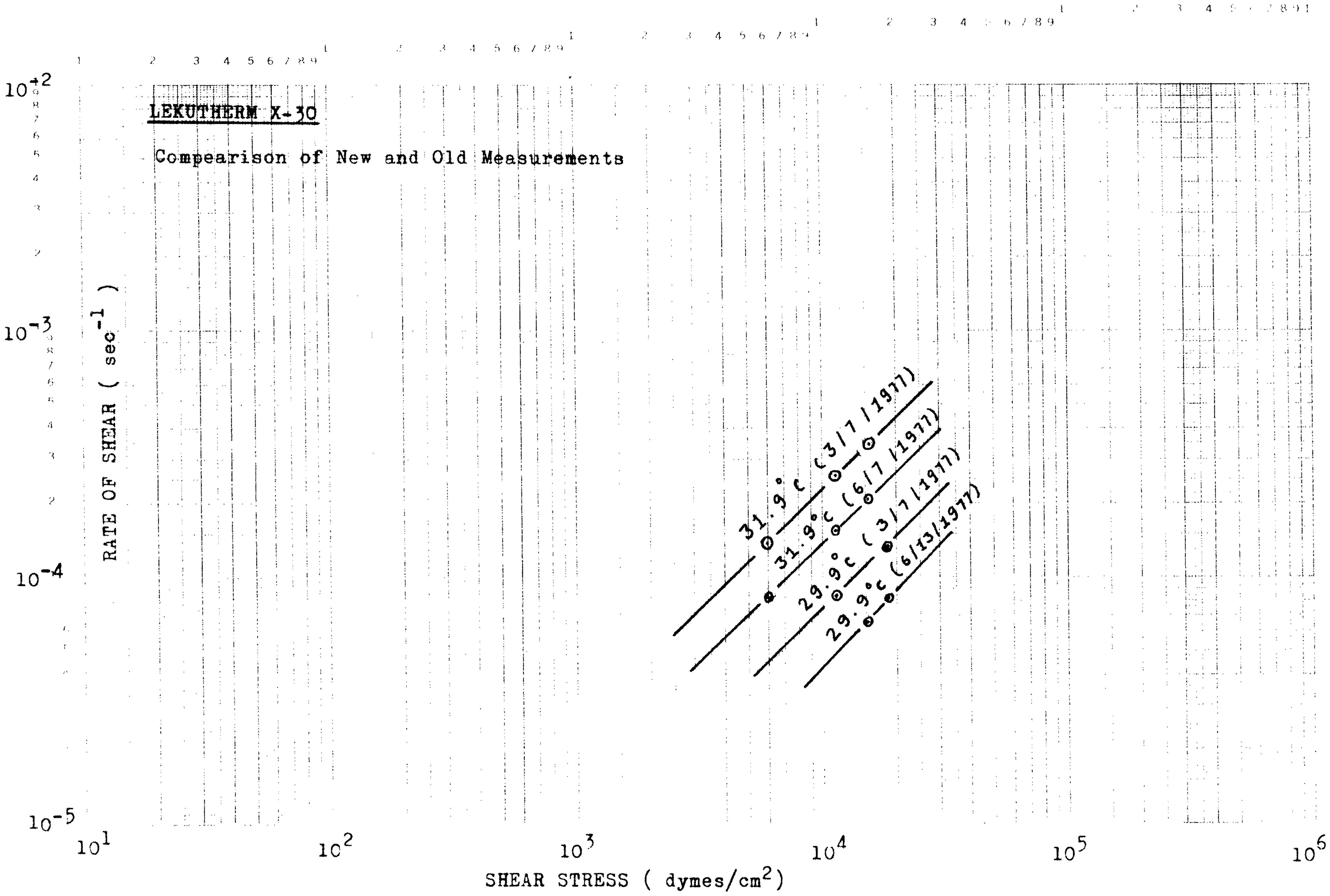
LEKUTHERM X-30

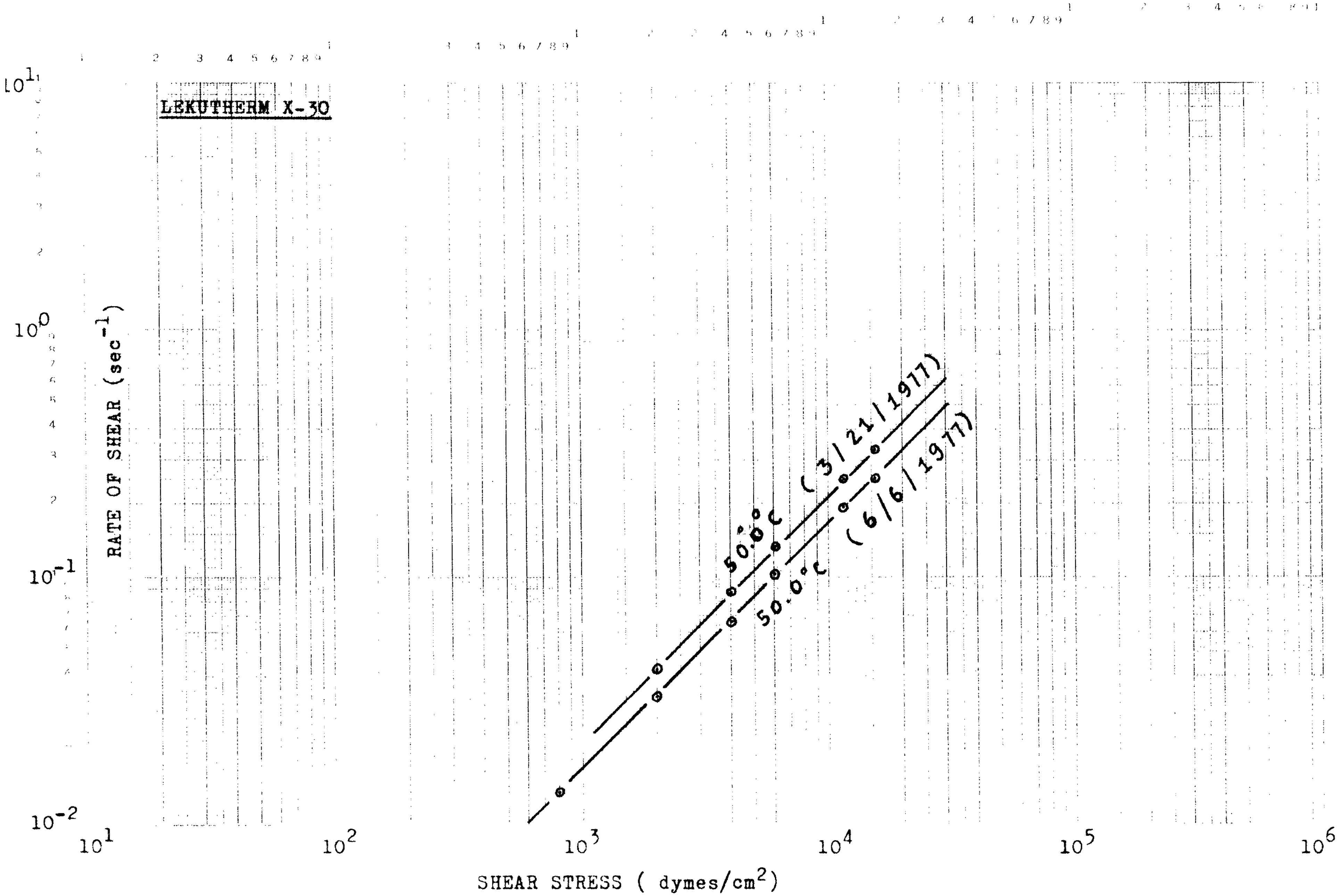
T (°C)	$\frac{1}{T} \times 10^6$
29.9	33444.82
31.9	31347.96
33.9	29458.53
35.9	27855.15
37.9	26385.22
39.9	25062.65
41.9	23866.35
43.9	22779.04
45.9	21786.49
47.9	20876.83
50.0	20000.00
55.0	18181.81
60.0	16666.67
65.0	15384.60
70.0	14285.70
75.0	13333.33
85.0	11764.70
95.0	10526.30

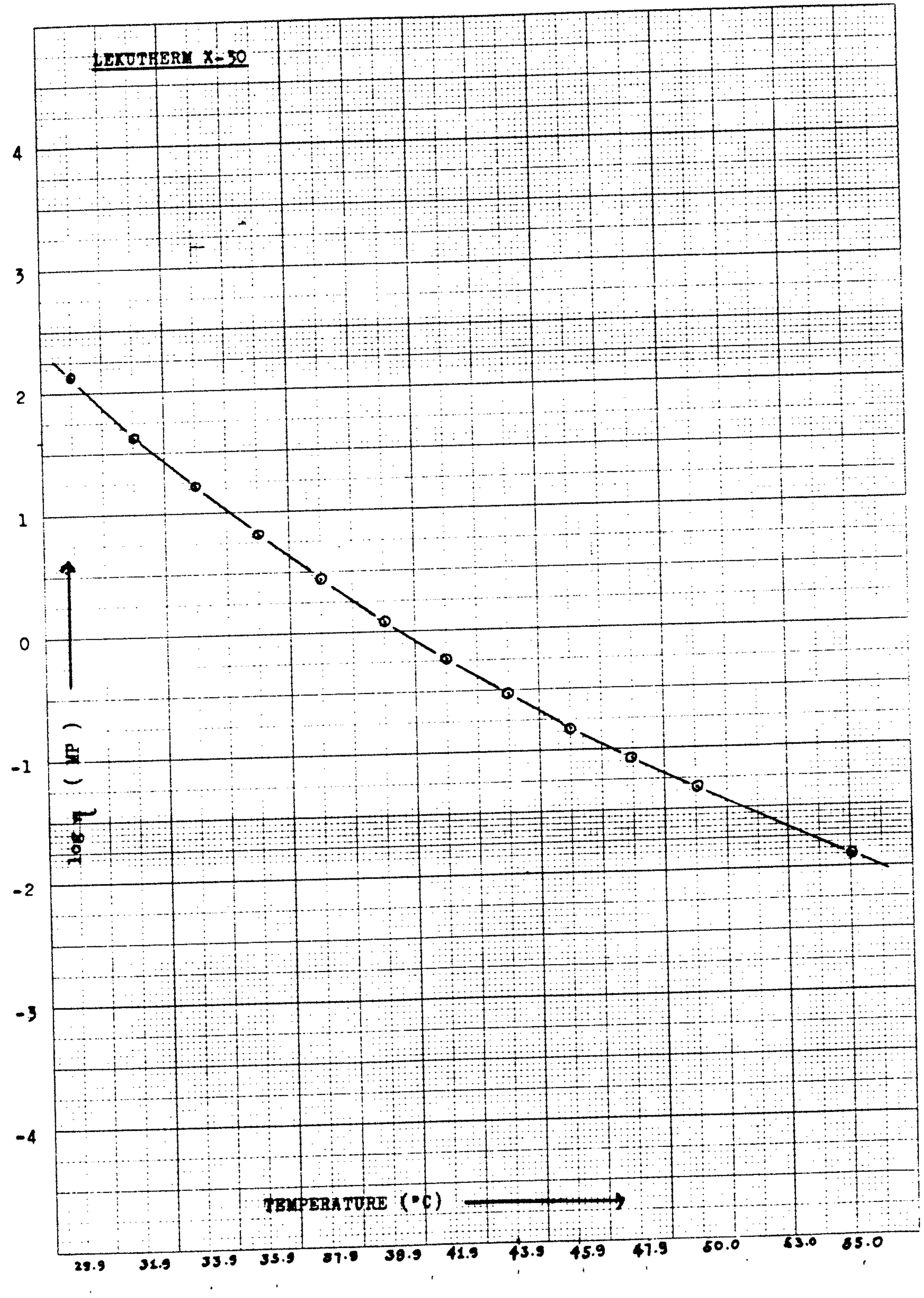

LEKUTHERM X-30
37.9°C
35.9°C
33.9°C
31.9°C
29.9°C
RATE OF SHEAR (sec^{-1})
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{1}
10^{2}
10^{3}
10^{4}
10^{5}
10^{6}
SHEAR STRESS (dymes/cm^{2})

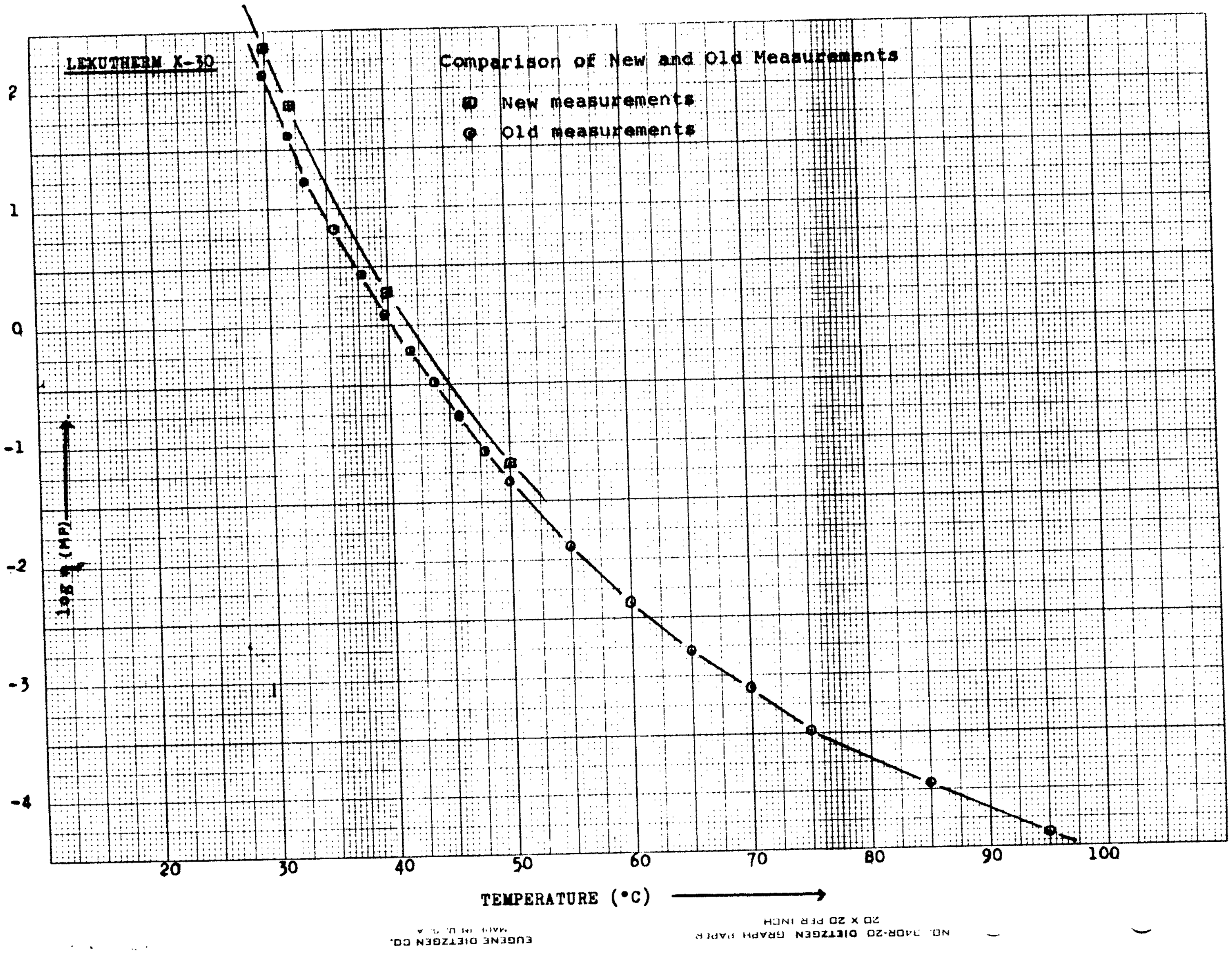

LEKUTHERM X-30
45.9°C
43.9°C
41.9°C
39.9°C
RATE OF SHEAR (sec^{-1})
SHEAR STRESS (dymes/cm^2)
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^1
10^2
10^3
10^4
10^5
10^6

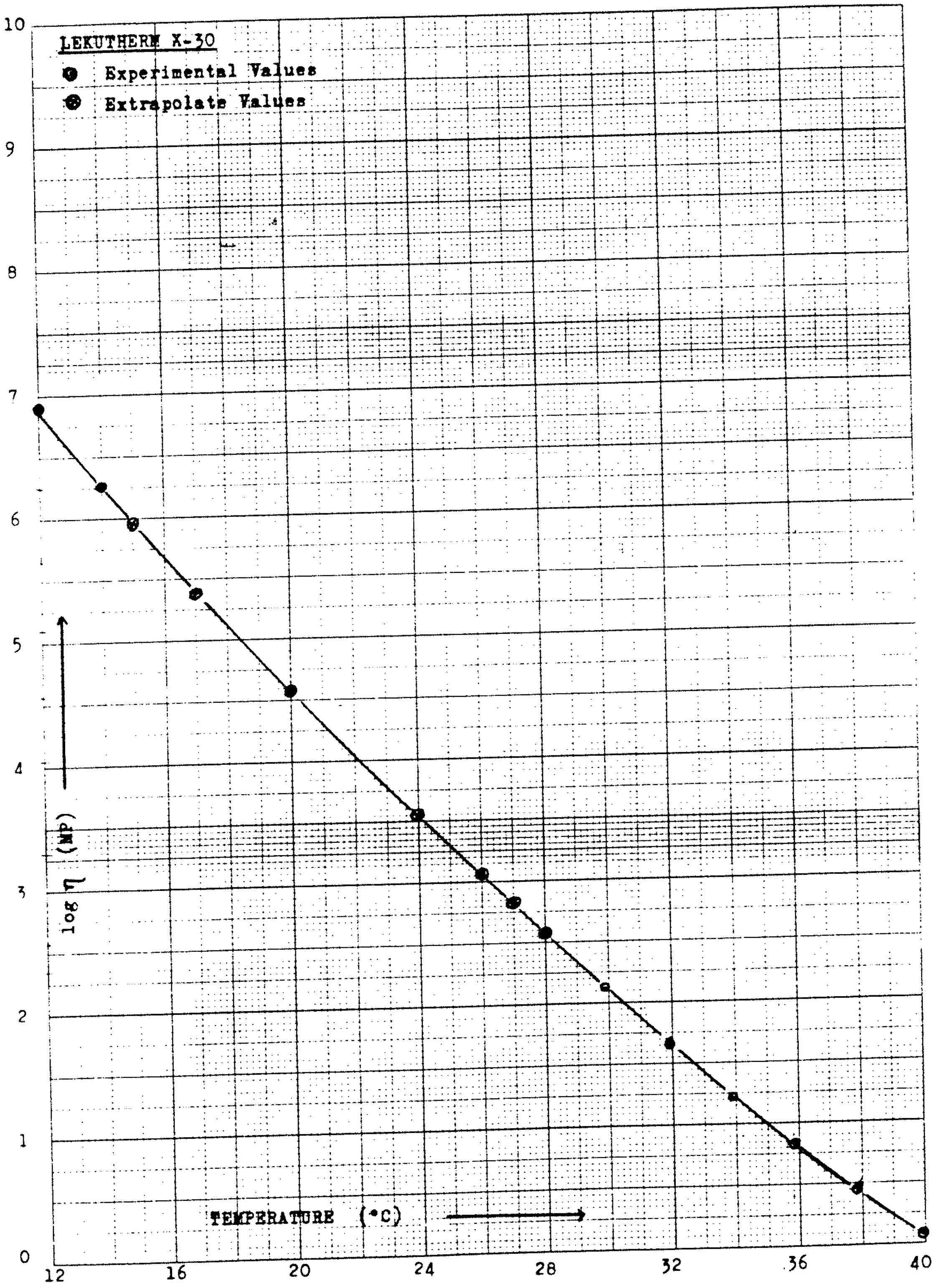

LEKUTHERM X-30
95.0°C
85.0°C
75.0°C
70.0°C
65.0°C
60.0°C
55.0°C
50.0°C
47.9°C
RATE OF SHEAR (sec⁻¹)
10^1
10^0
10^-1
10^-2
SHEAR STRESS (dymes/cm²)
10^1
10^2
10^3
10^4
10^5
10^6

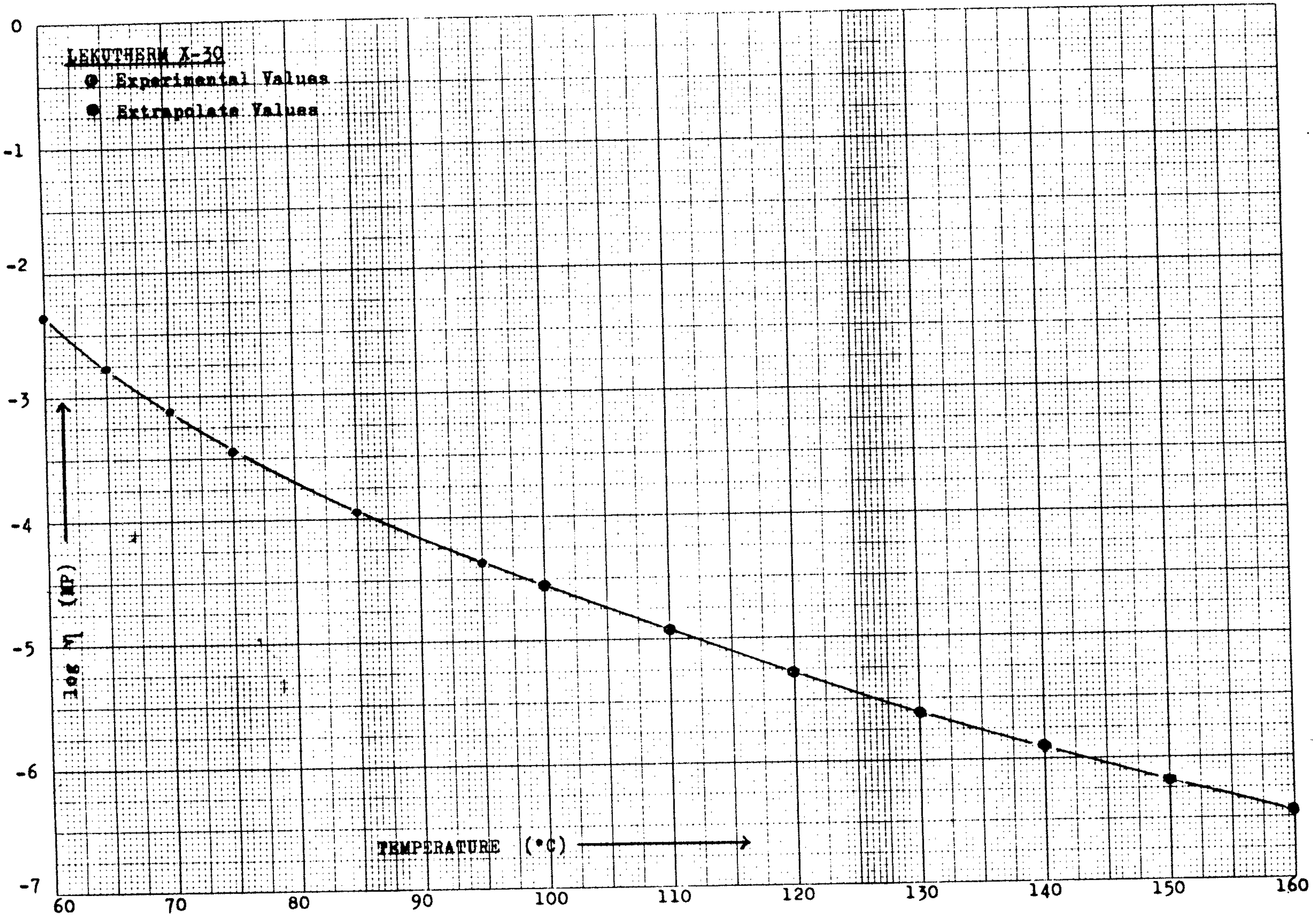

LEKUTHERM X-30
Compearison of New and Old Measurements
RATE OF SHEAR (sec^{-1})
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^1
10^2
10^3
10^4
10^5
10^6
SHEAR STRESS (dymes/cm^2)
31.9° C (3/7/1977)
31.9°C (6/7/1977)
29.9°C (3/7/1977)
29.9°C (6/13/1977)

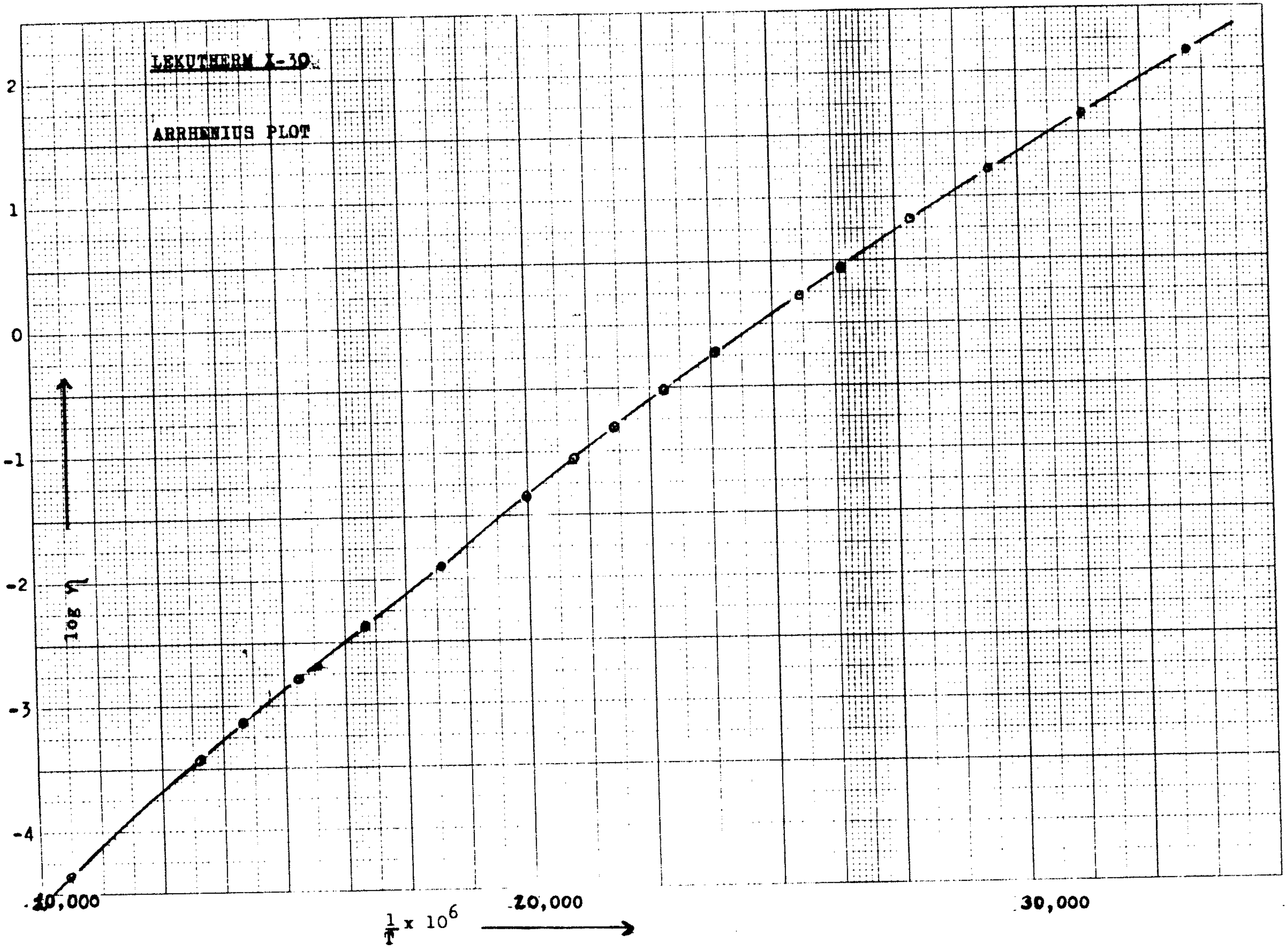

LEKUTHERM X-30
RATE OF SHEAR (sec^{-1})
SHEAR STRESS (dymes/cm^2)
10^1
10^0
10^{-1}
10^{-2}
10^1
10^2
10^3
10^4
10^5
10^6
50.0°C
(3/21/1977)
50.0°C
(6/6/1977)

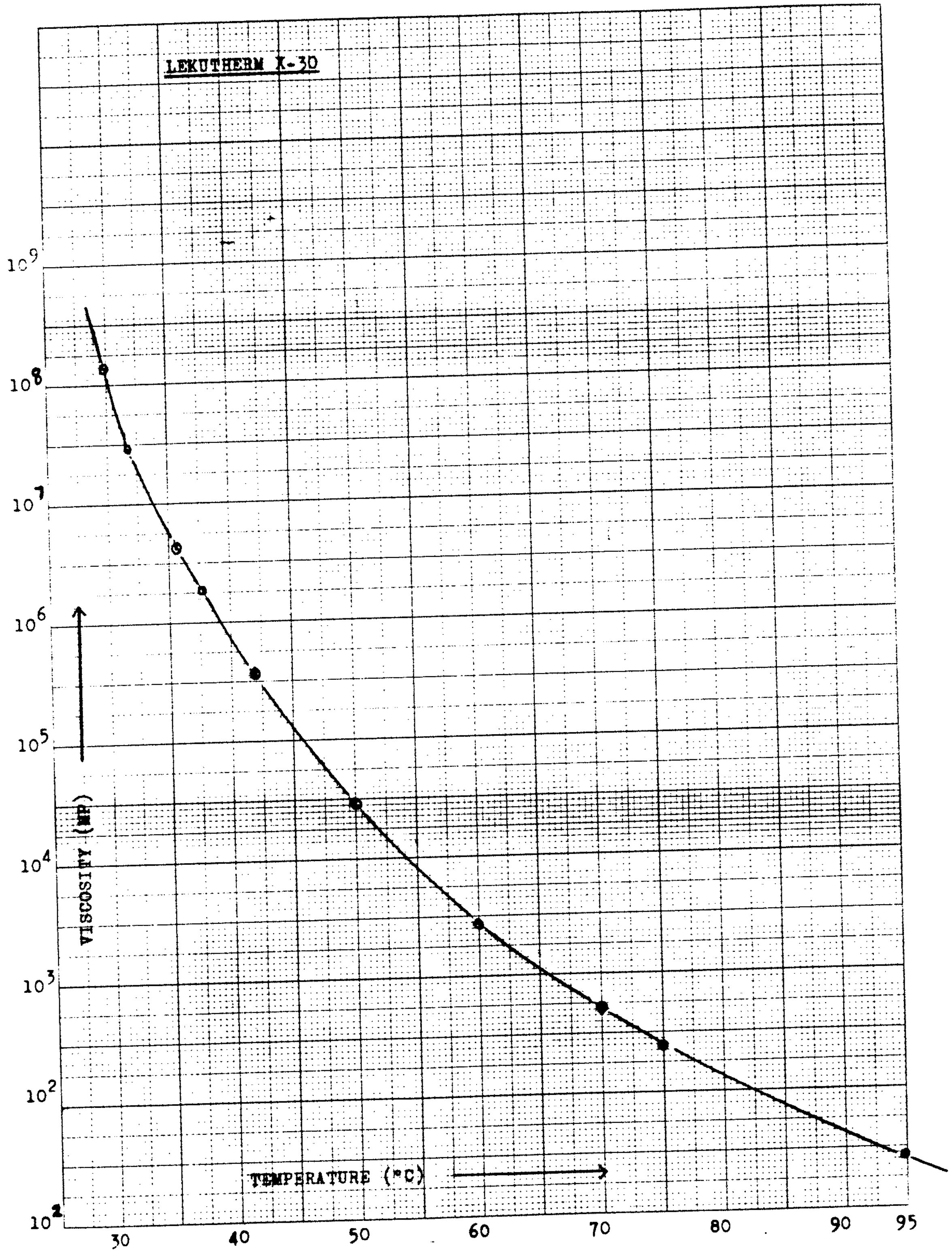

LEKUTHERM X-50
4
3
2
1
0
-1
-2
-3
-4
log η (MP)
TEMPERATURE (°C)
29.9
31.9
33.9
35.9
37.9
39.9
41.9
43.9
45.9
47.9
50.0
53.0
55.0


LEKUTHERM X-30
Comparison of New and Old Measurements
New measurements
Old measurements
log η (MP)
2
1
0
-1
-2
-3
-4
20
30
40
50
60
70
80
90
100
TEMPERATURE (°C)
NO. 340R-20 DIETZGEN GRAPH PAPER
20 X 20 PER INCH
EUGENE DIETZGEN CO.
MADE IN U. S. A.


LEKUTHERM X-30
● Experimental Values
⊗ Extrapolate Values
log η (MP)
TEMPERATURE (°C)
10
9
8
7
6
5
4
3
2
1
0
12
16
20
24
28
32
36
40


LEKUTHERM X-30
● Experimental Values
● Extrapolate Values
0
-1
-2
-3
-4
-5
-6
-7
log η (MP)
60
70
80
90
100
110
120
130
140
150
160
TEMPERATURE (°C)


LEKUTHERM X-30
ARRHENIUS PLOT
2
1
0
-1
-2
-3
-4
log η
10,000
20,000
30,000
$\frac{1}{T} \times 10^6$


LEKUTHERM X-30
10^9
10^8
10^7
10^6
10^5
10^4
10^3
10^2
10^2
VISCOSITY (MP)
TEMPERATURE (°C)
30
40
50
60
70
80
90
95

C. The Calculation of C_1, C_2 and a_T of The Temperature of Relaxation Mechanisms in Lekutherm x-30

There is a single empirical function to describe dependence of all mechanical and electrical relaxation processes in an amorphous polymer above its glass transition temperature.[30, 31] This single empirical function is the function of $a_T(T)$. It is a very important function in describing the physical properties of a polymer system. The ratio a_T (or K)[32] of any mechanical relaxation time at temperature T to its value at a reference temperature T_0, derived from transient[32] or dynamic viscoelastic measurements or from steady flow viscosity.[33, 34] In the corresponding ratio b_T of any electrical relaxation time values appear to be identical over wide ranges of time scale.[35] The theories of polymer viscoelastic,[36, 37] $a_T(=b_T)$ reflects mainly the temperature dependence of a segmental friction coefficient or mobility on which it is the dependence of the rate of all configurational rearrangements. In general, one chooses the same arbitrary reference temperature T_0 for one system. In this case it is 29.9°C for Lekutherm x-30 resin.

For the analytical expression, an empirical formula of a_T[33] shows as the following:

$$a_T = \frac{\eta\, T_0 \rho_0}{\eta_0 T \rho} \qquad \text{-------(1)}$$

From equation 1, a_T can be inferred by modifying an expression which had previously been applied to the viscosity (η) and dielectric dispersion[47] of super-cooled liquids, as well as to creep[40] of polymers:

$$\log \eta = \frac{A + B}{T - T_\infty} \text{ --------(2)}$$

where A, B and T_∞ are constants, T_∞ falling well below the glass transition temperature. This equation would imply the following form for a_T[41]

$$\log a_T = \frac{-C_1 (T - T_0)}{C_2 + (T - T_0)} \text{ -----(3)}$$

<u>Calculation for C_1 and C_2</u> (Constant Values)

$$C_2 = \frac{B - A}{A/t_1 - B/t_2}$$

$$C_1 = -\frac{A}{t_1}\,(C_2 + t_1)$$

Reference temperature at 29.9°C

$$\begin{aligned}
\log \eta_o &= 2.137 \\
T_{t_1} &= 31.9°\text{C} \\
T_{t_2} &= 70.0°\text{C} \\
t_1 &= 31.9° - 29.9° = 2° \\
t_2 &= 70.0° - 29.9° = 40.1° \\
A &= \log \eta - \log \eta_o \\
&= \log \eta_{31.9°} - \log \eta_o \\
&= 1.647 - 2.137 = -0.491 \\
B &= \log \eta_{70.0°} - \log \eta_o \\
&= -3.140 - 2.137 = -5.278
\end{aligned}$$

$$\begin{aligned}
C_2 &= \frac{(-5.278) - (-0.491)}{\dfrac{(-0.491)}{2} - \dfrac{(-5.278)}{40.1}} \\
&= \frac{-4.789}{(-0.2455)-(-0.1316)} \\
&= \frac{-4.787}{-0.1139} = 42.03
\end{aligned}$$

$$\begin{aligned}
C_1 &= -\frac{(-0.491)}{2}\,(42.03 + 2) \\
&= 0.2455 \times 44.03 \\
&= 10.81
\end{aligned}$$

Data for $A = \log\frac{\eta_1}{\eta_0} \Longrightarrow t_1$; $B = \log\frac{\eta_2}{\eta_0} \Longrightarrow t_2$

T° C	log η	$\log\frac{\eta}{\eta_0}$
31.9	1.647	- 0.491
33.9	1.209	- 0.928
35.9	0.822	- 1.3162
37.9	0.439	- 1.698
39.9	0.0828	- 2.054
41.9	- 0.236	- 2.373
43.9	- 0.538	- 2.675
45.9	- 0.824	- 2.961
47.9	- 1.092	- 3.229
50.0	- 1.338	- 3.475
55.0	- 1.903	- 4.040
60.0	- 2.365	- 4.502
65.0	- 2.778	- 4.915
70.0	- 3.140	- 5.278
75.0	- 3.441	- 5.578
85.0	- 3.9292	- 6.0662
95.0	- 4.3556	- 6.4926

Reference value ⟹ Temperature at 29.9°C

$\log \eta_0 = 2.137$

Data for the calculation of WLF equations (AM)

B - A	C_2	$t_1 + C_2$	C_1	T_{t_1} (°C)	T_{t_2} (°C)	t_1	A	A/t_1	t_2	B	$-B/t_2$	$A/t_1 - B/t_2$
- 4.787	42.03	44.03	10.81	31.9	70.0	2	- 0.491	- 0.2455	40.1	- 5.278	0.1316	- 0.1139
- 2.738	41.42	43.42	10.66	31.9	47.9	2	- 0.491	- 0.2455	18.0	- 3.229	0.1794	- 0.0661
- 3.224	43.68	53.68	11.03	39.9	70.0	10	- 2.054	- 0.2054	40.1	- 5.278	0.1316	- 0.0738
- 4.262	44.50	50.50	11.08	35.9	75.0	6	- 1.316	- 0.2194	45.1	- 5.578	0.1237	- 0.0957
- 5.821	42.99	44.99	11.05	31.9	85.0	2	- 0.491	- 0.2455	55.1	- 6.066	0.1101	- 0.1345
- 3.217	44.50	52.50	11.15	37.9	65.0	8	- 1.698	- 0.2123	35.1	- 4.915	0.1400	- 0.0723
- 2.129	44.17	56.17	11.11	41.9	60.0	12	- 2.373	- 0.1978	30.1	- 4.520	0.1496	- 0.0482
- 1.365	45.35	59.35	11.34	43.9	55.0	14	- 2.675	- 0.1911	25.1	- 4.040	0.1610	- 0.0301
- 3.105	41.40	57.40	10.63	45.9	85.0	16	- 2.961	- 0.1851	55.1	- 6.066	0.1101	- 0.0750
- 4.650	42.94	46.94	10.89	33.9	75.0	4	- 0.928	- 0.2320	45.1	- 5.578	0.1237	- 0.1083
- 2.591	41.26	61.36	10.61	50.0	85.0	20.1	- 3.475	- 0.1729	55.1	- 6.066	0.1101	- 0.0628
- 4.424	41.93	43.93	10.79	31.9	65.0	2	- 0.491	- 0.2455	35.1	- 4.915	0.1400	- 0.1055
- 4.350	43.33	47.33	10.98	33.9	70.0	4	- 0.928	- 0.2320	40.1	- 5.278	0.1316	- 0.1004
- 4.262	44.53	50.53	11.09	35.9	75.0	6	- 1.316	- 0.2194	45.1	- 5.578	0.1237	- 0.0957
- 4.368	42.37	50.37	10.74	37.9	85.0	8	- 1.698	- 0.2132	55.1	- 6.066	0.1101	- 0.1031
- 6.002	41.16	43.16	10.60	31.9	95.0	2	- 0.491	- 0.2455	65.1	- 6.493	0.0997	- 0.1458

WLF equations (AM)

$$C_2 = \frac{B - A}{A/t_1 - B/t_2}$$

$$C_1 = - \frac{A}{t_1} (C_2 + t_1)$$

Reference value: temperature at 29.9°C

$\log \eta_0 = 2.137$

Average C_2 = 42.973°C Error --- ± 1.33, 3.09%

Average C_1 = 10.908, Error --- ± 0.15, 1.34%

Data for the calculation of WLF equations (WAM)

t_1	t_2	$t_2 - t_1$	C_2	$C_2(t_2 - t_1)$	C_1	$C_1(t_2 - t_1)$
2	40.1	38.1	42.03	1601.343	10.81	411.861
2	18.0	16.0	41.42	662.720	10.66	170.560
10	40.1	30.1	43.68	1314.768	11.03	332.003
6	45.1	39.1	44.50	1739.950	11.08	433.228
2	55.1	53.1	42.99	2282.769	11.05	586.490
8	35.1	27.1	44.50	1205.950	11.15	302.030
12	30.1	18.1	44.17	799.477	11.11	201.091
14	25.1	11.1	45.35	503.385	11.34	125.896
16	55.1	39.1	41.40	1618.740	10.63	415.438
4	45.1	44.1	42.94	1893.654	10.89	480.205
20.1	55.1	35.0	41.26	1444.100	10.61	371.315
2	35.1	33.1	41.93	1387.883	10.79	356.984
4	40.1	36.1	43.33	1564.213	10.98	396.378
6	45.1	39.1	44.53	1741.123	11.09	433.502
8	55.1	47.1	42.37	1995.627	10.74	505.807
2	65.1	63.1	41.16	2597.196	10.60	668.608

WLF equations (WAM)

$$C_2 = \frac{\Sigma\, C_2(t_2 - t_1)}{\Sigma\, (t_2 - t_1)}$$

$$C_2 = \frac{24352.898}{569.4} = 42.7694^{\circ}\mathrm{C},\ \text{Error --- } \pm 1.34$$

3.14%

$$C_1 = \frac{\Sigma\, C_1(t_2 - t_1)}{\Sigma\, (t_2 - t_1)}$$

$$C_1 = \frac{6191.396}{569.4} = 10.8735,\ \text{Error --- } \pm 0.22$$

2.04%

Data for the calculation of WLF equations (Cor WAM)

t_1	t_2	t_2-t_1	C_2	$C_2(t_2-t_1)$	C_1	$C_1(t_2-t_1)$
10	40.1	30.1	43.37	1305.437	10.96	329.896
6	45.1	39.1	44.32	1732.912	11.04	431.664
2	55.1	53.1	42.62	2263.122	10.95	581.445
2	65.1	63.1	40.88	2579.528	10.52	663.812
2	40.1	38.1	42.03	1601.343	10.81	411.861
2	18.0	16.0	41.42	662.720	10.66	170.560
8	35.1	27.1	44.50	1205.950	11.15	302.030
12	30.1	18.1	44.17	799.477	11.11	201.091
14	25.1	11.1	45.35	503.385	11.34	125.896
16	55.1	39.1	41.40	1618.740	10.63	415.438
4	45.1	44.1	42.96	1893.654	10.89	480.205
20.1	55.1	35.0	41.26	1444.100	10.61	371.315
2	35.1	33.1	41.93	1387.863	10.79	356.984
4	40.1	36.1	43.33	1564.213	10.98	396.378
6	45.1	39.1	44.53	1741.123	11.09	433.502
8	55.1	47.1	42.37	1995.627	10.74	505.807

WLF equations (Cor WAM)

$$C_2 = \frac{C_2(t_2-t_1)}{(t_2-t_1)}$$

$$C_2 = \frac{24299.214}{569.4} = 42.675^\circ C, \quad \text{Error --- } \pm 1.35 \quad 3.17\%$$

$$C_1 = \frac{C_1(t_2-t_1)}{(t_2-t_1)}$$

$$C_1 = \frac{6177.884}{569.4} = 10.85, \quad \text{Error --- } \pm 0.22 \quad 2.06\%$$

WLF Equations

(AM) C_1 = 10.908, C_2 = 42.973

(WAM) C_1 = 10.874, C_2 = 42.769

(Cor WAM) C_1 = 10.850, C_2 = 42.675

T_o = 29.9°C

Comparison of Calculated and Experimental Values of log a_T

T (°C)	log a_T (AM)	log a_T (WAM)	log a_T (Cor WAM)	log a_T (Experiment)
31.9	- 0.4851	- 0.4858	- 0.4857	- 0.4910
33.9	- 0.9288	- 0.9300	- 0.9298	- 0.9280
35.9	- 1.3364	- 1.3378	- 1.3374	- 1.3162
37.9	- 1.7120	- 1.7135	- 1.7129	- 1.6980
39.9	- 2.0592	- 2.0607	- 2.0598	- 2.0540
41.9	- 2.3811	- 2.3825	- 2.3813	- 2.3730
43.9	- 2.6804	- 2.6817	- 2.6802	- 2.6750
45.9	- 2.9595	- 2.9605	- 2.9587	- 2.9610
47.9	- 3.2202	- 3.2209	- 3.2188	- 3.2290
50.0	- 3.4761	- 3.4766	- 3.4741	- 3.4750
55.0	- 4.0220	- 4.0215	- 4.0182	- 4.0400
60.0	- 4.4932	- 4.4917	- 4.4938	- 4.5020
65.0	- 4.9040	- 4.9015	- 4.8966	- 4.9150
70.0	- 5.2654	- 5.2619	- 5.2562	- 5.2780
75.0	- 5.5859	- 5.5812	- 5.5749	- 5.5780
85.0	- 6.1284	- 6.1220	- 6.1144	- 6.0662
95.0	- 6.5707	- 6.5626	- 6.5538	- 6.4926

D. Calculation of Viscosity from Constants C_1 and C_2

for Cor WAM: $C_1 = 10.850$

$C_2 = 42.675$

$$\log \eta = \log \eta_o + \frac{-C_1 t}{C_2 + t}$$

Reference Temperatuer at 29.9°C

$\log \eta_o = 2.1384$

For Temperature at 35.0°C

$t = 35.0 - 29.9$

$= 5.1$

$$\log \eta = 2.1384 + \frac{(-10.85 \times 5.1)}{42.675 + 5.1}$$

$= 0.9802$

$\eta = 9.5543$

For WAM: $C_1 = 10.874$

$C_2 = 42.769$

Reference Temperature at 29.9°C

$\log \eta_o = 2.1384$

For Temperature at 30.0°C

$t = 30.0 - 29.9$

$= 0.1$

$$\log \eta = 2.1384 + \frac{(-10.874 \times 0.1)}{42.769 + 0.1}$$

$= 2.113$

$\eta = 129.8317$

Cor WAM: $C_1 = 10.850$

$C_2 = 42.675$

$$\log \eta = 2.1384 + \frac{(-10.850 \times 0.1)}{42.675 + 0.1}$$

$= 2.113$

$\eta = 129.8317$

For WAM: $C_1 = 10.874$

$C_2 = 42.769^\circ C$

Reference Temperature at 29.9°C

$\log \eta_0 = 2.1384$

For Temperature at 80.0°C

$t = 80.0 - 29.9$

$= 50.1$

$$\log \eta = 2.1384 + \frac{(-10.874 \times 50.1)}{42.769 + 50.1}$$

$= -3.7278$

$\eta = 0.0001869$

Cor WAM: $C_1 = 10.850$

$C_2 = 42.675$

$$\log \eta = 2.1384 + \frac{(-10.850 \times 50.1)}{42.675 + 50.1}$$

$= -3.7208$

$\eta = 0.0001899$

Calculation for T_g

For the glass-transition temperature $T_g {}^\circ C$, the viscosity is 10^{15} P or $\log \eta_a = +15$ --- used here is in MP, therefore $\log \eta_a = +9$.

Then the glass-transition temperature is

$$-T_g = \frac{9 \times C_1 - \log \eta_0}{9 + C_2}$$

$$= \frac{9 \times 42.675 - 2.1384}{19.85}$$

$$= 19.2^\circ C$$

$$T_g = 29.9 - 19.2 = 10.7^\circ C$$

$$\approx 11^\circ C \text{ or } 284^\circ K$$

Measurements are all above T_g!

Data for calculation of Viscosity from constants C_1 and C_2

T (°C)	t	$C_2 + t$	$C_1 t$	$\frac{C_1 t}{C_2 + t}$	log η	η
90	60.1	102.775	652.085	6.3448	- 4.2064	0.00006206
95	65.1	107.869	707.897	6.5626	- 4.4154	0.00003842
45	15.1	57.775	163.835	- 2.8360	- 0.6973	0.200700
40	10.1	52.775	109.585	2.0765	0.0619	1.153190
37	7.1	49.775	77.035	1.5480	0.5907	3.898000
35	5.1	47.775	55.335	- 1.158	0.9802	9.554300
25	- 4.9	37.775	- 53.165	- 1.4074	3.5458	3513.986
23	- 6.9	35.775	- 74.865	- 2.0927	4.2311	17025.504
20	- 9.9	32.775	-107.415	- 3.2773	5.4157	260435.39
19	-10.9	31.775	-118.265	- 3.7220	5.8604	725103.50
18	-11.9	30.775	-129.115	- 4.1955	6.3339	2157247.6
15	-14.9	27.775	-161.665	- 5.8205	7.9589	90970378

Reference Temperature at 29.9°C ⟶ $\log \eta_0 = 2.1384$

Cor WAM: $C_1 = 10.850$, $C_2 = 42.675$

95	65.1	107.869	707.897	6.5626	- 4.4242	0.00003765
90	60.1	102.869	653.5274	6.3530	- 4.4246	0.00006090
25	- 4.9	37.869	- 53.2826	- 1.4070	3.5454	3510.75100
23	- 6.9	35.869	- 75.0306	- 2.0918	4.2302	16990.2590
20	- 9.9	32.869	-107.6526	- 3.2752	5.4136	259179.110

Reference Temperature at 29.9°C ⟶ $\log \eta_0 = 2.1384$

WAM: $C_1 = 10.874$, $C_2 = 42.769$

Comparison of Calculated and Experimental Viscosity

T (°C)	η (MP) (Experiment)	η (MP) (Calc. AM)	η (MP) (Calc. WAM)	η (MP) (Calc. Cor WAM)
31.9	44.38	45.0091	44.9366	44.9469
33.9	16.20	16.2032	16.1585	16.1659
35.9	6.6405	6.3387	6.3183	6.3241
37.9	2.7568	2.6693	2.6601	2.6638
39.9	1.2145	1.2001	1.1959	1.1984
41.9	0.5826	0.5719	0.5700	0.5716
43.9	0.2907	0.2871	0.2862	0.28[illegible]2
45.9	0.1505	0.1510	0.1506	0.1513
47.9	0.0812	0.0828	0.0827	0.0831
50.0	0.0461	0.0460	0.0459	0.0462
55.0	0.0125	0.0131	0.0131	0.0132
60.0	0.004315	0.004418	0.004433	0.004412
65.0	0.001667	0.001716	0.001725	0.001745
70.0	0.000742	0.000746	0.000752	0.000762
75.0	0.000362	0.000357	0.000361	0.000366
85.0	0.000118	0.000102	0.000104	0.000106
95.0	0.000044	0.000037	0.000038	0.000038

Reference Temperature at 29.9°C ⟶ $\log \eta_0 = 2.1384$

E. Recheck Viscosity of LEKUTHERM x-30 (in One month and Three months later)

times (sec)
217.89
220.01
222.76
220.09
222.86
222.95
224.63
223.00
222.06

Temperature at	31.9°C	
Displacement	1.0	cm
Weight	3767.0	g
Shear stress With air	15068.0	$\frac{\text{dynes}}{\text{cm}^2}$
Shear rate	2.019×10^{-4}	sec^{-1}
Viscosity	77460.880×10^{4}	poises
$t_{1\,cm}$(average)	221.58	sec
$t_{10°}$	17726.40	sec
$t_{1\,cm}$(old data)	132.40	sec
$t_{10°}$	10592.00	sec

$$\% \text{ difference} = \frac{17726 - 10592}{10592} \times 100$$

$$= 67.36$$

times (sec)
285.71
287.88
286.61
290.70
288.70
290.00
285.81
282.80

Temperature at	31.9°C	
Displacement	1.0	cm
Weight	2860.0	g
Shear stress With air	11440.0	$\frac{\text{dynes}}{\text{cm}^2}$
Shear rate	1.558×10^{-4}	sec^{-1}
Viscosity	7342.740×10^{4}	poises
$t_{1\,cm}$(average)	287.29	sec
$t_{10°}$	22982.80	sec
$t_{1\,cm}$(old data)	174.88	sec
$t_{10°}$	13990.00	sec

$$\% \text{ difference} = \frac{22982.80 - 13990.00}{13990.00} \times 100$$

$$= 64.28$$

<u>times</u> (sec)
539.41
542.92
544.11
549.82
554.75
541.75
550.05

Temperature at 31.9°C
Displacement 1.0 cm
Weight 1500.0 g
Shear stress 6000.0 $\frac{\text{dynes}}{\text{cm}^2}$
With air
Shear rate 8.194×10^{-5} sec^{-1}
Viscosity 732.240×10^{5} poises
t_{1cm}(average) 546.12 sec
$t_{10°}$ 43689.26 sec
t_{1cm}(old data) 327.30 sec
$t_{10°}$ 26184.00 sec

$$\% \text{ difference} = \frac{43689.26 - 26184.00}{26184.00} \times 100$$

$$= 66.85$$

<u>times</u> (sec)
90.48
90.92
90.43
90.50
90.45
90.08
90.18
90.05

Temperature at 39.9°C
Displacement 2°
Weight 3767.0 g
Shear stress 15068.0 $\frac{\text{dynes}}{\text{cm}^2}$
With air
Shear rate 7.921×10^{-3} sec^{-1}
Viscosity 1902.2900×10^{3} poises
$t_{2°}$(average) 90.39 sec
$t_{10°}$ 451.95 sec
$t_{2°}$ (old data) 57.80 sec
$t_{10°}$ 289.00 sec

$$\% \text{ difference} = \frac{451.95 - 289.00}{289.00} \times 100$$

$$= 56.38$$

<u>times</u> (sec)	Temperature at	39.9°C	
59.22	Displacement	1°	
59.32	Weight	2860.0 g	
59.54	Shear stress	11440.0	$\frac{dynes}{cm^2}$
59.62	With air		
59.32	Shear rate	6.023×10^{-3}	sec^{-1}
59.54	Viscosity	1899.39×10^{3}	poises
59.50	$t_{1°}$ (average)	59.44	sec
	$t_{10°}$	594.40	sec
	$t_{1°}$ (old data)	38.10	sec
	$t_{10°}$	381.00	sec
	% difference	56.01	

<u>times</u> (sec)	Temperature at	39.9°C	
113.68	Displacement	1°	
113.34	Weight	1500.0 g	
113.96	Shear stress	6000.0	$\frac{dynes}{cm^2}$
113.32	With air		
113.11	Shear rate	3.156×10^{-3}	sec^{-1}
113.42	Viscosity	1901.140×10^{3}	poises
113.56	$t_{1°}$ (average)	113.44	sec
	$t_{10°}$	1134.40	sec
	$t_{1°}$ (old data)	75.5	sec
	$t_{10°}$	755.0	sec
	% difference	54.34	

times (sec)
553.01
550.62
555.54

Temperature	29.9°C	
Displacement	1.0 cm	
Weight	4596.0 g	
Shear stress	18384.0 $\frac{dynes}{cm^2}$	
With out air		
Shear rate	8.0914 $\times 10^{-5}$	sec^{-1}
Viscosity	2272.04 $\times 10^{5}$	dynes.sec/cm^2
t_{1cm}(average)	553.06	sec
$t_{10°}$	44244.53	sec
t_{1cm}(old data)	336.14	sec
$t_{10°}$	26890.80	sec
% difference	64.53	

Data of C_1 and C_2 from old value $\log\eta_0 = 2.137$ $T_{ref.} =$ 29.9°C

T_{t_1}(°C)	T_{t_2}(°C)	t_1	$\frac{A}{t_1}$	t_2	A	B
31.9	50.0	2	- 0.2455	20.1	- 0.491	- 3.475
31.9	39.9	2	-.0.2455	10.0	- 0.491	- 2.054
39.9	50.0	10	- 0.2054	20.1	- 2.054	- 3.475

$\frac{B}{t_2}$	$\frac{A}{t_1} - \frac{B}{t_2}$	B - A	C_2	$C_2 + t_1$	C_1	
- 0.1729	- 0.0173	- 2.966	40.854	42.854	10.521	
- 0.2054	- 0.0401	- 1.563	38.978	40.978	10.060	
- 0.1729	- 0.0325	- 1.421	43.723	53.723	11.035	

$$\left.\begin{array}{l}\text{Average } C_1 = 10.539,\ \text{Error --- } \pm 0.40,\ 3.78\% \\ \text{Average } C_2 = 41.185,\ \text{Error --- } \pm 2.03,\ 4.92\%\end{array}\right\}\ \text{AM-I}$$

Data of Recheck Viscosity of LEKUTHERM X-30 (New I)

T_{t_1}(°C)	T_{t_2}(°C)	A	$\frac{A}{t_1}$	t_1	t_2	$T_{ref.}$
31.9	50.0	- 0.48772	- 0.2411	2.	20.1	29.9
31.9	39.9	- 0.48772	- 0.2411	2	10.0	"
39.9	50.0	- 2.0765	- 0.2076	10	20.1	"

B	$\frac{B}{t_2}$	$\frac{A}{t_1} - \frac{B}{t_2}$	B - A	C_2	$C_2 + t_1$	C_1
- 3.5775	- 0.1780	- 0.06311	- 3.0898	48.959	50.959	12.286
- 2.0765	0.0207	- 0.03345	- 1.5888	47.497	49.497	11.934
- 3.5775	- 0.1780	- 0.02970	- 1.5010	50.608	60.608	12.585

New value of $\log \eta_0 = 2.3555$ **(from experiment)**

(Average)C_1 = 12.268 ⟶ 6/13/77 Error --- ±0.27, 2.17%

(Old value)C_1 = 10.539 ⟶ 3/14/77 Error --- ±0.40, 3.78%

% change = 16.406

(Average)C_2 = 49.021°C, Error --- ±1.27, 2.59%

(Old value) = 41.185°C, Error --- ±2.03, 4.92%

% change = 19.026

WLF - Equations:

$$C_1 = -\frac{A}{t_1}(C_2 + t_1)$$

$$C_2 = \frac{B - A}{\frac{A}{t_1} + \frac{B}{t_2}}$$

** Note that -- 1°C change in T_g, accounts for 20% difference (see graph on page 50)

Data of C_1 and C_2 from new value of $\log\eta_0 = 2.35$ (from graph) $T_{ref} = 29.9°C$

T_{t_1}(°C)	T_{t_2}(°C)	t_1	A	$\frac{A}{t_1}$	t_2	B
31.9	50.0	2	- 0.4822	- 0.2411	20.1	- 3.572
31.9	39.9	2	- 0.4822	- 0.2411	10.0	- 2.071
39.9	50.0	10	- 2.0710	- 0.2071	20.1	- 3.572

$\frac{B}{t_2}$	$\frac{A}{t_1} - \frac{B}{t_2}$	B - A	C_2	$C_2 + t_1$	C_1
- 0.1777	- 0.0634	- 3.0898	48.735	50.735	12.232
- 0.2071	- 0.0340	- 1.5888	46.729	48.729	11.749
- 0.1777	- 0.0294	- 1.5010	51.054	61.054	12.644

Average C_1 = 12.208, Error --- ±0.37, 2.996% } New II
Average C_2 = 48.893°C, Error --- ±1.77, 3.62%

Calculation of C_1 and C_2 from reference value of $\log \eta_0 = 1.647$

Reference Temperature at 31.9°C (old value)

$T_{t_1} = 39.9°C \longrightarrow t_1 = 8$

$T_{t_2} = 50.0°C \longrightarrow t_2 = 18.1$

$A = -1.5642,$ $\frac{A}{t_1} = -0.1955$

$B = -2.985,$ $\frac{B}{t_2} = -0.1649$

$\frac{A}{t_1} - \frac{B}{t_2} = -0.0306$

$B - A = -1.4208$

$C_2 = 46.431,$ $C_2 + t_1 = 64.53$

$C_1 = 12.616$

Calculation of C_1 and C_2 from reference value of $\log \eta_0 = 1.8678$

reference temperature at 31.9°C (New value)

$T_{t_1} = 39.9°C \longrightarrow t_1 = 8$

$T_{t_2} = 50.0°C \longrightarrow t_2 = 18.1$

$A = -1.5888$ $\frac{A}{t_1} = -0.1986$

$B = -3.0898$ $\frac{B}{t_2} = -0.1707$

$\frac{A}{t_1} - \frac{B}{t_2} = -0.0279$

$B - A = -1.501$

$C_2 = 53.799$ $C_2 + t_1 = 61.799$

$C_1 = 12.273$

Comparison of different types of C_1 and C_2, New and Old Values

Types of constants	C_1	Errors	C_2 (°C)	Errors
<u>Old Values</u>				
T_{ref} = 29.9°C				
AM	10.91	± 0.15 1.34%	42.97	± 1.32 3.09%
WAM	10.87	± 0.22 2.04%	42.77	± 1.34 3.14%
Cor WAM	10.85	± 0.22 2.06%	42.67	± 1.35 3.17%
AM-I	10.54	± 0.398 3.78%	41.18	± 2.03 4.92%
<u>New Values</u> three months later				
T_{ref} = 29.9°C				
New I	12.27	± 0.27 2.17%	49.02	± 1.27 2.59%
New II	12.21	± 0.37 2.996%	48.89	± 1.77 3.62%
Old Value				
T_{ref} = 31.9°C	12.616	-	46.431	-
New Value				
T_{ref} = 31.9°C	12.273	-	53.799	-

F. Recoil (Reversible of Lekutherm X-30

Viscoelastic material is material which has recoverable shear properties such as epoxy resin. It has characateristics in between pure elastic solid when stretched which will return to its original shape on condition its elastic limit has not been exceeded. The rotational viscometer is the apparatus for recoverable shear measurement. This is done by suddenly removing the weight while a constant shear stress is applied. This can be aided by a stop-load mechanism for light weights and by hand for heavy weights. By doing this the material stops moving forward and at the same time it recoils.

The recoverable shear is a measurement of a distance by a moving weight on a rotational viscometer. Then let it run until it reaches a certain distance then remove the weight. The distance of movement at the stop weight and the distance reverse from the point of stopped weight are recorded. In this first experiment a weight of 1000 grams is applied at the shear stress of 4000 dynes/cm^2, displacement of 1 degree and obtained recoil is 0.5 mm. For the second experiment a weight of 2860 grams is applied at the shear stress of 11440 dynes/cm^2, displacement of 2 degrees and obtained recoil of 1.0 mm. From this information, one can calculate the time of the recoil (see page 77).

Data of Recoil of LEKUTHERM X-30

Expt. #	Wt (g)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Displacement (degree)	Recoil (mm)	% error
1	1000	4000	1	0.5 $\pm \frac{1}{4}$	50.00
2	2860	11440	2	1.0 $\pm \frac{1}{4}$	25.00
3	4596	18384	5	4.0 $\pm \frac{1}{4}$	6.25

Temperature at 39.9°C

Calculations

Experiment #1

τ = 4000 dynes/cm^2

1° = 80 mm

$\gamma = \frac{0.358}{80} \times 0.5 = 0.00224$

Modulus $= \frac{4000}{0.00224} = 1.79\times10^6$ dynes/cm^2

$\eta = 1.9009\times10^6$ dynes.sec/cm^2

Relaxation time T $= \frac{1.9009\times10^6}{1.79\times10^6}$ $\frac{\text{dynes.sec/cm}^2}{\text{dynes/cm}^2}$

$= 1.06$ sec

Experiment #2

τ = 11440 dynes/cm^2

$\gamma = 0.004475 \times 1.0 = 0.004475$

Modulus $= \frac{11440}{0.004475} = 2.56\times10^6$ dynes/cm^2

$\eta = 1.9009\times10^6$ dynes.sec/cm^2

Relaxation time T $= \frac{1.9009\times10^6}{2.56\times10^6}$ sec

$= 0.75$ sec

Experiment #3

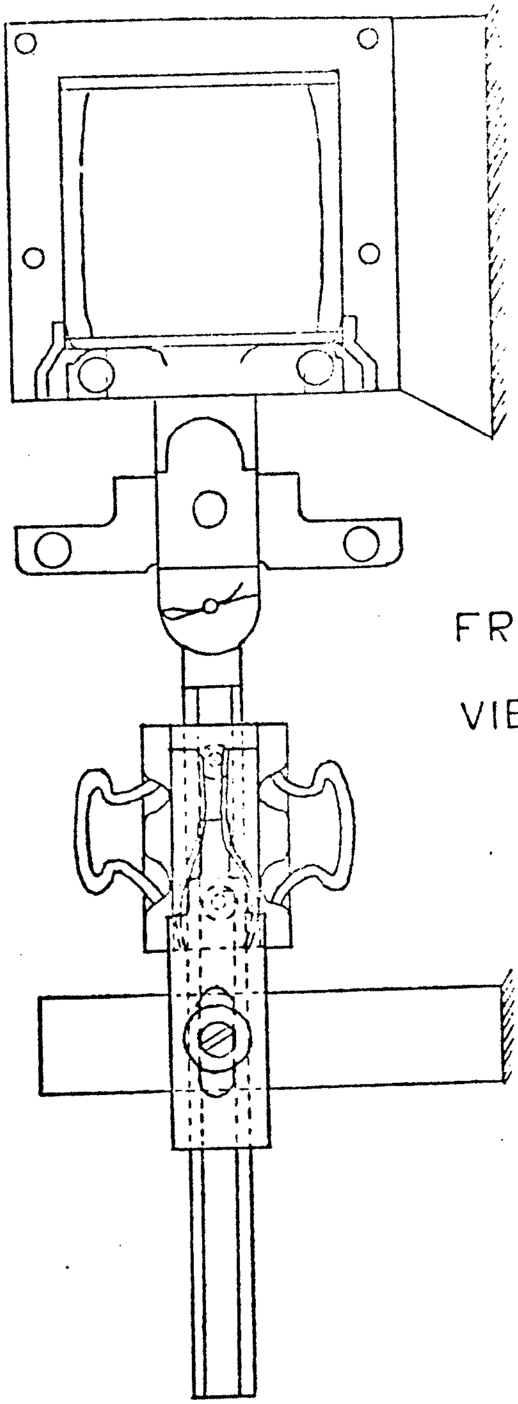
τ = 18384 dynes/cm^2

$\gamma = 0.004475 \times 4.0 = 0.0179$

Modulus $= \frac{18384}{0.0179} = 1.027\times10^6$ dynes/cm^2

$\eta = 1.9009\times10^6$ dynes.sec/cm^2

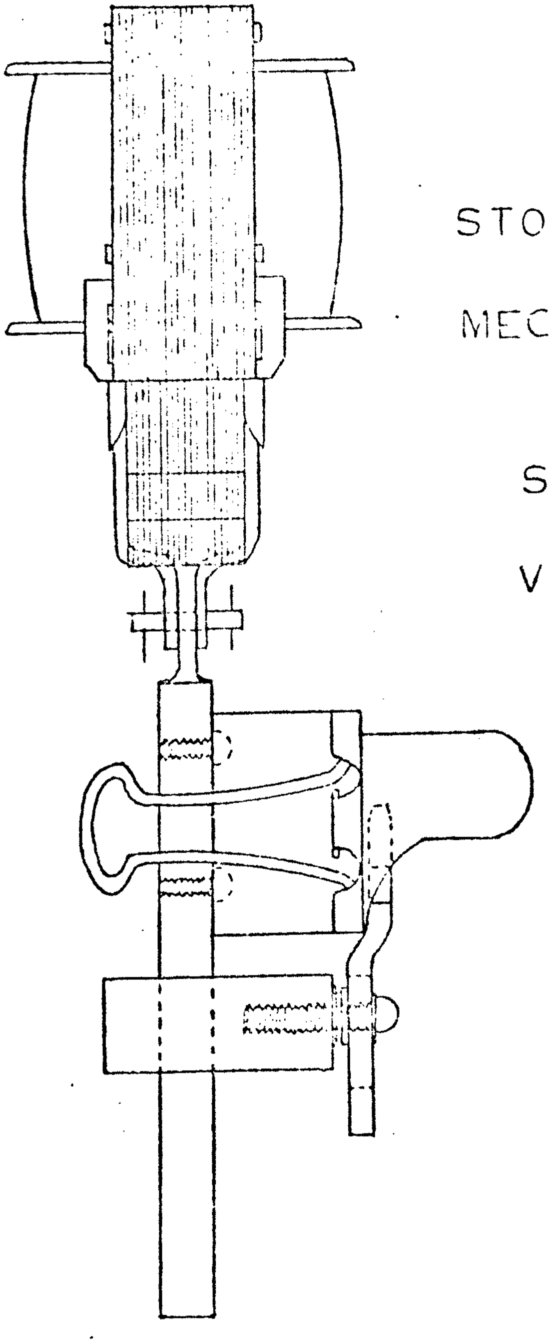
Relaxation time T $= \frac{1.9009\times10^6}{1.027\times10} = 1.85$ sec



STOP-LOAD MECHANISM

FRONT VIEW

FIGURE 9[42]



STOP-LOAD

MECHANISM

SIDE

VIEW

FIGURE 10 43

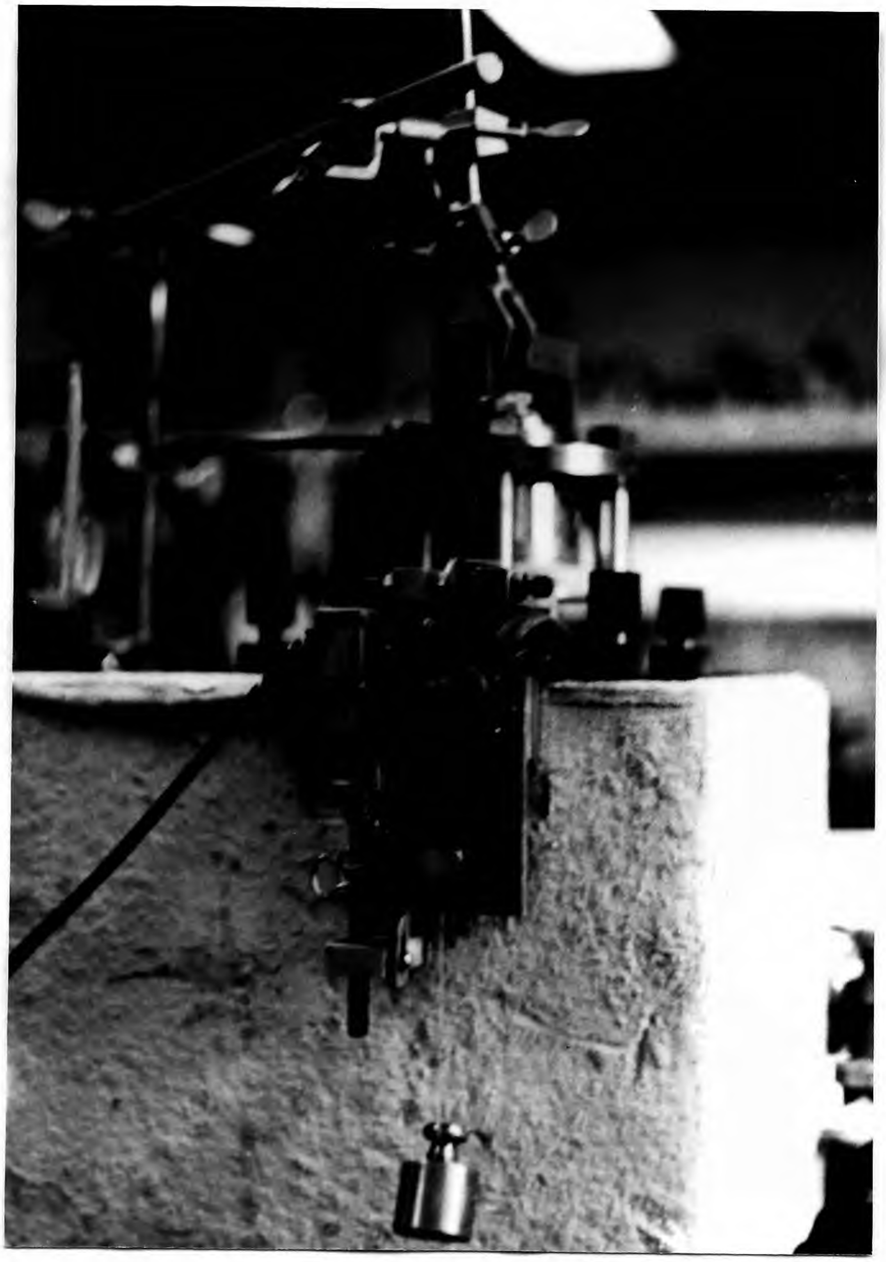


FIGURE 11[44]

Thermometer Correction

Correction for Emergent Stem of Liquid-in-Glass Thermometers

Tc = To + f x l x (To - Tm) where Tc = corrected temperature

Tm = 25°C; l = To - 4°C (4°C which emerges in H_2O)

* This is important for long length thermometer to do the correction but is not necessary for short length thermometer.

** For this experiment corrected temperature was not necessary since the thermometer used is made from SGA which is already calibrated.

Used: T-3420 Thermometer, Etched Stem with permanent filler, fractional degree, Centigrade, yellow back, general laboratory, Mercury-filled, 76 mm Immersion. Stem has 6 to 7 mm, O.D., and is nitrogen-filled above mercury with top suspension ring. Specify type - D -1 to +101 Division 0.1°C length 610 mm. range °C.

G. Comparing Viscosity of LEKUTHERM X-30 with Viscosity of the other materials

1. ORONITE N-16

   molecular weight (Mn) = 500
   Viscosity = 23.6 poise (low viscosity)
   Temperature at 25.0°C

2. INDOPOL H-25 (polyisobutylene liquid)

   molecular weight = 593 670
   density = 0.8691 g/cc (at 25.0°C)
   Viscosity = 29.45 poise
   Temperature at 25.0 C

3. ORONITE N-24

   molecular weight = 900
   Viscosity = 209 poise (a moderately viscous)
   Temperature at 25.0°C

4. INDOPOL H-1900 (polyisobutylene produce by AMICO)

   molecular weight = 1900 - 2560
   density = 0.9224 g/cc (at 25.0°C)
   Viscosity = 5049 poise
   Temperature at 25.0°C

5. VISTANEX LM/MS (polyisobutylene produce by Enjay)

   molecular weight = 25,000 70,000
   Viscosity = 1.15×10^6
   It begins to exhibit non-Newtonian characteristics for shear stresses above 10,000 dynes/cm^2

6. VISTANEX L-200 Solution (polyisobutylene solution composed of 4.5 wight % VISTANEX L-200 in PRIMOL

355, a white mineral oil. The solution is produced by dissolving the Vistanex in hexane and then mixing it with the oil. The hexane is then driving off, leaving the final solution, which is later filtered. The solution exhibits very strong non-Newtonian characteristics and has a zero shear viscosity of about 48,000 poise, molecular weight is about 5.5 x 10^6.

7. NBS 2-35967 Solution

This liquid is polystyrene solution of 7.14 weight % NBS 2-35967 in a 35-65 mixture of Aroclor and TPC. The solution is supplied by the National Bureau of Standards and produced by the Pressure Chemical Company. It has zero shear viscosity of about 681 poise and becomes quite non-Newtonian beyond a shear stress of 1000 dynes/cm^2.

46

Viscosity-Temperature Relation for PRIMOL 355

T (° C)	Kin.Visc. V CST	density (g/cc)	Viscosity CP.
0	1256.6	(0.8954)	1125.00
15	340.46	0.8853	301.50
25	166.81	0.8788	146.60
37.78	77.49	0.8704	67.50
54.45	34.65	(0.8580)	29.75
98.89	8.202	(0.8275)	6.80

Interpolated Values by Dr. W. Philippoff
(1/29/1962)

H. Collection of Mathematatic Operations

Viscosity

$$\text{Rate of shear } (\dot{\gamma}) = \frac{3.58}{t_{10^\circ}} \quad \text{sec}^{-1}$$

$$\text{Shear stress } (\tau) = 4 \times (g) \quad \text{dynes/cm}^2$$

$$\text{Viscosity } (\eta) = \frac{\tau}{\dot{\gamma}}$$

WLF Equation

$$\log a_T = \frac{-C_1 t}{C_2 + t} = \frac{-C_1 (T - T_o)}{C_2 + (T - T_o)}$$

$$a_T \sim \frac{\eta}{\eta_o}$$

$$\log \frac{\eta}{\eta_o} = \frac{-C_1 t}{C_2 + t}$$

η_o is reference value

$$A = \frac{-C_1 t_1}{C_2 + t_1}$$

$$B = \frac{-C_1 t_2}{C_2 + t_2}$$

$$\frac{A}{B} = \frac{t_1 (C_2 + t_2)}{t_2 (C_2 + t_1)}$$

$$C_2 + t_2 = C_2 \frac{t_2}{t_1} \frac{A}{B} + \frac{t_2}{t_1} \frac{A}{B} t_1$$

$$t_2 \left(1 - \frac{A}{B}\right) = C_2 \left(\frac{t_2}{t_1} \frac{A}{B} - 1\right)$$

$$C_2 = \frac{t_2 \left(1 - \frac{A}{B}\right)}{\frac{t_2}{t_1} \frac{A}{B} - 1}$$

$$C_2 = \frac{B - A}{\frac{A}{t_1} - \frac{B}{t_2}}$$

$$A = \frac{-C_1 t_1}{\left[\frac{B-A}{\frac{A}{t_1}+\frac{B}{t_2}}\right] + t_1}$$

$$-C_1 t_1 = A\left\{\left[\frac{B-A}{\frac{A}{t_1}+\frac{B}{t_2}}\right] + t_1\right\}$$

$$C_1 = -\frac{A}{t_1}\left\{\left[\frac{B-A}{\frac{A}{t_1}+\frac{B}{t_2}}\right] + t_1\right\}$$

$$C_1 = -\frac{A}{t_1}\left(C_2 + t_1 \right)$$

$$A = \log \frac{\eta_1}{\eta_0} \longrightarrow t_1$$

$$B = \log \frac{\eta_2}{\eta_0} \longrightarrow t_2$$

$$t_1 = T_1 - T_{ref}$$

$$t_2 = T_2 - T_{ref}$$

Calculation of Viscosity from Constants C_1 and C_2

$$\log \frac{\eta}{\eta_0} = \frac{-C_1 t}{C_2 + t}$$

$$t = T - T_{ref}$$

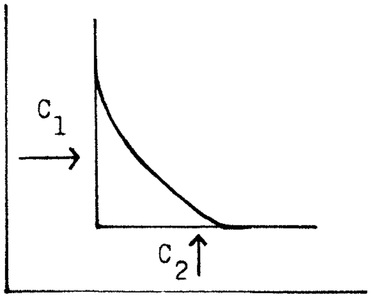
$$\log \frac{\eta}{\eta_0} = \log \eta - \log \eta_0$$

$$\log \eta = \log \eta_0 + \frac{-C_1 t}{C_2 + t}$$

$$10^{\eta} = \eta$$

or $$\ln \eta = \log \eta \times 2.303$$

$$e^{\eta} = \eta$$



Relationship between C_1 and C_2

IV. DISCUSSION AND CONCLUSIONS

Viscosity of 6% L-200 in PRIMOL 355 (polyisobutylene) was remeasured to observe the behavior of the material for a long period of time. Two years prior to my remeasurement, Dr. Philippoff had measured this polymer solution in order to obtain its viscosity in different shear stresses at a temperature of 25°C. The measurements I obtained had higher viscosity values than the one which D. Philippoff observed. For example at the shear stress of 4,000 dynes/cm^2 the new viscosity was 1284.934 poises and the old viscosity was 650 poises (see page 33 and 34 for the other values). The new viscosity was increased to almost double the old value. These results have shown the material has changed to become more viscous which is quite contradictory to the general assumption that the older the material the less viscous it will be. One would expect that this polymer solution would become liquified. Another interesting proof of this observation is that 6% L-200 in PRIMOL 355 will not deteriorate over this long period of time. The graph that shows the comparison of new and old viscosities of 6% L-200 in PRIMOL 355 is on page 35.

On page 36 to 40 are data of Lekutherm x-30 resin viscosity which shows the value of viscosity in million poises, log of the average viscosity, shear rate and shear stress at its temperature, time and weight. The lowest temperature was 29.9°C and the value of its viscosity was 137.53 million poises. The highest temperature was 95.0°C and its viscosity was 0.00004409 (44.09×10^{-6}) million poises or only 44.09 poises. From the values obtained one can see that this material has a Newtonian-liquid behavior. It is very viscous at room temperature and even at about 5°C above. But at higher temperatures the viscosity become less and less which proves that this polymer resin is very sensitive to temperature change. It is very much temperature dependent. To my knowledge no one ever measured this high viscosity value. The graphs of shear stress V.S. shear rate are shown on pages 44, 45 and 46 and the graphs of log η (viscosity) V.S. temperature are shown on pages 49 and 50.

After completing the first experiment, the material was kept at room temperature. A few days later the resin was reheated to 50°C and rechecked for its viscosity. There was no change in viscosity and the values were the same. (see page 39) Another experiment was conducted 70 days later. This time there was a change in viscosity. The new viscosity values were higher than the old measurements, 64.75%, 66.19%, 57.10% and 30.32% higher at the temperatures of 29.9°C, 31.9°C, 39.9°C and 50°C respectively. See the comparison values between new and old viscosity on page 41 and also the comparison graph of shear stress V.S. shear rate on pages 47, 48 and 50. One can assume from this increasing viscosity in a longer period of time that it is possible that the material slowly polymerize and therefore it became more viscous. The table of extrapolated values of Lekutherm x-30 viscosity is shown on page 42 and the graphs are shown on pages 51 and 52.

WLF equations were introduced for the calculation of constants C_1 and C_2. These constants were the parameter of the viscosity for which C_1 was applied at the x-coordination and C_2 was applied at the y-coordination. The temperature at 29.9°C was chosen for the reference temperature. The experimental value of viscosity at 29.9°C was chosen for the reference viscosity also. The calculation for C_1 and C_2 and their data are shown on pages 55 to 61. There are three types of calculation for C_1 and C_2, AM, WAM and Cor WAM. These different values were calculated from the same value reference temperature and reference viscosity; the difference is in collecting new data by selecting only some data from AM values in different ranges of temperatures and then apply these values in the new formulas of C_1 and C_2 (see pages 61 61). These three sets of C_1 and C_2 values had only a slight difference among them (see page 75). AM, WAM and Cor WAM for C_1 and C_2 value were applied to equation 3 (see page 56) for the calculation of log a_T. The comparison of calculated and experimental values were closed in their values (see page 62). The further useful application for C_1 and C_2 was to apply them to the viscosity equation in order to calculate the new values of viscosity at any temperature. The calculation values of viscosity can be very accurate as experimental values if one can get the best values of C_1 and C_2. Pages 63, 64 and 6 show the calculated values of viscosity at different temperatures. The comparison of calculated and experimental values of viscosity is shown on page 66. Their values fluctuated, some calculated values were higher and others were lower than experimental values. Over all, their values only slightly differed from each other.

There are some of the C_1 and C_2 values from the other experiments, for example in "Viscoelastic Properties of Polymers" by John D. Ferry the WLF parameters of poly-n-octyl methacrylate for $C_1 = 7.60$ and $C_2 = 227.3$, choosing T_o = 373° K.[51] The "Time-Temperature Superposition in Styrene/Butadiene/Styrene Block Copolymers" by D. G. Fesko and N. W. Tschoegl show the value of shell 16/78/16 for $C_1 = 7.76$ and $C_2 = 51.0$°C, the reference temperature of -78°C;(52) the value of NBS 10/30/10 for $C_1 = 13.36$ and $C_2 = 109.2$°C at a reference temperature of -80.91° C. (53) The third triblock was a commercial material, shell Kraton 102, $C_1 = 9.14$ and $C_2 = 52.4$°C at a reference temperature of -60°C.(54) Comparing the Lekutherm x-30, C_1 about 11 and C_2 about 43°C at a reference temperature of 29.9°C for the old measurements and C_1 about 12.5 and C_2 in between 46°C to 54°C for the new measurements (see page 75), these Lekutherm x-30 values are in the same range of poly-n-octyl methacrylate and styrene/butadiene/styrene block copolymers values.

Pages 67 to 70 show the calculation of the percent difference of time between the new and old viscosity of Lekutherm x-30 resin. The percent differences were between 54% to 68%. Pages 71 to 74 show the calculation of C_1 and C_2 from the new values of viscosity. There was a considerable difference between their values (see page 72 for percent differences).

Only three experiments were done for recoil measurements (see pages 76 and 77). These recoil values show that the heavier the weight or higher the shear stress, the larger the recoil values one receives. This also holds true for the displacement values and times. This is not true for the modulus values obtained in the contrasting situation. For example, experiment #2 applied 2860 g by weight, shear stress 11440 dynes/cm^2 with the displacement value of 2 degrees, obtained 1.0 mm of recoil value. The calculated value of modulus was 2.56x10^6 dynes/cm^2 and relaxation time was 0.75 sec. For experiment #3 applied 4596 g by weight, shear stress 18384 dynes/cm^2 with displacement of 5 degrees and obtained 4.0 mm of recoil value, the calculated value of modulus was 1.027 dynes/cm^2 and relaxation time value was 1.85 sec. Notice that "The converging lens increases image, sharpens to produce a scale reading of $\pm$ ¼ mm" (see page 17), therefore, for example experiment #1, the recoil reading was 0.5 $\pm$ ¼ mm or 0.5 $\pm$ 0.25 mm, percent error was 50. Experiment #2, the recoil value was 1.0 $\pm$ ¼ mm and percent error was 25. Experiment #3 had the recoil value of 4.0 mm and it had the lowest percent error, 6.25% and it had the longest relaxation time, 1.85 seconds. The other experiments, percent errors were too high. Therefore the valid value was experiment #3 only, which had the highest weight of the three experiments. Lower weight generally had a lower effect on recoil measurements and had higher percent errors. In taking the value of recoil measurements one must be certain of the reverse movement. This is checked by moving the apparatus by hand and stopping immediately (do this without string). If the chart shows the reverse reading, this is proof the the material is reversible by itself.

The measurements of viscosity at a different temperatures and measurements of the amount of elastic property as a function of displacements and shear stress in terms of recoil were operated by the rotational viscometer. The components were designed by Dr. Wladimir Philippoff. The rotational viscometer is able to determine the transient properties that are mentioned above. It is also able to determine the time for attaining constant shear rate as a function of shear stress used. It can separate the elastic property from the viscous property by its flow curves by using the constant stress method. It can be used to study shear rate and irreversible shear rate growth as a function of time and shear stress. Nikolans Zwetkow[48] was one of the researchers who studied these transient properties by using this rotational viscometer. I found it very helpful to study his masters thesis on "Transient Phenomena of Polymer Solution", written in 1975.

The rotation viscometer is valuable for the study of transient properties but attention has to be paid to its ability to operate under uniform stress. To obtain the rheological measurements, it is essential to use an instrument in which the material is subjected to continuous and uniform or essentially uniform stresses. Otherwise the data will be questionable for their accuracy.

In 1934, M. Mooney and R. H. Ewart had developed the conicylindrical viscometer for measurements of rubber latex. They found that their conicylindrical viscometer was an absolute instrument of considerable precision in measuring viscosities of 0.05 poise or more.[49]

In 1959, Dr. W. Philippoff and Frederick Gaskins presented a paper to the Journal of Applied Polymer Science entitled "Instrumentation for the Rheological Investigation of Viscoelastic Materials". In this paper it was stated that:

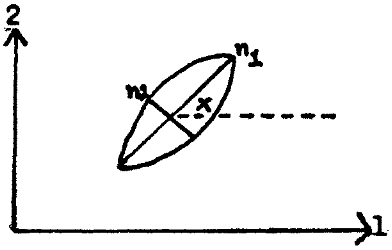
> "The investigation of mechanical properties under "steady-state" conditions is probably the most general technique used in "Steady-state conditions" means that the material is sheared unidirectionally and continuously until an equilibrium value for the rate of shear is obtained under a constant shear stress, or the converse. It is desirable that the instrumentation be so designed that the parameters can be precalculated from the geometry and cross-checked against the calibrated values. One of the primary instruments used for the purpose is the rotational viscometer, of which there are many types.
>
> In our investigations the coni-cylindrical assembly is employed. The assemblies have been designed according to the development of Mooney and Ewart in order to obtain a reasonably constant distribution of the rate of shear profile across the annulus." 50

This confirms that the rotation viscometer which was used for the measurements in this research was a cone-and-plate system that was developed by Mooney and Ewart.

The rheology phenomena has been studied for about fifty years. There are a lot of knowledgable scientists in this field and the amount of research has been growing in the United States over the past thirty five years.[55] One of the scientists among them is Dr. W. Philippoff who is an important figure in this area of research both in instrumentation and transient properties. His kind help has enabled me to learn much in this field.

V. INTRODUCTION

The birefringence, Δn is defined as the difference between the refractive index in various planes of orientation in space. This is where the refractive index is described as the ratio of the velocity of light in a transparent substance to the one in vacuum. One theory of the refractive index assumes that the electrons generate an electric field. These electrons in the atom retard the movement of the light wave. When more electrons are aligned in one direction than another, a difference in the refractive index occurs. This happens when a material is stressed by either mechanical means or subjected to flow when it is a liquid. Preceeding investigations of experimental results have shown that the refractive index difference is proportional to the pressure or stresses. The birefringence is measured with the use of polarized light. When the light passes through the stressed material it is divided into two component waves. Each wave with its plane of polarization parallel to one of the principal planes. An interference pattern can be produced in the polariscope, since one beam will be hindered a little more than the other. These interference patterns become visible as $\frac{\Delta n.l}{\lambda} = 2 k \pi$, black bands where the two beams completely cancel one another. With a compensator, one can measure fractions of a band. The birefringence, Δn of n_1 and n_2 planes shows the diagram as follows:

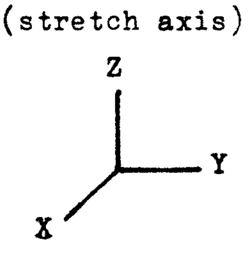


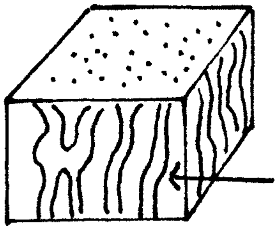
The orientation of the principal axes of stress of refractive index in the simple shear flow birefringence experiment.

The following are the types of birefringence observed which are categories of relative importance in polmeric materals.

1. Orientation Birefringence.

This occures when there is a physical ordering of optically anisotropic elements along some preferential direction for example chemical bonds. This can occur by an extension or drawing deformation as in polymers by aligning amorphous or a chrystalline chain. Simple illustration depicting molecular orientation which will result in orientation birefringence.





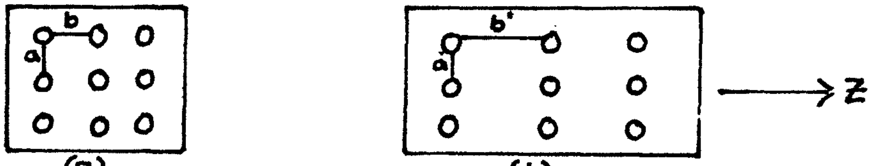
Simple illustration depicting molecular orientation which will result in orientation birefringence.

Chain backbone preferentially aligned along Z

A special case of orientation birefringence is intrinsic birefringence, Δn, by definition it is the maximum in orientation birefringence. But it will depend on whether it is an amorphous chain or crystal. For crystal, three intrinsic birefringence values exist due to the three dimensionality of a unit cell. However, only two of these are independent. The sum determines the average n, usually quoted.

2. <u>Deformation Birefringence</u>

Deformation birefringence occurs in a collection of optical isotropic particles as well as anistropic systems. For example an axial dilatation or compression due to a force could change the lattice spacing. Hence one obtains the resulting in a refracaive index difference between axes Z and Y. Distortion of bond angles and or bond lengths from equilibrium may also result in a finite birefringence, for example within glasses. Illustration showing how deformation birefringence may arise as a result of a change in packing caused by an external deformation.

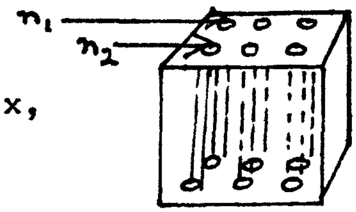


(a) (b)

3. <u>Form Birefringence</u>

The phenomenon takes place when the medium contains at least two phases each having a different refractive index and at least one dimension comparable with the wavelength of light. The classical cases treated by Wiener showed that if one had an isotropic two component system (see diagram) then a final birefringence from original could result.

Also with isotropic rods and matrix, where $\Delta n \sim (n_1 - n_2)^2$.



Folkes and Keller stated that all the observed birefringence in an extended cylinder of an ABA block copolymer was due to form effects, but it is not from molecular orientation.

Double refractive index measurements were used in a study of deformation behaviour, directly for stress analysis in liquid and glasses, and also used to study the local molecular conformation and over all orientation of polymer molecules. Recently this field has been of much interest, which is due to the uniqueness of this method in measuring the stress and flow without disturbing the medium.

VI. HISTORICAL DEVELOPMENT OF BIREFRINGENCE

According to the literary sources, Mach was the first person to investigate double refraction in very viscous substances - for example, Canada balsam when poured. In 1866, Clerk Maxwell built a concentric cylinder instrument. He was investigating the transiency of Canada balsam to shearing. He obtained results in 1874.[55] Quincke obtained similar results by immersing a heated rod in various liquids in 1880.

The first quantitative study was done by Kundt.[56] He observed movement of an interference band produced with a gypsum plate using a nitrocellulose solution. Kundt used Maxwell's concepts to express the decay birefringence as

$$\Delta n = Ktj$$

where t is the relaxation time, j is shear rate. Kündt concluded that the incompressible liquid in the angülar gap is subjected to compressive and tensile stresses perpendicular to one another and oriented 45° to the direction of flow. These stresses were proportional to viscosity times shear rate for Newtonian liquids. Raman and Krishman proposed the equation shown as the following:[57]

$$\frac{\Delta n}{n\eta j} = \frac{(n^2-1)\ (n^2+2)(a_1-a_2)(\alpha_{11}-\alpha_{22})+(a_2-a_3)(\alpha_{22}-\alpha_{33})+(a_3-a_1)(\alpha_{33}-\alpha_{11})}{10n^2N_o\ k\ T\ (a_1+a_2+a_3)\ (\alpha_{11}+\alpha_{22}+\alpha_{33})}$$

where n=index of refraction, No=number of particles/cm^3, T= absolute temperature in ^{o}K, k=Boltzmann's constant, a=geometrical axes of the triaxial ellipsoid and α = principal polarizabilities of the triaxial ellipsoids. By assuming rotational symmetry where $\alpha_2 = \alpha_3$ and $a_2 = a_3$.

Introducing the Lorentz-Lorentz equation simplifies the equation to

$$\frac{\Delta n}{2\eta j} = \frac{2\pi(n^2 + 2)^2(\alpha_1 - \alpha_2)f}{45\ K\ T\ n}$$

where f is a geometric form factor.

In 1932 Haller proposed the theory which predicted why the extinction angle changes from 45° to 0° with increasing shear rate.[58]

W. Kuhn presented his theory stating that particles are isotropic and flexible or anisotropic and rigid, with the rigid particles being strings of rigidly connected spheres, which executes an irregular rotational motion about its center of gravity in addition to translation. He presents the models which have birefringence present as a function of the diffusion constant. His models were two dimensional in nature with various geometries. In the same year (1932) R. Siguor and H. Gross discovered that the extinction angle is not 45° for polymer identical but diminishes to zero.[59]

In 1939 Peterlin, Stuart, Snellman and Bjornstahl tried to improve Kuhn's theory by treating it as a three-dimensional model and taking into account the effect of light absorption by the particle. Their theory was useless to practical research. During 1943 W. Kuhn studied the behavior of polystyrene and rubberlike materials. He concluded that birefringence was due to the deformation of the particles as well as their orientation. W. Kuhn and H. Kuhn studied solutions through probability and entropy relationships.[60] They developed a two dimensional equation for birefringence which is assumed to be an ellipse in revolution for each straight element. The equation follows:

$$\Delta n = n_x - n_y = \frac{8\pi}{15n_o}\left(\frac{n_o^2+2}{3}\right)^2 N_p(\alpha_1-\alpha_2)\sigma'\bar{h}^2\,(S_1^2+T_1^2)^{\frac{1}{2}}$$

$$\text{and } S_1 = \frac{\sigma'\bar{h}^2 f_1(\sigma'\bar{h}^2)}{f(\sigma'\bar{h}^2)} \quad ; \quad T_1 = \frac{f_2(\sigma'\bar{h}^2)}{f(\sigma'\bar{h}^2)}$$

$$\text{where } \bar{h}^2 = N_m A_m^2 \quad \text{and} \quad \sigma' = j/16D_t$$

in which D_t is the translatory diffusion constant perpendicular to h, A_m is the average length of the statistical dicular to h, A_m is the average length of the statistical element and N_m is the number of elements per molecule. Since W. Kuhn and H. Kuhn present the functions f, f_1, f_2 as complicated integrals, their formula has only been evaluated for specific cases where assumptions of S_1 and T_1 can be made. Similarly, for the extinction angle equation, W. Kuhn and H Kuhn derived the following:

$$X = \pi/4 - \tfrac{1}{2}\tan^{-1} S_1/T_1$$

Lodge-

using a model similar to the statistical theory of rubber-like elasticity, assumed that birefringence is caused by the orientation of the deforming network of optically aniso-tropic chain links.[61] He started that the stress and the optic ellipsoids are coaxial as in solids and that the extinction angle diminishes - with shear rate, and the difference of principle axes of the optic ellipsoids increase proportionately to the differences of the corresponding principle axes of the stress ellipsoid, as also Kuhn and experimentally. Lodge's stress optical coefficient equation is similar to that of F. Muller, and Kuhn, and it is very similar to the equation derived from Raman and Krishnan. The equation is as follows:[62]

$$\frac{\Delta n}{\Delta s} = \frac{\Delta p C_o}{\Delta s C} = \frac{C_o}{kT} = \frac{2\pi \bar{n}}{5kT}\left(\frac{n^2+2}{3n}\right)^2 (\alpha_1 - \alpha_2)$$

similarly from equation

$$\frac{\Delta n \sin 2\chi}{\bar{n}} = \frac{4\pi}{5}\left(\frac{n^2+2}{3\bar{n}}\right)^2 \frac{(\alpha_1 - \alpha_2)}{kT} (n - n_o)\, j$$

Lodge concluded that:

$$\frac{\Delta n}{\Delta p} = \frac{\Delta n \sin 2\chi}{2j\,(\eta - \eta_o)} = \frac{\Delta n \sin 2\chi}{2\,\tau} = C$$

Where C is the stress-optical coefficient, identical to the one for solid.

LEKUTHERM X-30, epoxy resin was investigated for its rheo-optical properties. The temperature effect on the stress optical co-efficient, $n_{11} - n_{33}$ refractive index difference and $n_{22} - n_{33}$ refractive index difference were studied in various temperatures. The experimental investigation for this thesis was observed by concentric cylinder apparatus, $n_{11} - n_{33}$ flow apparatus and $n_{22} - n_{33}$ flow apparatus, respectively.

VII. DESCRIPTION OF THE APPARATUS:

Optical Arrangement:

The optical arrangement is composed of the light source in a 100 watts, high pressure, high intensity mercury arc lamp, whose light passes through a compound projector lens (18 mm focal length) and is then passed through a green interference filter (5461 Å) and limited by two sets of variable Bjornstahl slits.

Two sets of horizontal slits whose images are focused on the entrance of the flow chamber and the half wave plate was used in the Bjornstahl arrangement. A vertical slit is used to control the width of the beam. With this arrangement a light beam of about four times the intensity of a parallel slit is produced.

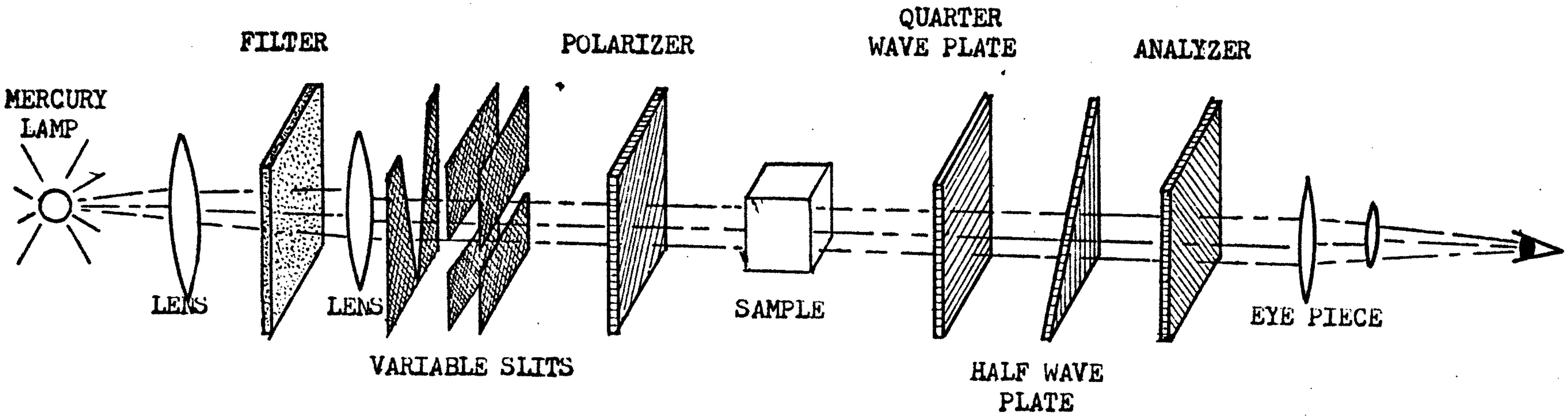
Hence the light then becomes a parallel beam by passing through another compound lens, and is polarized by a Glan Thompson prism. The light beam is now transmitted through the sample container and then through a quarter wave plate.

Half of the image passes through a quartz half wave plate by using the half shadow technique of Senarmont compensator. By matching the light intensity of the two fields one can find the correct angle. In order to operate this the image must be transmitted through the analyser and focused by eye piece.

The analyser and polarizer can be operated independently. The analyser half-wave plate is free to move a complete 360° while the analyser combination is capable of a 180°rotation.

Their rotations are divided into fractions of a degree which may be read to within a minute of an arc with the help of a vernier scale. Further precision is unjustified by individuals which is caused from the limitations of the human eye. Inhomogeneities of sample will cause inconsistant reading results. An additional lens is placed between the sample and the quarter wave plate to magnify the image when observing to 2-3 plane of flow.

All of the optical data was obtained through the use of a polariscope designed by Dr. W. Philippoff and built in the Franklin Institute of Philadelphia, Pennsylvania.



OPTICAL ARRANGEMENT OF THE POLARISCOPE[63]

VIII. TEMPERATURE EFFECT ON THE STRESS OPTICAL COEFFICIENTS

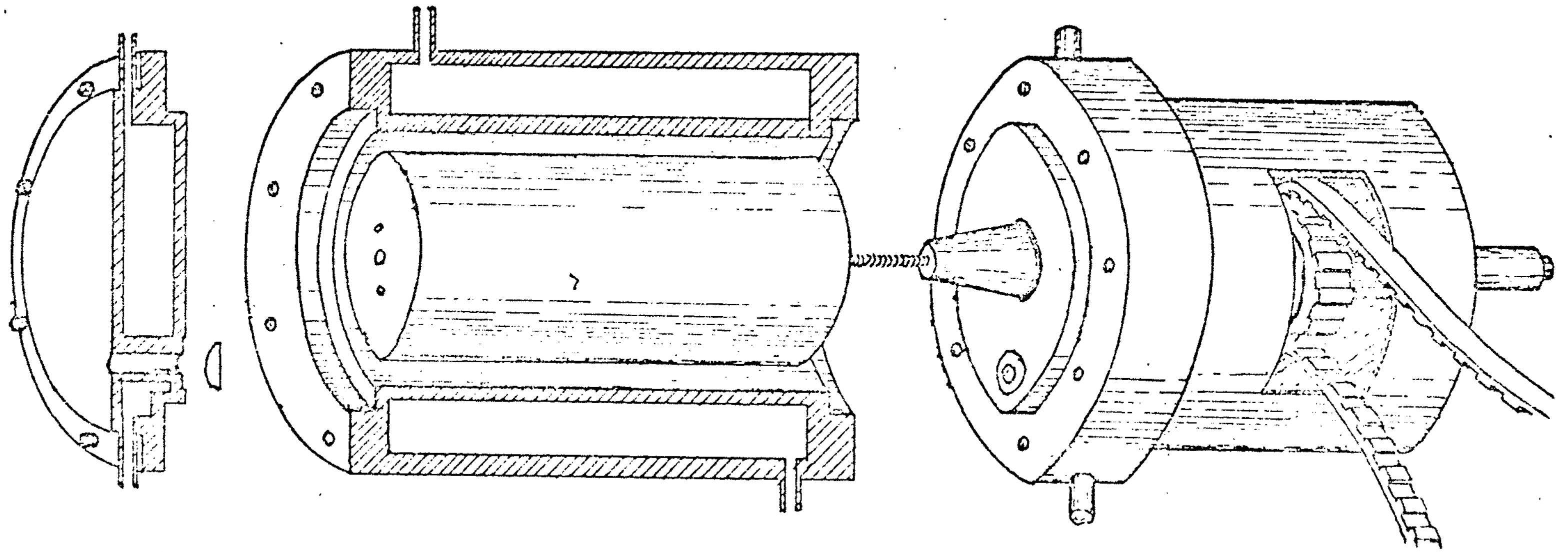
A. Concentric Cylinder Apparatus

An optical arrangement of the polariscope and a concentric cylinder arrangement compose the apparatus which was used to obtain the double refraction data. Two concentric stainless steel cylinders are the main device of this apparatus. A series of timing belt and gear boxes operate the rotation of the inner cylinder. The synchronous constant speed motor drives the gear boxes.

The apparatus is operated at different rate of shear. The rate of shear range is from 0.0000793 to 4570 sec^{-1}. The difference rate of shear is dependent on the cylinder used. For this particular experiment Cylinder I, a large gap was used. Cylinder I has a radius of 2.522 centimeters, and a length of 6.985 centimeters.

The angular gap is 3.35 millimeters. Two small circular glass windows of 12 millimeters diameter by 0.15 millimeters are mounted on each end of the stationary cylinder. The light beam passes through these two windows.

There is a water jacket which functions to keep the temperature constant. It is located on the outer cylinder. A water jacket which was divided into three sections --one section is a constant temperature bath from which the water originates. Its accuracy can be maintained within o.01°C. An insulated jar which contains a calibrated thermometer is circulated throughout by water from a constant temperature bath. A calibrated thermometer has the accuracy of ± 0.02°C. The water travels through the flexible rubber tubing. The inner concentric cylinder which contains the material is kept a constant temperature by the water which comes from the other flexible tube connected with an insulated jar connected to the middle jacket. One can set up any temperature and keep it constant for the experiment. In order to minimize the heat losses, the flexible tube is designed to be used along with the entire cylinder.



CONCENTRIC CYLINDER INSTRUMENT[64]

Temperature Effect on Stress-Optical Coefficient

B. Experimental Procedure

The common practice to correct the coefficient C is by Brownian motion with the equation:

$$C = C' \quad \frac{T'}{T}$$

where C' is the stress-optical coefficient at some reference temperature T'.

To test this equation, a highly birefringent and temperature sensitive agent was used. A highly viscous epoxy resin (Lekutherm X-30) was used to perform the experiment.

One can calculate the viscosity and birefringence values by using either one of its data and C. But there is still doubt that their experiment values are the same as their calculated values. Therefore, it is better to run the experiment for both of them and check with the calculated data. By having both devices available, it is possible to obtain the data on the same batch of material. The same thermometer was used for the viscosity and the birefringence measurements to eliminate any thermometer errors. The measurements were conducted in a temperature range of +30° - 80°C.

The inconsistent birefringence values will be obtained if large bubbles appear in the concentric cylinder device. Therefore, it is very important to be careful while filling the sample to ensure that no air bubbles will be introduced into the resin. Dispersion of air due to shearing will cause the resin to become opaque.

A period of time -- 24 hours or more -- was allowed for thermal equilibrium to occur. The material was operated in a clockwise and then a counter-clockwise direction and an average of the two values was used to compensate for any optical misalignments.

Temperature Effect on the Stress-Optical Coefficient Procedure

In order to obtain the value of birefringence, one has to set the analyzer to zero for a Newtonian liquid setup at 45°. The extinction angle X is obtained by rotating, the analyzer and the polarizer are locked at an angle of 89° perpendicular to each other. The reason being to allow for the balancing of the half-wave plate field. If one is locked at an angle of 90°, the total cancellation is zero light intensity, therefore, there is no reading at this setting. The polarizer is then set at one angle of 45-X degree and the compensation angle is read from the analyzer. Hence, the ' birefringence value is obtained by multiplying the angle by the factor of 4.32×10^{-8}. The factor is derived from the following equation:

$$\Delta n = \frac{\theta \lambda \left(0.1745 \frac{\text{radius}}{\text{degree}}\right)}{\pi \ell}$$

where θ is the compensator angle in degree, ℓ is the length of cylinder, and λ is the wavelength.

C. Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 1 Temperature at 30.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	Angle (min) / Shear Rate (sec^{-1})
4	0.000177	64° 00′	3840	21700000
5	0.000121	46° 20′	2780	22986000
6	0.0000793	30° 10′	1810	22820000
			Average	22300000
*eliminate too small!				
Experiment 2				
4	0.000177	61° 40′	3700	21637426.9
5	0.000121	44° 30′	2670	22066115.7
			Average	21851771.3
*eliminate too small!				
Experiment 3				
4	0.000177	84° 00′	5040	28500000.0
5	0.000121	57° 40′	3460	28500000.0
6	0.0000793	38° 10′	2290	28800000.0
			Average	28600000.0
Error--- ±141421.36, 0.49%				
Experiment 1		Temperature at 32.0°C		
3	0.000254	46° 30′	2790	10984252.0
4	0.000177	32° 00'	1920	10847457.0
5	0.000121	21° 40′	1300	10744380.1
6	0.0000793	14° 37'	877	11059268.0
			Average	10908839.0
Error--- ±121584.33, 1.11%				
Experiment 2				
3	0.000254	43° 30′	2610	10300000
4	0.000177	29° 30′	1770	10000000
5	0.000121	20° 00′	1200	9920000
6	0.0000793	12° 40′	760	9570000
			Average	9947500
*eliminate too small!				

Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 1 Temperature at 35.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	$\frac{\text{Angle (min)}}{\text{Shear Rate (sec}^{-1})}$
5	0.001210	47°30′	2850	2350000
6	0.000793	31° 40′	1900	2400000
1	0.000564	21° 25′	1285	2280000
2	0.000370	14° 20′	860	2330000
3	0.000254	10° 00′	600	2360000
4	0.000177	7° 00′	420	2370000
			Average	2350000

*eliminate too small!

Experiment 2

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	$\frac{\text{Angle (min)}}{\text{Shear Rate (sec}^{-1})}$
5	0.001210	60° 20′	3620	2990000
6	0.000793	38° 17′	2297	2900000
1	0.000564	27° 30′	1650	2925000
2	0.000370	17° 50′	1070	2890000
3	0.000254	12° 20′	740	2910000
4	0.000177	8° 40′	520	2940000
5	0.000121	5° 40′	340	2810000
6	0.0000793	3° 50′	230	2900000
			Average	2910000

Error--- ±47598.58, 1.64%

Experiment 3

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	$\frac{\text{Angle (min)}}{\text{Shear Rate (sec}^{-1})}$
5	0.001210	55° 00′	3300	2725000
6	0.000793	35° 20′	2120	2670000
1	0.000564	24° 40′	1480	2620000
2	0.000370	15° 30′	930	2510000
3	0.000254	10° 40′	640	2520000
4	0.000177	7° 00′	420	2370000
			Average	2569167

Error--- ±119512.9, 4.65%

Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 1 Temperature at 37.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	$\frac{\text{Angle (min)}}{\text{Shear Rate (sec}^{-1})}$
3	0.00254	49° 30′	2970	1170000
4	0.00177	35° 20′	2120	1198000
5	0.00121	24° 30′	1470	1215000
6	0.000793	15° 50′	950	1198000
			Average	1195000
Error--- ±16147.76,		1.35%		
Experiment 2				
3	0.00254	50° 00′	3000	1180000
4	0.00177	35° 20′	2120	1190000
5	0.00121	24° 15′	1465	1210000
6	0.000793	15° 30′	930	1172000
1	0.000564	11° 10′	670	1187000
2	0.000370	7° 20′	440	1190000
3	0.000254	4° 50′	290	1145000
			Average	1180000
Error--- ±18662.41,		1.58%		

Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 1 Temperature at 40.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	$\frac{\text{Angle (min)}}{\text{Shear Rate (sec}^{-1}\text{)}}$
1	0.00564	39° 00′	2340	414000
2	0.00370	25° 00′	1500	406000
3	0.00254	17° 30′	1050	413000
4	0.00177	11° 20′	680	384000
5	0.00121	8° 00′	480	397000
6	0.000793	5° 20′	320	403000
Error--- ±10222.52, 2.54%			Average	403000
Experiment 2				
5	0.01090	70° 30′	4230	388000
6	0.0714	45° 50′	2750	385000
1	0.00564	36° 00′	2160	383000
2	0.00370	24°20′	1460	394000
3	0.00254	16° 40′	1000	393000
4	0.00177	11° 20′	680	384000
5	0.00121	7° 50′	470	388000
6	0.000793	5° 20′	320	403000
1	0.000564	3° 40′	220	393000
2	0.000370	2° 30′	160	405000
Error--- ±7213.87, 1.84%			Average	391600
Experiment 3				
1	0.00564	36° 40′	2200	390000
2	0.00370	24° 50′	1490	403000
3	0.00254	17° 00′	1020	402000
4	0.00177	11° 20′	680	384000
5	0.00121	7° 40′	460	380000
6	0.000793	5° 20′	320	403000
Error--- ±9469.25, 2.40%			Average	394000

Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 1 Temperature at 45.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	Angle (min) / Shear Rate (sec^{-1})
4	0.0159	21° 20′	1280	80500
5	0.0109	14° 40′	880	80700
6	0.00714	9° 37′	577	80800
1	0.00564	8° 3′	483	85600
2	0.00370	5° 14′	314	84600
3	0.00254	3° 28′	208	81900
4	0.00177	2° 30′	150	84600
			Average	82670
Error--- ±2025.35,	2.45%			
Experiment 2				
1	0.0508	63° 00′	3980	(74300)
2	0.0333	44° 00′	2640	79200
3	0.0229	30° 40′	1840	80300
			Average	79700
Error--- ±552.27,	0.69%			
Experiment 3				
1	0.0508	73° 00′	4380	86200
2	0.0333	48° 5′	2885	86600
3	0.0229	33° 00′	1980	86400
4	0.0159	23° 7′	1387	87200
5	0.0109	16° 40′	1000	91700
6	0.00714	10° 20′	620	86800
1	0.00564	8° 3′	483	85600
2	0.00370	5° 15′	315	85000
3	0.00254	3° 32′	212	83400
4	0.00177	2° 40′	160	90400
5	0.00121	1° 40′	100	91500
			Average	87350
Error--- ±2571.66,	2.94%			

Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 4 Temperature at 45.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	$\frac{\text{Angle (min)}}{\text{Shear Rate (sec}^{-1}\text{)}}$
1	0.0508	70° 10′	4210	82800
2	0.0333	45° 00′	2700	81200
3	0.0229	30° 50′	1850	80800
4	0.0159	21° 20′	1280	80600
5	0.0109	14° 50′	890	81600
6	0.00714	9° 40′	580	81300
			Average	81400
Error---	±712.97,	0.88%		
Experiment 1		Temperature at 50.0°C		
1	0.0508	17° 45′	1065	21100
2	0.0333	12° 26′	746	22400
3	0.0229	8° 35′	515	22900
4	0.0159	5° 58′	358	23100
6	0.00714	2° 39′	159	23600
			Average	22600
Error---	±852.06,	3.77%		
Experiment 2				
4	0.159	60° 50′	3650	22900
5	0.109	42° 30′	2550	23400
6	0.0714	28° 20′	1700	23800
1	0.0508	19° 30′	1143	22500
2	0.0333	12° 40′	760	22800
3	0.0229	8° 40′	520	22700
4	0.0159	6° 10′	370	23300
5	0.0109	4° 00′	240	22000
6	0.00714	2° 40′	160	22400
			Average	22870
Error---	±524.94,	2.30%		

Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 3 Temperature at 50.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	$\frac{\text{Angle (min)}}{\text{Shear Rate } (sec^{-1})}$
4	0.159	53° 30′	3210	20200
5	0.109	37° 00′	2220	20400
6	0.0714	24° 00′	1440	20200
1	0.0508	17° 30′	1050	20700
2	0.0333	11° 20′	680	20400
3	0.0229	7° 45′	465	20300
4	0.0159	5° 30′	330	20700
5	0.0109	3° 44′	224	20600
6	0.00714	2° 30′	150	21000
			Average	20500
Error--- ±253.86,	1.24%			
Experiment 1		Temperature at 60.0°C		
1	0.508	18° 29′	1109	2183.071
2	0.333	12° 17′	737	2213.213
3	0.229	8° 51′	531	2318.778
4	0.159	6° 10′	370	2327.044
5	0.109	4° 27′	267	2449.541
6	0.0714	2° 43′	173	2422.969
1	0.0508	1° 45′	115	2263.780
2	0.0333	1° 4′	74	2222.222
			Average	2300.077
Error--- ±91.61,	3.98%			
Experiment 2				
4	1.59	66° 00′	3960	2490
5	1.09	47° 00′	2820	2597
6	0.714	29° 45′	1785	2500
1	0.508	19° 40′	1180	2322
2	0.333	14° 10′	850	2552
3	0.229	8° 50′	530	2314
4	0.159	6° 40′	400	2525
Error--- ±100.63,	4.07%			

Data and Calculations of Flow Birefringence of LEKUTHERM X-30

Experiment 2 (continue)   Temperature at 60.0°C

Setting	Shear Rate (sec^{-1})	Angle (degree)	Angle (min)	Angle (min) / Shear Rate (sec^{-1})
5	0.109	4° 40′	280	2569
6	0.0714	2° 50′	170	2381
			Average	2470
Experiment 3				
1	0.508	19° 10′	1140	2240
2	0.333	12° 40′	760	2280
3	0.229	8° 30′	510	2230
4	0.159	6° 00′	360	2265
5	0.109	4° 20′	260	2380
6	0.0714	2° 30′	150	2100
			Average	2250
Error--- ±82.69, 3.68%				
Experiment 1			Temperature at 70.0°C	
4	1.59	10° 52′	652	410.063
5	1.09	6° 50′	410	376.147
6	0.714	4° 49′	289	404.762
1	0.508	3° 25′	205	403.543
2	0.333	2° 10′	130	390.390
3	0.229	1° 34′	94	410.480
4	0.159	1° 10′	70	440.252
			Average	405.091
Error--- ±18.34, 4.53%				
Experiment 1			Temperature at 80.0°C	
1	5.08	8° 50′	530	104.33
2	3.33	5° 53′	353	106.01
3	2.29	4° 2′	242	105.68
4	1.59	2° 38′	158	99.37
5	1.09	1° 50′	110	100.92
6	0.714	1° 16′	76	106.44
			Average	103.79
Error--- ±2.70, 2.60%				

RATE OF SHEAR

Cylinder 1 (large gap) Constant = 4.32×10^{-8}

Setting	Straight	1:10	1:100	1:900
1	4570	457	45.7	5.08
2	3000	300	30.0	3.33
3	2060	206	20.6	2.29
4	1428	142.8	14.28	1.59
5	979	97.9	9.79	1.09
6	642	64.2	6.42	0.714

Setting	1:9000	1:90,000	1:810,000	1:1000	1:10,000
1	0.508	0.0508	0.00564	4.57	0.457
2	0.333	0.0333	0.00370	3.00	0.300
3	0.229	0.0229	0.00254	2.06	0.206
4	0.159	0.0159	0.00177	1.43	0.143
5	0.109	0.0109	0.00121	0.979	0.0979
6	0.0714	0.00714	0.000793	0.642	0.0642

Stress - Optical Coefficient C_{br} of LEKUTHERM X-30

Expt.	$\bar{M}'$	$M \times 10^8$	η (P)	2η (P)	C_{br}
Temperature at 30.0°C					
1	22300000	1605600	*129831700	259663400	⊛618
2	21851771	1573328	"	"	⊛605
3	28600000	2059200	"	"	793
				Average	793
⊛ eliminate experiment #1 and #2, values too small!					
Temperature at 32.0°C					
1	10908839	785436	*42674000	85348000	920
2	9947500	716220	"	"	⊛839
				Average	920
⊛ eliminate					
Temperature at 35.0°C					
1	2350000	169200	*9552500	19105000	⊛887
2	2910000	209520	"	"	1097
3	2569167	184980	"	"	1050
				Average	1073
Error--- ±23.5, 2.19%					
Temperature at 37.0°C					
1	1195000	86040	*3898000	7796000	1158
2	1180000	84960	"	"	1143
				Average	1151
Error--- ±7.52, 0.65%					
Temperature at 40.0°C					
1	403000	29061	*1153325	2306647	1258
2	391600	28195	"	"	1225
3	396000	28368	"	"	1230
				Average	1240
Error--- ±14.70, 1.19%					

* intrapolated value

Stress - Optical Coefficients C_{br}

Expt.	$\bar{M}'$	$M \times 10^8$	η (P)	2η (P)	C_{br}
Temperature at 45.0°C					
1	82670	5952.2	*190546	389969	1526
2	79700	5738.4	"	"	1471
3	87350	6289.2	"	"	1612
4	81400	5860.8	"	"	1502
Error--- ±52.40, 3.42%				Average	1528
Temperature at 50.0°C					
1	22600	1627.2	46020	92040	1768
2	22870	1646.64	"	"	1789
3	20500	1476.00	"	"	1604
Error--- ±82.71, 4.81%				Average	1720
Temperature at 60.0°C					
1	2300	165.6	4315	8630	1919
2	2470	177.8	"	"	2061
3	2250	162.0	"	"	1877
Error--- ±78.73, 4.03%				Average	1952
Temperature at 70.0°C					
1	405.09	29.17	742	1484	1965
Temperature at 80.0°C					
1	103.79	7.47	190	380	1967

Stress - Optical Coefficients C from Experiment 1 Values

T (°C)	η (P)	C_{br}- 1
30.0	129831700	⊛618.34
32.0	42674000	920.27
35.5	9552500	⊛887.00
37.0	3898000	1157.90
40.0	1153325	1258.00
45.0	190546	1526.34
50.0	46020	1767193
60.0	4315	1918.89
70.0	742	1965.40
80.0	190	1966.57

Stress - Optical Coefficients C_{br} from Experiment 2 Values

T (°C)	η (P)	C_{br}- 2
30.0	129831700	⊛605.91
32.0	42674000	⊛839.18
35.0	9552500	1097.00
37.0	3898000	1143.40
40.0	1153325	1225.00
45.0	190546	1471.50
50.0	46020	1789.05
60.0	4315	2060.70

⊛ eliminate, values too small!

Stress - Optical Coefficients C_{br} from Average Values

T (°C)	η (P)	C_{br}- Ave
30.0	129831700	793.03
32.0	42674000	920.27
35.0	9552500	1011.30
37.0	3898000	1160.60
40.0	1153325	1240.00
45.5	190546	1528.37
50.0	46020	1720.21
60.0	4315	1952.20
70.0	742	1965.40
80.0	190	1966.57

Stress - Optical Coefficients C_{br} from Experiment 3

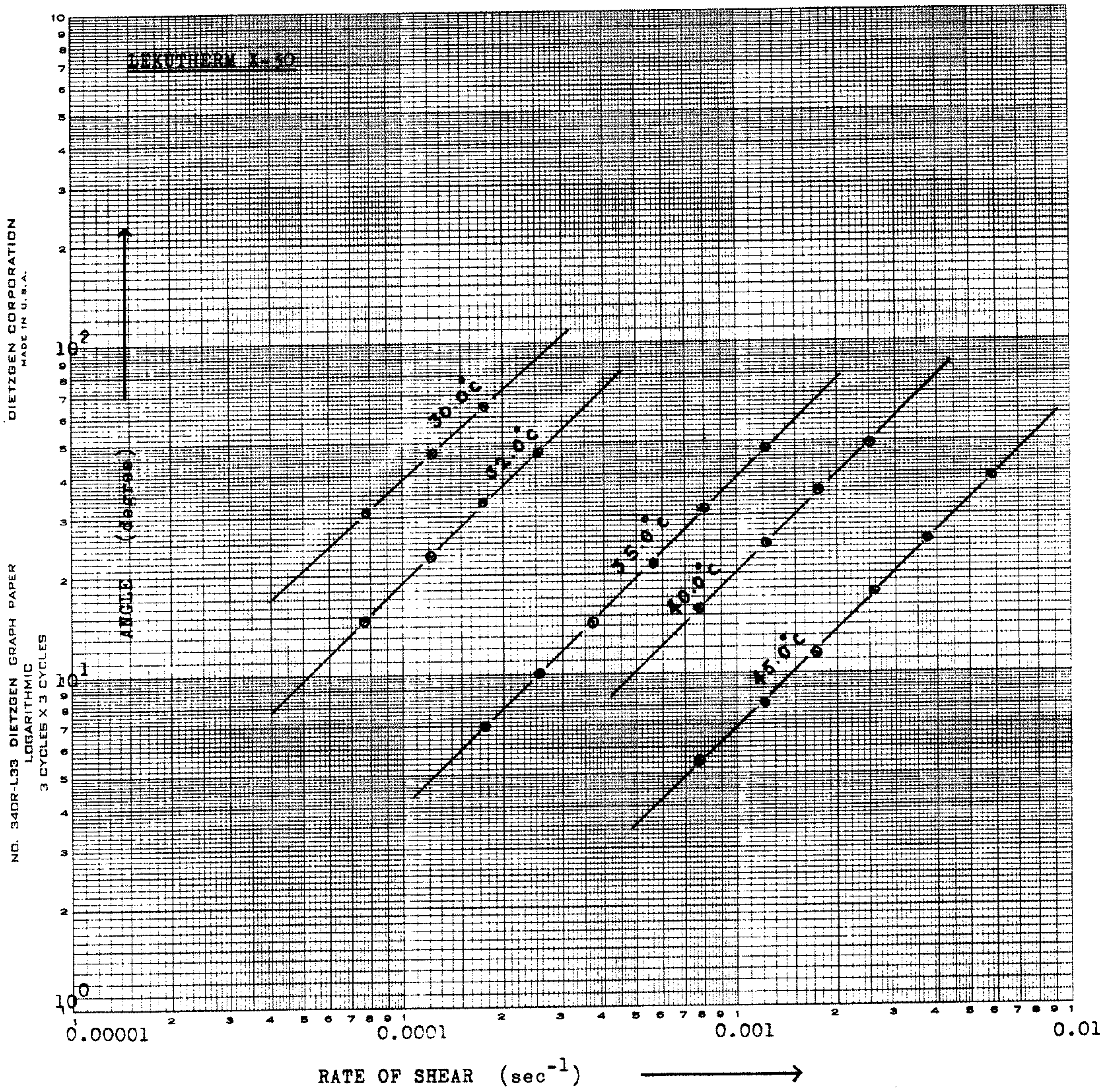
T (°C)	η (P)	C_{br}- 3
30.0	129831700	793.03
35.0	9552500	1050.00
40.0	1153325	1230.00
45.0	190546	1612.74
50.0	46020	1603.65
60.0	4315	1877.00

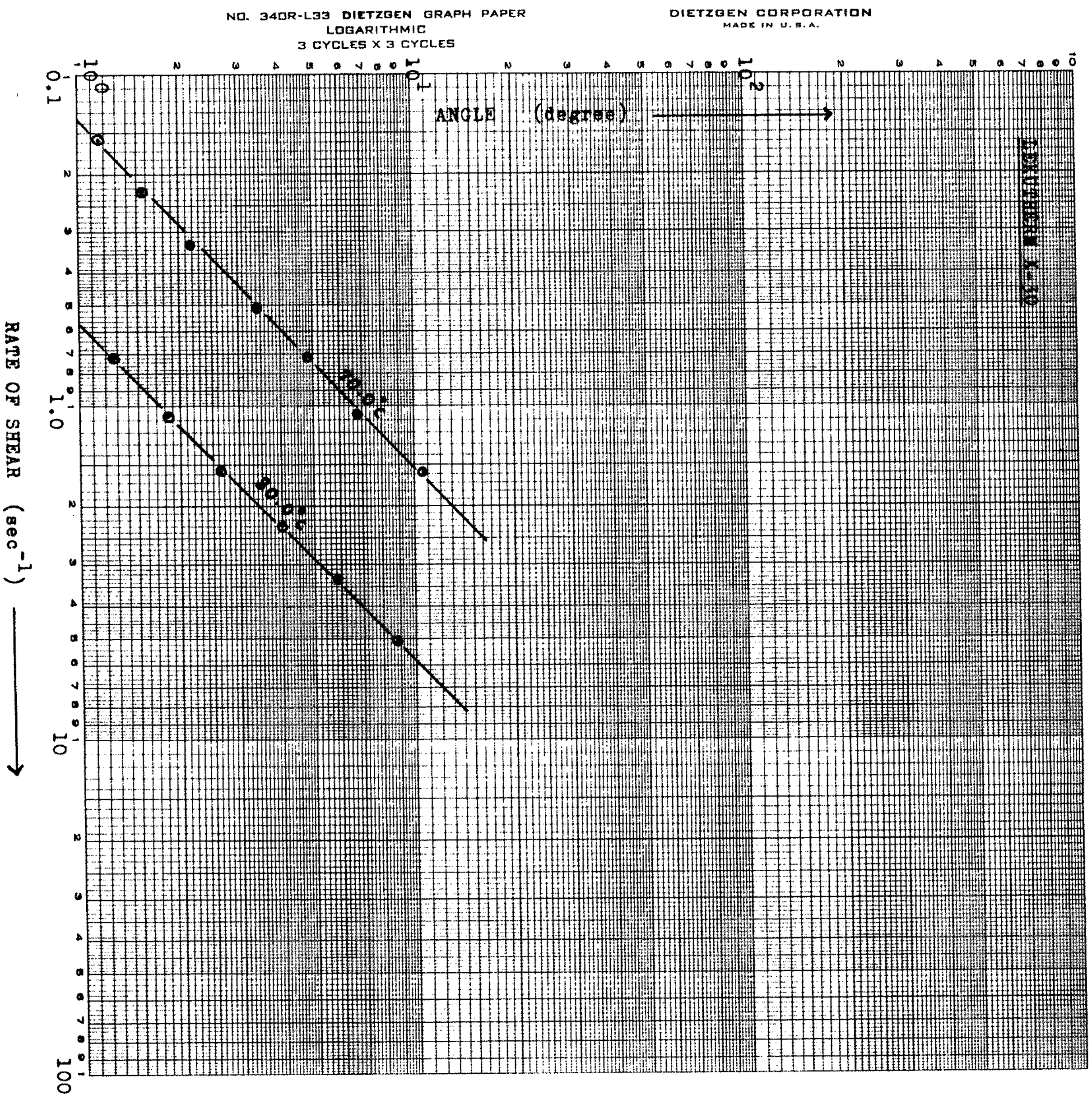
Stress - Optical Coefficients C_{br} from Average Values

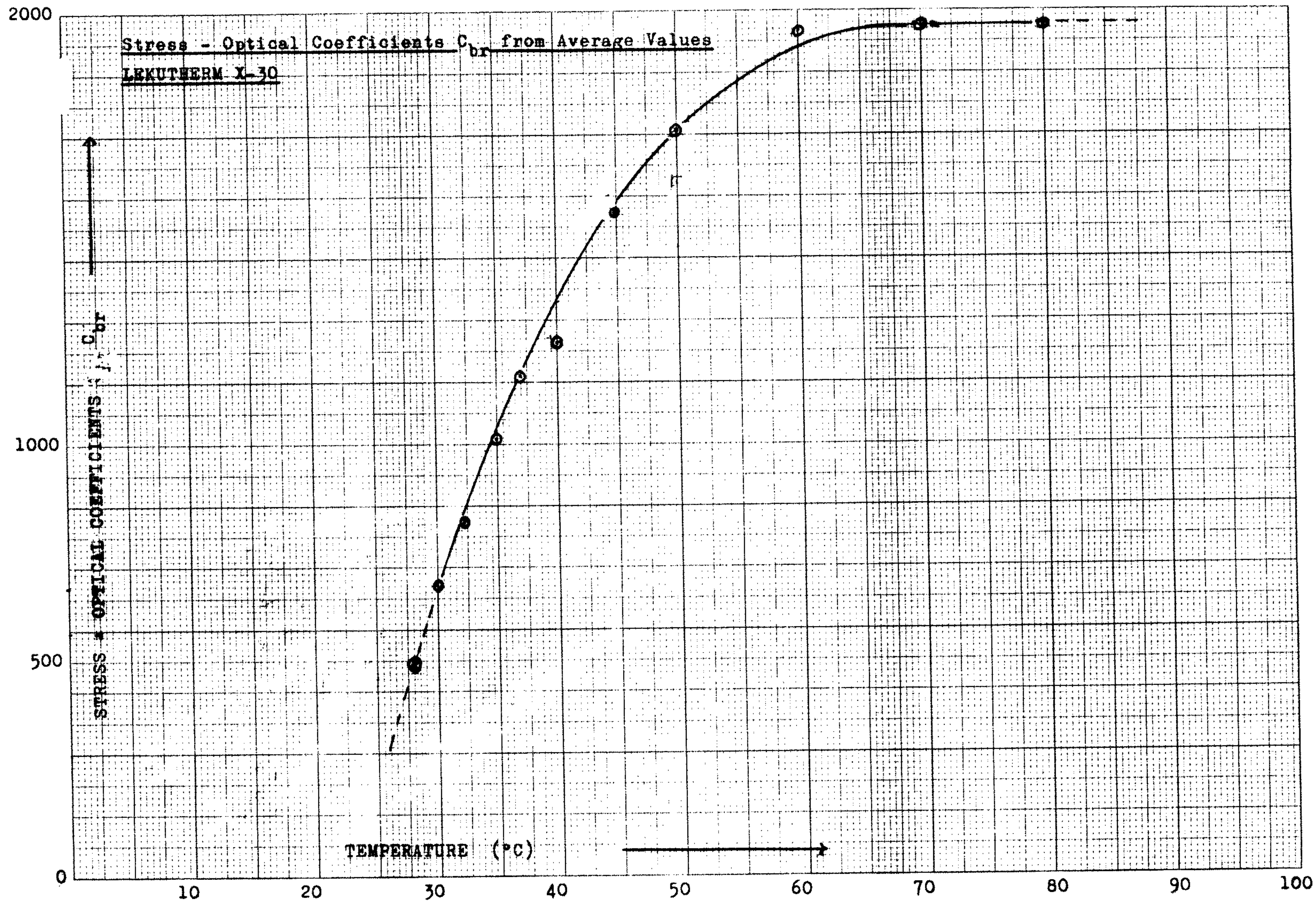
T (°C)	η (P)	C_{br}- Ave
30.0	129831700	793.03
32.0	42674000	920.27
35.0	9552500	1011.30
37.0	3898000	1160.60
40.0	1153325	1240.00
45.5	190546	1528.37
50.0	46020	1720.21
60.0	4315	1952.20
70.0	742	1965.40
80.0	190	1966.57

Stress - Optical Coefficients C_{br} from Experiment 3

T (°C)	η (P)	C_{br}- 3
30.0	129831700	793.03
35.0	9552500	1050.00
40.0	1153325	1230.00
45.0	190546	1612.74
50.0	46020	1603.65
60.0	4315	1877.00

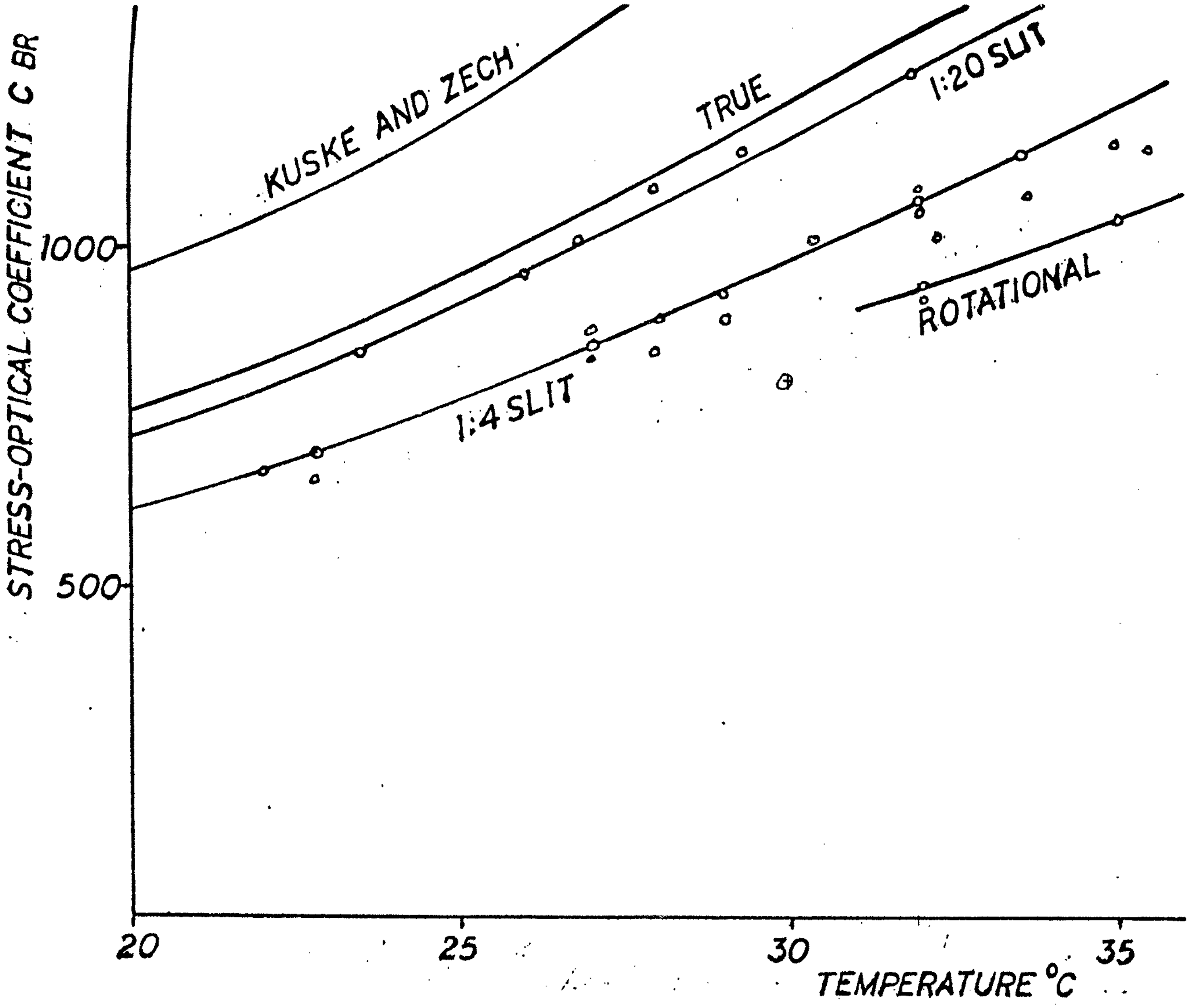

LEKUTHERM X-30
ANGLE (degree)
RATE OF SHEAR (sec^{-1})
10^0
10^1
10^2
10
0.00001
0.0001
0.001
0.01
30.0°C
32.0°C
35.0°C
40.0°C
45.0°C
NO. 340R-L33 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 3 CYCLES
DIETZGEN CORPORATION
MADE IN U.S.A.

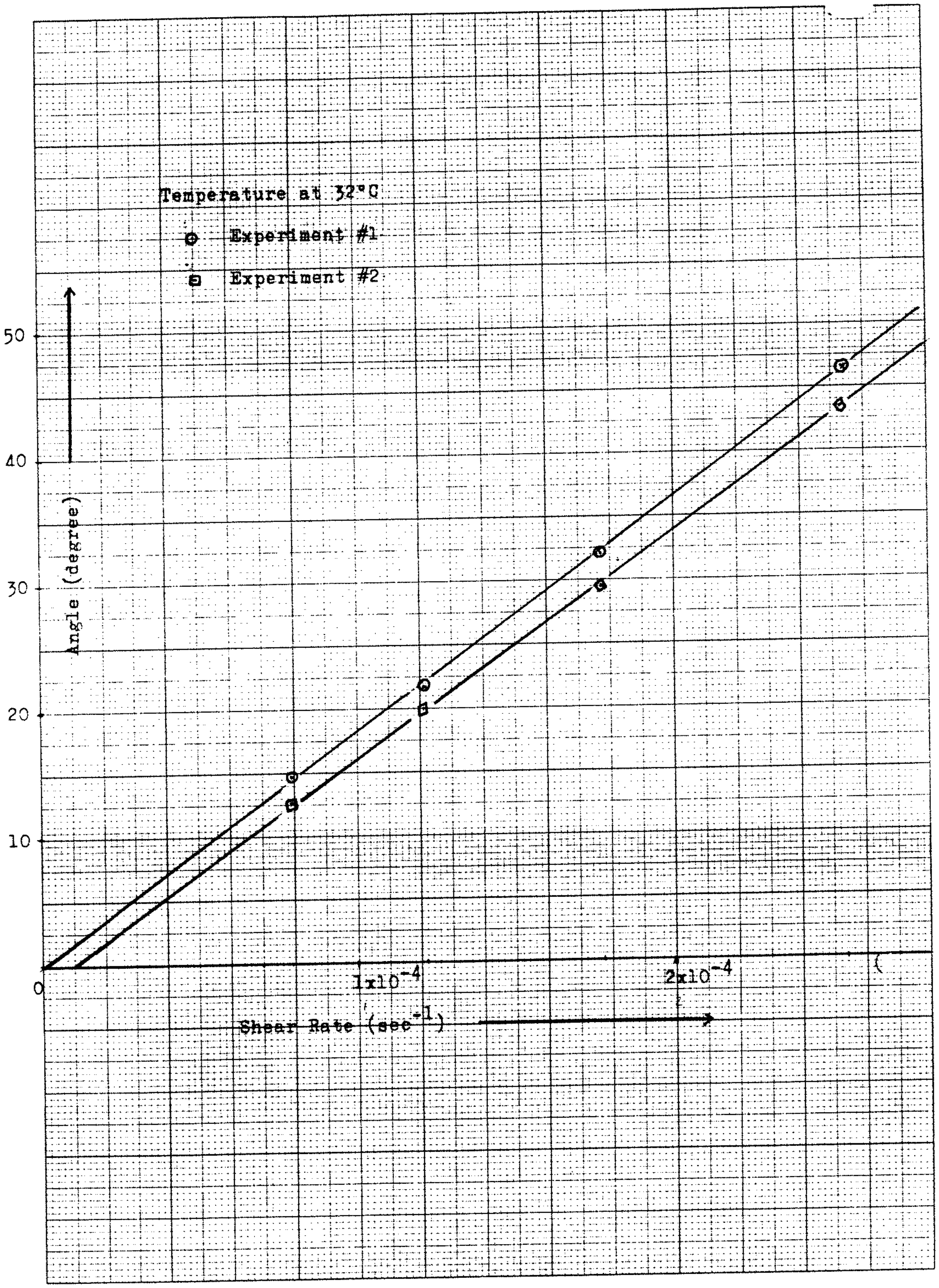

NO. 340R-L33 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 3 CYCLES
DIETZGEN CORPORATION
MADE IN U.S.A.
ANGLE (degree)
RATE OF SHEAR (sec^{-1})
0.1
1.0
10
100
10^0
10^1
10^2
70.0°C
50.0°C

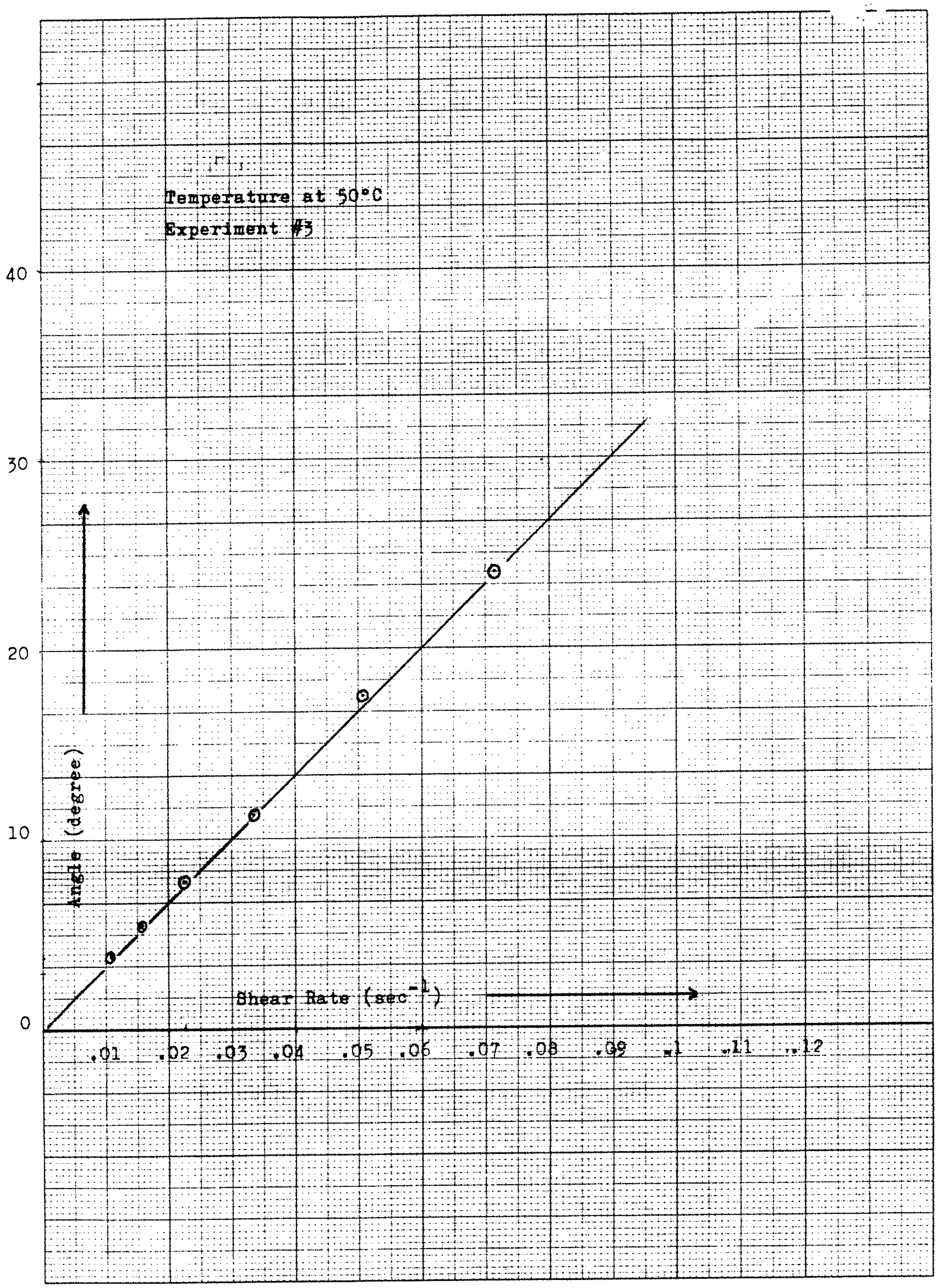


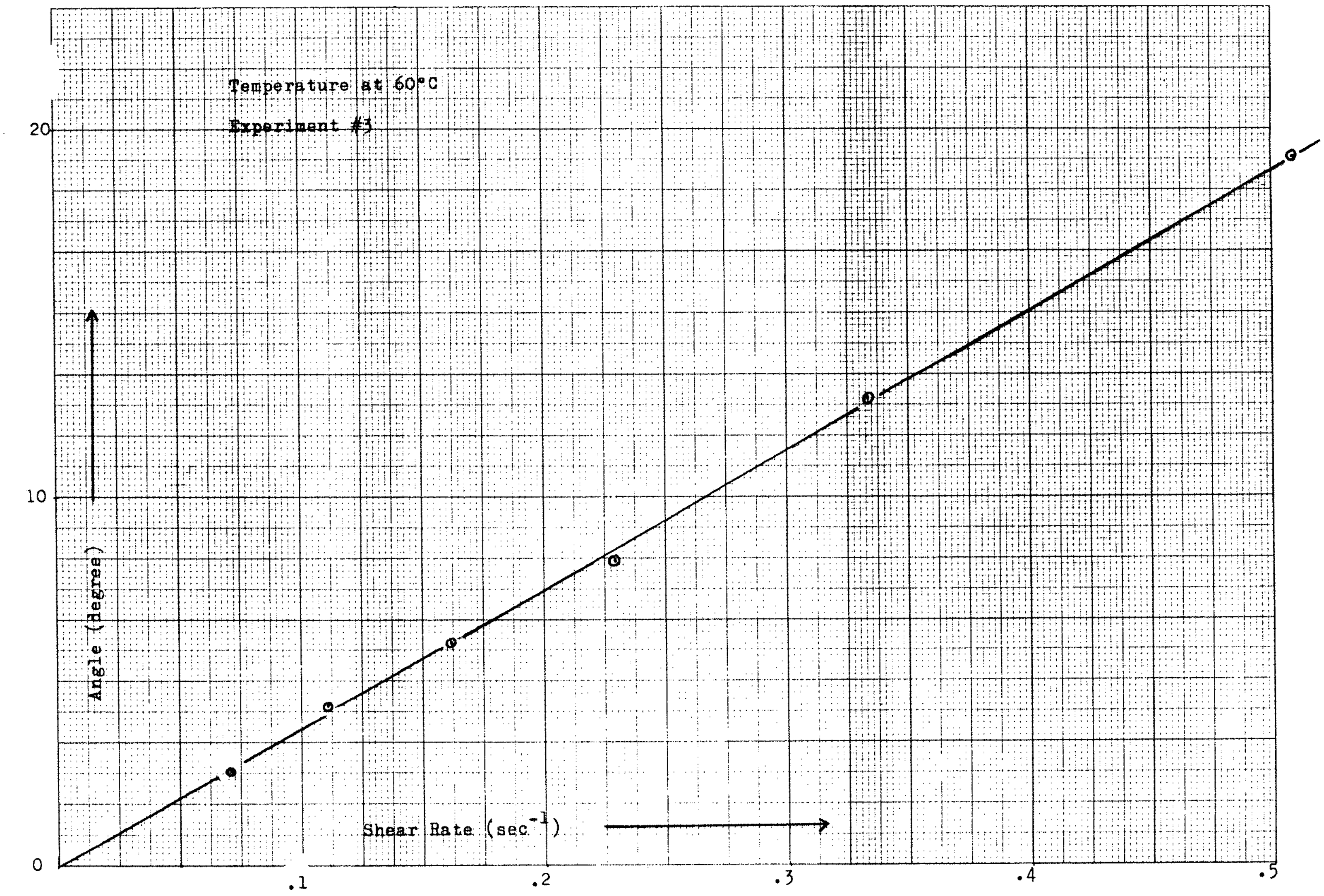
Stress - Optical Coefficients C_{br} from Average Values

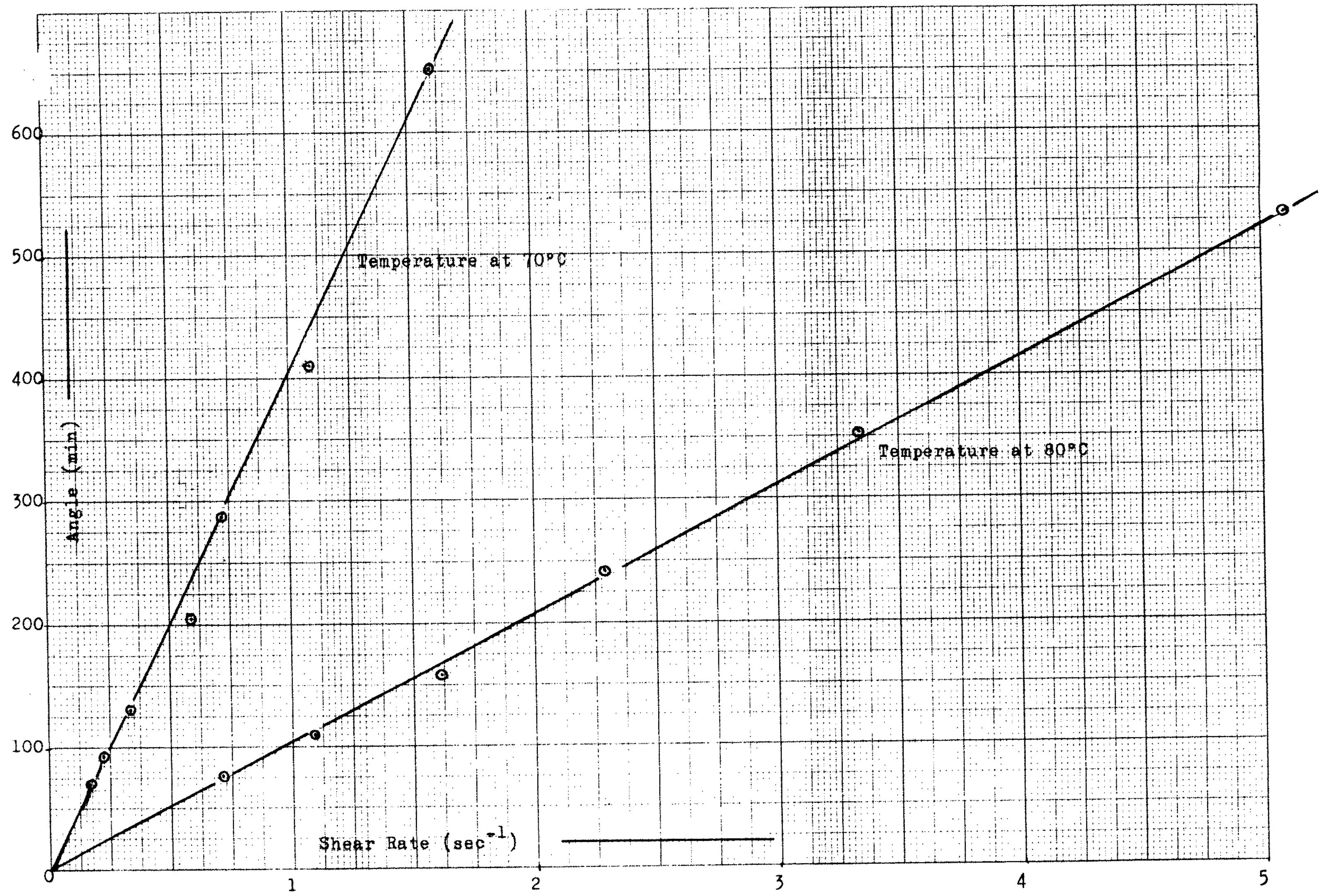
LEKUTHERM X-30


KUSKE AND ZECH
TRUE
1:20 SLIT
1:4 SLIT
ROTATIONAL
STRESS-OPTICAL COEFFICIENT C BR
1000
500
20
25
30
35
TEMPERATURE °C


Temperature at 32°C
Experiment #1
Experiment #2
Angle (degree)
50
40
30
20
10
0
1x10^{-4}
2x10^{-4}
Shear Rate (sec^{-1})


Temperature at 50°C
Experiment #3
Angle (degree)
Shear Rate (sec^{-1})
0
10
20
30
40
.01
.02
.03
.04
.05
.06
.07
.08
.09
.1
.11
.12


Temperature at 60°C
Experiment #3
Angle (degrees)
Shear Rate (sec^{-1})
0
10
20
.1
.2
.3
.4
.5



600
500
400
300
200
100
0
Angle (min)
1
2
3
4
5
Shear Rate (sec^{-1})
Temperature at 70°C
Temperature at 80°C

Birefringence of LEKUTHERM X-30

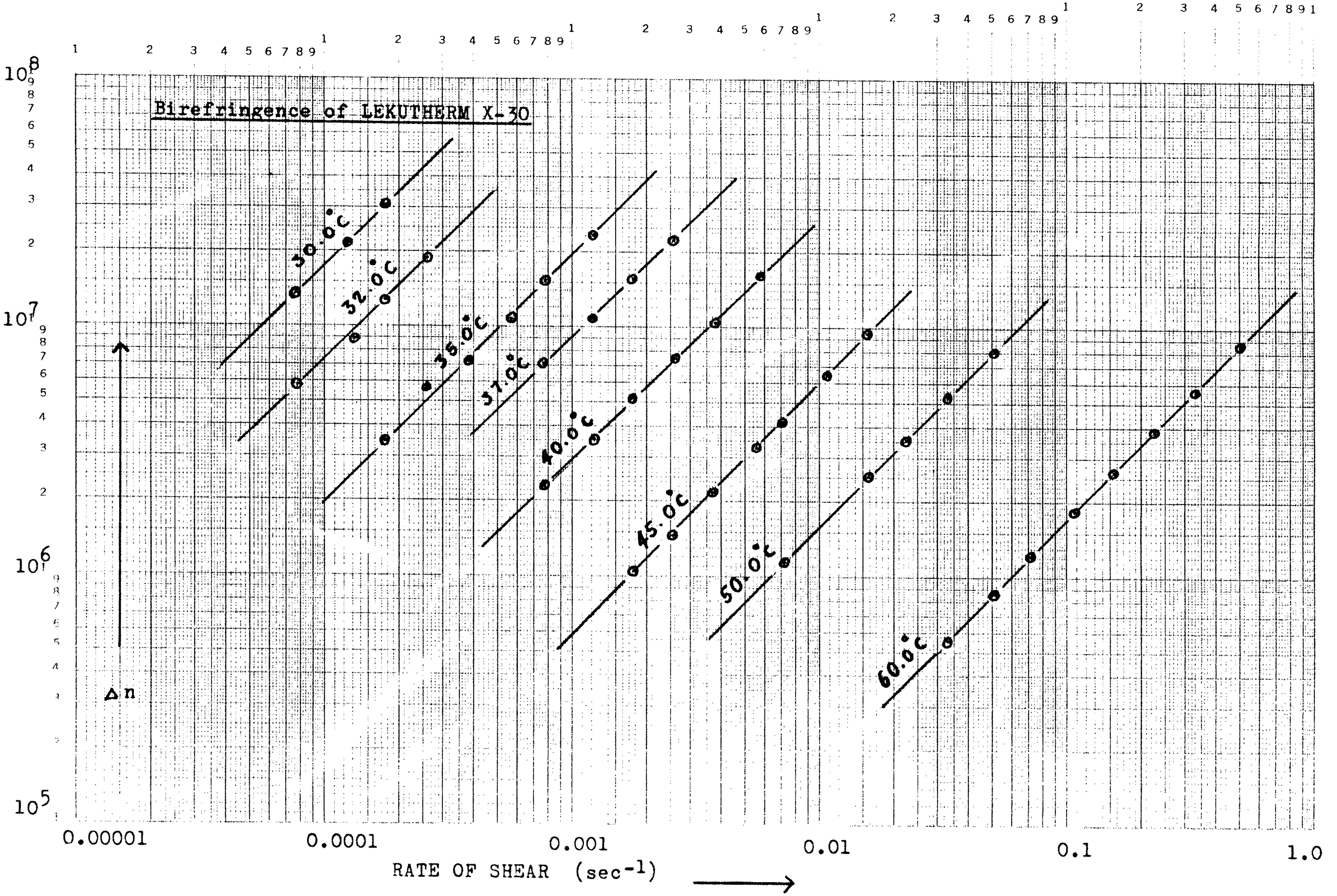
T (°C)	η (P)	C_{br}	$\dot{\gamma}$ (sec^{-1})	$\Delta n \times 10^8$
30.0	129831700	793.03	0.000177	3.6448×10^7
			0.000121	2.4916×10^7
			0.0000793	1.6330×10^7
32.0	42674000	920.27	0.000254	1.9950×10^7
			0.000177	1.3902×10^7
			0.000121	9.5037×10^6
			0.0000793	6.2285×10^6
35.0	9552500	1011.00	0.001210	2.3371×10^7
			0.000793	1.5317×10^7
			0.000564	1.0894×10^7
			0.000370	7.1466×10^6
			0.000254	4.9060×10^6
			0.000177	3.4188×10^6
37.0	3898000	1150.60	0.00254	2.2784×10^7
			0.00177	1.5877×10^7
			0.00121	1.0854×10^7
			0.000793	7.1133×10^6
40.0	1153325	1240.00	0.00564	1.6132×10^7
			0.00370	1.0583×10^7
			0.00254	7.2650×10^6
			0.00177	5.0626×10^6
			0.00121	3.4609×10^6
			0.000793	2.2682×10^6

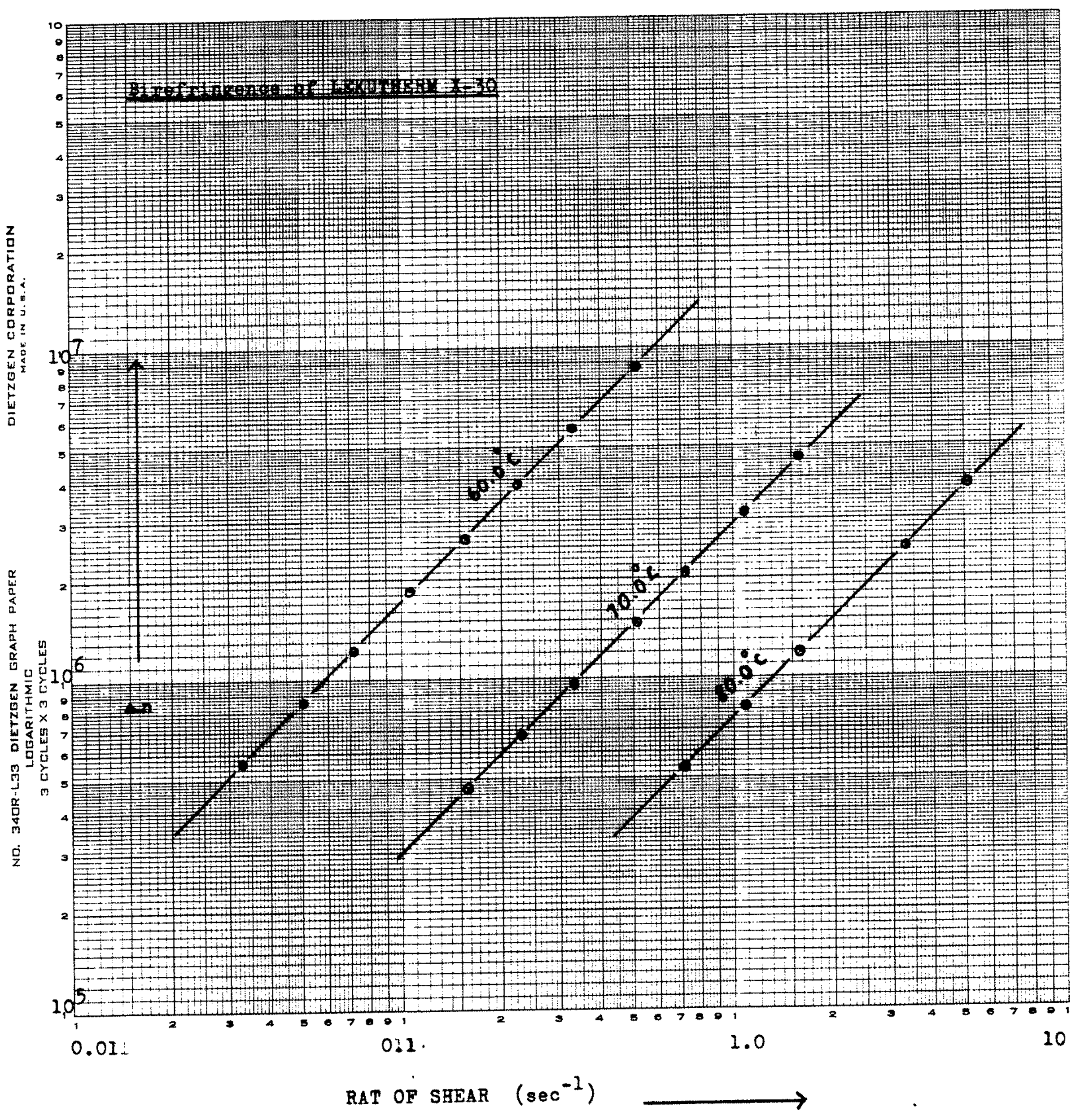
Birefringence of LEKUTHERM X-30

T (°C)	η (P)	C_{br}	$\dot{\gamma}$ (sec^{-1})	$\Delta n \times 10^8$
45.0	190546	1528.37	0.0159	9.2609×10^6
			0.0109	6.3087×10^6
			0.00714	4.1587×10^6
			0.00564	3.2850×10^6
			0.00370	2.1551×10^6
			0.00254	1.4794×10^6
			0.00177	1.0309×10^6
50.0	46020	1720.21	0.0508	8.0431×10^6
			0.0333	5.2723×10^6
			0.0229	3.6257×10^6
			0.0159	2.5174×10^6
			0.00714	1.1305×10^6
60.0	4315	1952.20	0.508	8.5585×10^6
			0.333	5.6102×10^6
			0.229	3.8581×10^6
			0.159	2.6788×10^6
			0.109	1.8364×10^6
			0.0714	1.2029×10^6
			0.0508	8.5585×10^5
			0.0333	5.6102×10^5

Birefringence of LEKUTHERM X-30

T (°C)	η (P)	C_{br}	$\dot{\gamma}$ (sec^{-1})	$\Delta n \times 10^8$
<u>70.0</u>	742	1965.40	1.59	4.6375×10^6
			1.09	3.1792×10^6
			0.714	2.0825×10^6
			0.508	1.4817×10^6
			0.333	9.7125×10^5
			0.229	6.6791×10^5
			0.159	4.6375×10^5
<u>80.0</u>	190	1966.57	5.08	3.7962×10^6
			3.33	2.4885×10^6
			2.29	1.7113×10^6
			1.59	1.1882×10^6
			1.09	8.1455×10^5
			0.714	5.3357×10^5


Birefringence of LEKUTHERM X-30
30.0°C
32.0°C
35.0°C
37.0°C
40.0°C
45.0°C
50.0°C
60.0°C
Δn
10^8
10^7
10^6
10^5
0.00001
0.0001
0.001
0.01
0.1
1.0
RATE OF SHEAR (sec^{-1})


Birefringence of LEKUTHERM X-30
Δn
10^5
10^6
10^7
60.0°C
10.0°C
80.0°C
0.01
0.1
1.0
10
RAT OF SHEAR (sec^{-1})
NO. 340R-L33 DIETZGEN GRAPH PAPER
LOGARITHMIC
3 CYCLES X 3 CYCLES
DIETZGEN CORPORATION
MADE IN U.S.A.

D. Results and Discussion

The quantitative experimental data on various shear rates and temperatures of flow birefringence of Lekutherm x-30 was investigated. The cylinder I, large gap was employed. It has a constant of 4.32×10^{-8}. From the apparatus set up one can derive the equation of shear rate as the following:

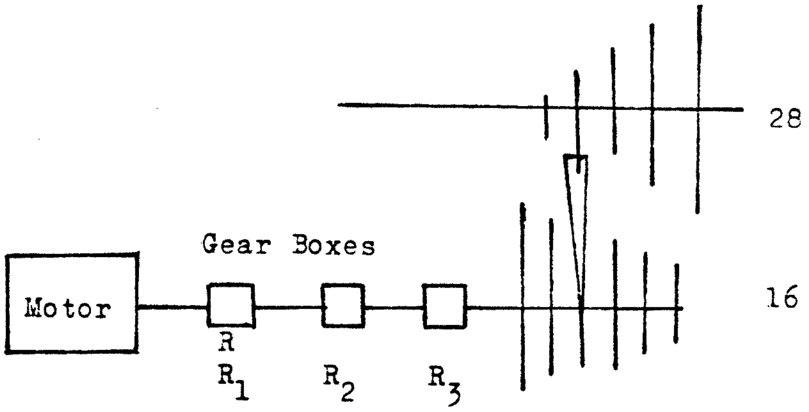
$$\dot{\gamma} = \frac{2\Omega}{1-C^2} \qquad \text{-----(1)}$$

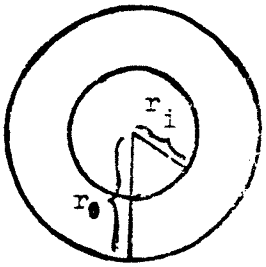
where Ω is radians per sec, hence

$$\dot{\gamma} = \frac{4\pi n}{60\,(1-C^2)} \qquad \text{-----(2)}$$

where n is revolution per min (RPM)

ratio of radii is $\frac{r_i}{r_\theta}$, RPM is $\frac{1800}{R_1R_2R_3}$





There are six steps equal on log plot in one decade of change in rate of shear by i gear boxes, and log plot equal spacing due to ratio of teeth (r = a ratio of teeth of gear box) on timing belt.

For birefringence in 1-2 plane equation shows:

$$\Delta n_{(1-2)} = \frac{\pi\lambda}{180} \times \frac{1}{L} (\ S'en) \qquad \text{------------(3)}$$

$$= K. (^{\circ}S'en) \qquad \text{------------(4)}$$

°Sen is the value of the angle read from the analyzer. K value is obtained from cylinder I, large gap.

Stress-optical coefficient, C_{br} is proportional to birefringence and the reciprocal of shear stress:

$$\text{Since } \tau = \dot{\gamma}\eta \qquad C_{br} = \frac{\Delta n_{(1-2)}}{2\tau} \qquad \text{-------------(5)}$$

$$\text{Hence} \qquad C_{br} = \frac{\Delta n_{(1-2)}}{2\dot{\gamma}\eta} \qquad \text{-------------(6)}$$

$$\text{From equation (4)} \quad C_{br} = \frac{K\ .\ (^{\circ}S'en)}{2\tau}$$

$$\text{For} \qquad 2\tau = 271.3 \quad \text{dynes/cm}^2$$

$$C_{br} = \frac{(4.32\text{x}10^{-8})\ (10^{13})\ (^{\circ}\ S'en)}{271.3}$$

$$= 1592\text{x}(^{\circ}S'en)$$

Where 10^{13} is the BREWSTER, Br unit.

Calculations of the stress-optical coefficient C_{br} from the experimental data is obtained in the following manner. The experimental values are obtained in the angle from the matching light intensity of the two fields (see VII. Description of Apparatus page 102. The angle is read from the analyzer in degrees and minutes (A° B').

Combine the degrees into minutes and divide by the shear rate, (the shear rate values from different settings and gear boxes are calculated, see page 119. This new value represented by M was multiplied by $\frac{K}{\text{min}} = \frac{4.32\text{x}10^{-8}}{60}$ $= 0.072$ and called M. M was then divided by two times the viscosity (2η) in order to obtain C_{br}. The simple construction is shown as the following:

$$A^{\circ}\ B' \longrightarrow D' \text{ --- } \frac{D}{\dot{\gamma}} \longrightarrow M(0.072) = M \qquad \text{(Maxwell Constant)}$$

$$M \longrightarrow \frac{M}{2\eta} = \quad C_{br}$$

For this experiment the lowest shear rate is $0.0000793\ \text{sec}^{-1}$ and the highest is $5.08\ \text{sec}^{-1}$. The temperatures obtained are 30, 32, 35, 37, 40, 45, 50, 60, 70 and 80 degrees centigrade. The graph of stress-optical coeficients, C_{br} V.S. temperatures were ploted on pages 127. For the higher temperatures at 60°C, 70°C and 80°C, the values of C_{br} are 1952.20, 1965.40 and 1966.57 respectively. These values are close to each other which shows that at these high temperature ranges the stress-optical coefficients have very little effect on temperature. Kuske and Zech had measured some of C_{br} values of Lekutherm x-30 resin and found that the liquid C_{br} value is 1960. This value is in the same range as my value. At the low temperatures the stress-optical coefficients have a great effect on temperature as the slope of the graph declines sharply. There is some doubt as to the accuracy of C_{br} values at low temperatures as compared to the Kuske and Zech values and 1:4 slit, 1:20 slit and the true values which were measured by Dr. W. Philippoff (see page 128. The

C_{br} values aae much higher than my values, especially those measured by Kuske and Zech. Generally it would be expected that the values measured by Dr. W. Philippoff that lie between the Kuske and Zech values and mine would be more accurate. This is because we do not know how Kuske and Zech did their measuring. My values at this low temperature range had many problems due to the inability of apparatus to perform well. Some of the experimental values at 30°C, 32°C and 35°C had to be eliminated because they were too small.

The birefringences $\Delta n_{(1-2)}$ were calculated from the experimental value of C_{br} as a function of shear rate and viscosity. The study shows that $\Delta n_{(1-2)}$ is proportional to shear rate and shear stres. The graph of $\Delta n_{(1-2)}$ V.S. shear rate is shown on pages 136 and 137.

Dr. W. Philippoff has done extensive research on birefringence in different planes. On his work with Gaskins and Brodnyan on the topic of "Flow Birefringence and Stress. V. Correlation of Recoverable Shear Strains with Other Rheological Properties of polymer Solutions", the results show that the principal axes of the tensors of stress, strain and optical anistropy coincide even when no constant shear modulus or viscosity (shear compliance) exists.[65]

There is still some doubt about the accuracy of values for measurement at low temperatures (as mentioned above). This is because of a variety of technological and mechanical problems. For example, with the temperature at 35°, the shear rate of 0.000121 and 0.0000793 could not be measured, this is because the values became quite large and took too much time to reach equilibrium. This was due to the apparatus set up. It took one hundred and thirty one and a half hours per one revolution for the machine to rotate, the calculation of hours came from:

$$\text{RPM} = \frac{1800}{\text{gear box}} \times (16{,}28 \text{ teeth on wheel for timing belt})$$

$$= \frac{1800}{810000} \times \frac{16}{28}$$

$$= 0.000127, \text{ RPM} = 7875 \quad \text{min/rev}$$

$$= 131\tfrac{1}{2} \quad \text{hrs/rev}$$

Sometimes the movement of turning the machine caused the measurement values to fluctuate. For example, I obtained one value too high and the other values too small. When this situation took place it was necessary to try to get a value in the middle range or use the average values. It usually occured at the low temperature range.

Another mechanical problem was the rubber belt. At times a solution came from the rubber belt and got between the connected gear, it caused a loosening of the belt (or took a long time for the belt to tighten). When checked, the angle of the back plate was too large, about 10 degrees instead of zero degrees. A metal belt will not cause such a problem.

When the reading of the measurement obtained are not in agreement, there is a possible need to check the zero point by plotting the graph of angle V.S. shear rate, (see pages 129 to 132). For example the new Zero point at 60°C had to be changed by minus two degrees. This was checked by setting the plate angle to Zero, then moving the front angle plate to a homogeneous intensity without the movement of the gear. If there is some angle shown at the front plate this angle is due to the stress of the material at low temperatures. To be free of stress the front plate angle should read at zero. Before accurate measurements are read the front plate angle has to come down to zero degrees, which is called free stress.

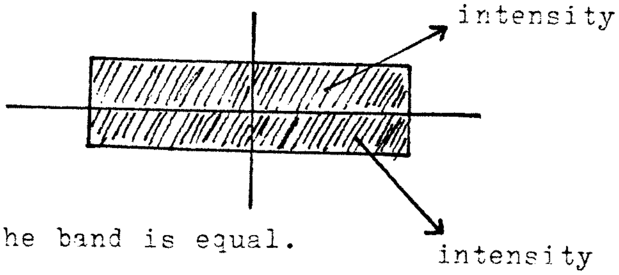
Low Temperature correction of the angle is derived as follows:

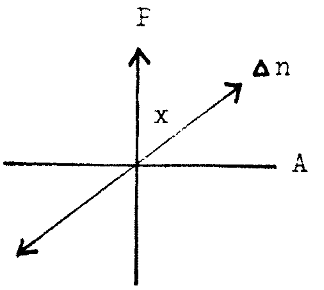
$$I = I_o \sin^2 2x$$

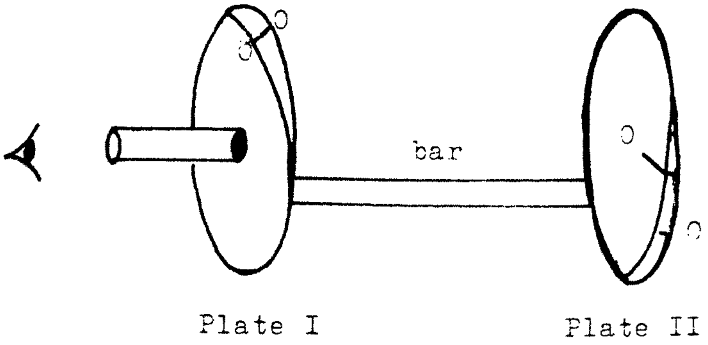
when $x = 45°$ is the maximum

let $x = 0°$ then $I = 0$

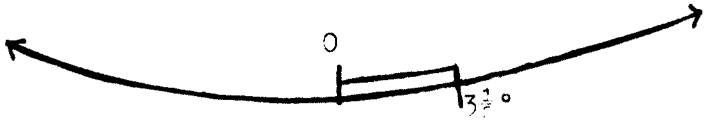
when $I = 0$, then the intensity of the band is equal.







Adjust the reading by adjusting the first plate reading to zero then loosen the bar and move the bar until the band has the same intensity. Then read from plate II to see how much the reading is off. For example the reading at plate II is 3° 30'.



For the left direction, move plate II to 45° + 3½° = 48½° and for the right direction move plate II to 45° -3½° = 41½°. After plate II is moved to the corrected position then lock the bar, the measurement can then be read as usual on plate I.

The window stress and the resin stress could cause some minor inaccuracy for the measurements. For example when setting plate II at 45°, the angle stress of the front plate should be zero but it was -20'. This negative result was due to the window stress. When setting plate II at 33°, plate I is read at 22', this also is caused by window stress but it is a small amount, as the calculation shows:

$$22'(\cos 66^{\circ}) = 0.41 \times 22 = 9'$$

when setting back plate II at 45°, front plate I will read at 9'.

The resin stress is shown in a similar manner by setting plate II at 45° and plate I read at -10, this can be caused from the stress of the resin. But in over all results these two stress problems may be considered minnor.

One of the other things which can give a major problem in the reading of measurement values is the unhomogeneous material. One can raise the temperature to a higher range if only slight cloudiness intensity appears, otherwise it needs to be refilled with new material.

Even though so many minor problems exist they can be eliminated by studying more about the machine and material behaviors and more so the mistakes of experience could help the researcher know how to get a better result.

In addition, there is a limitation of experiment which one may take into account as the following:

1. lower S'en
2. lower rate of shear available
3. long time to equilibrium
4. belt skipped at too high torque due to viscosity of sample

The significance of this research is that it was done in a range of low rate of shear and viscosity (up to 137.5 MP). It is different from anything in the field until now, where the limit before for melt ≈ 10^5 P viscosity.

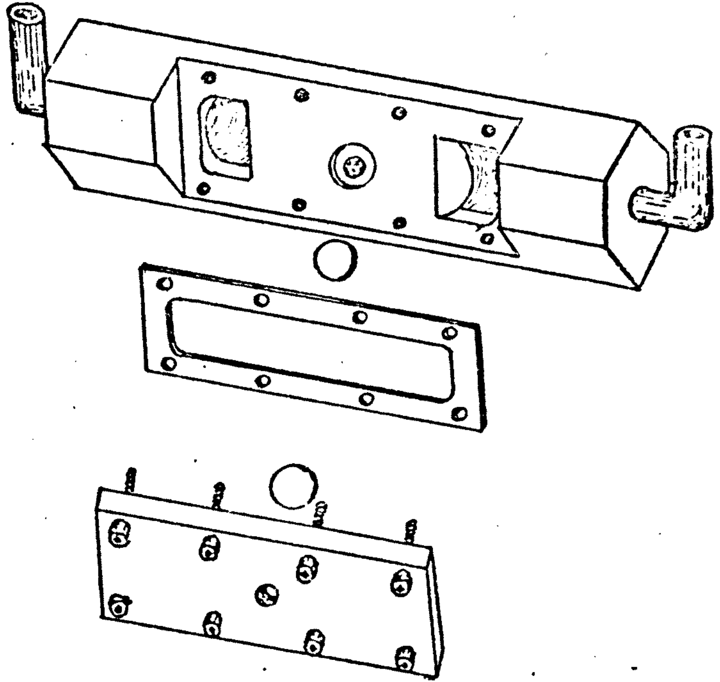
IX. $n_{11} - n_{33}$ REFRACTIVE INDEX DIFFERENCE

A. Refractive Index Difference $n_{11} - n_{33}$ Apparatus:

The apparatus is composed of a simple slit arrangement, which is made from stainless steel. Two thin glass windows similar to the one which is used in the concentric cylinder device are parts of the apparatus. One window is contained in the main body of the apparatus and the other window is contained in the slit which is determined by steel and brass spacers of known thickness. The slit is placed between a rigid stainless steel plate.

There are constructions of two different slits, one has the measurements of 2.54 centimeters in length, 1.27 centimeters in width, and 0.0635 centimeters in thickness. The other one has 2.54 centimeters in length, 1.27 centimeters in width and 0.127 centimeters in thickness. The apparatus contains no moving parts. The refractive index difference $n_{11} - n_{33}$ is measured by the fluid flowing horizontally in a plane perpendicular to the light beam.

The resin is supplied in the stainless steel vessel which is pressurized with nitrogen gas in various pressurized with nitrogen gas in various pressures up to 200 psig.



$n_{11} - n_{33}$ FLOW APPARATUS[66]

B. Refractive Index Difference $n_{11} - n_{33}$ Procedure

The epoxy (LEKUTHERM X-30) was applied in the refractive index difference $n_{11} - n_{33}$ apparatus for measuring. The variation of temperature permitted an evaluation of the temperature dependent which perform by stress varies with time upon the $n_{11} - n_{33}$ refractive index difference.

The apparatus is a single pass system where the resin is expelled in the chamber. The shearing can cause the heating effects, but it can be neglected for these short dimensions. Since the device has no provisions for constant temperature measurements, hence one has to conduct the experiment at room temperature.

The resin is contained in 0.050 inch gap which is pressurized by nitrogen gas. By timing the flow and knowing the viscosity, it is possible to measure the shear stress as a function of the gauge pressure.

The flow chamber was positioned perpendicular to the light beams for the optical orientation. The polarizer was set at a 90° angle which is a 45° angle to the direction of the flow. The readings were obtained from the Senarmont compensetor.

Data of $n_{11} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
Experiment 1				
22.7	0	0	- 6	0
$\eta \sim 0.63 \times 10^{10}$ p			- 8	10
			- 9	15
			- 6	30
			- 6	40
			- 6	60
			- 6	70
			Equilibrium point	
22.7	348000	200	- 2	0
			21	7
			25	15
			27	20
			40	30
			44	40
			49	55
			49	65
			48	73
			45	85
			40	90
			29	105
			27	115
			21	125
			9	144
			5	147

Data of $n_{11} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
Experiment 2				
21.5	0	0	- 16	0
$\eta \sim 14 \times 10^{10}$ P			- 20	10
			- 19	15
			- 18	30
			- 16	40
			- 16	60
			- 16	70
			- 16	80
			Equilibrium point	
21.5	348000	200	- 10	0
			18	5
			21	10
			25	20
			27	35
			41	55
			42	90
			50	115
			50	1
			47	170
			42	185
			38	200
			30	220
			26	245
			23	260
			20	275
			18	290

Data of $n_{11} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

T (°C)	τ $\frac{dynes}{cm^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
Experiment 3				
21.6	0	0	- 15	0
$\eta \sim 1.4 \times 10^{10}$ P			- 20	10
			- 19	15
			- 18	30
			- 16	40
			- 16	60
			- 16	70
			- 16	80
			Equilibrium point	
21.6	348000	200	- 15	0
			- 10	5
			- 9	12
			24	21
			27	35
			40	51
			50	77
			52	117
			18	229

Data of $n_{11}- n_{33}$ Refractive Index Difference of LEKUTHERM X-30

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
Experiment 4				
23.8	0	0	0	0
$\eta \sim 0.36 \times 10^{10}$			0	10
			1	15
			- 4	20
			1	30
			1	40
			1	50
		Equilibrium pt.	1	60
23.8	348000	200	60	0
			70	8
			70	13
			42	18
			25	33
			20	43
			9	63
			3	73
			0	82
			- 5	97
			-6.5	108
			- 9	148
			- 9	163
			-10	193
			-10	250
			-10	275
		Equilibrium pt.	-10	300

Data of $n_{11} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
<u>Experiment 5</u>				
<u>22.8</u>	0	0	- 10	0
η 1.2 x 10^{10} P			- 58	3
			- 67	5
			- 86	10
			- 77	15
			- 70	20
			- 58	30
			- 40	40
			- 30	50
			- 23	70
			- 10	165
			- 10	195
			- 10	210
			- 10	225

Calculations

Experiment #4

T = 23.8°C, Viscosity = 0.36×10^{10} P

τ = 348000 dynes/cm^2

C_{cr} = 421.43 cm^2/dynes (extrapolated value from this researc

C_{br} = 680 cm^2/dynes (from true value)

At P = 0 psi, equilibrium angle = 1 min

At P = 200 psi, equilibrium angle = -10 min

The difference effect of angle = 1 - (-10) = 11 min

$$\Delta n_{(1-3)} = 12 \times 10^{-8} \times \text{S'en}$$

$$= 12 \times 10^{-8}\ (\text{min}^{-1}) \times 11\ \text{min}$$

$$= 132 \times 10^{-8}$$

$$\Delta n_{(1-2)} = 2 \times \tau \times C_{br} \times 10^{-13}$$

$$= 2 \times 348000 \times 421.43 \times 10^{-13}$$

$$= 2933 \times 10^{-8}$$

$$\%\ \text{ratio} = \frac{\Delta n_{(1-3)}}{\Delta n_{(1-2)}} \times 100$$

$$= \frac{132 \times 10^{-8}}{2933 \times 10^{-8}} \times 100$$

$$= 4.5\%$$

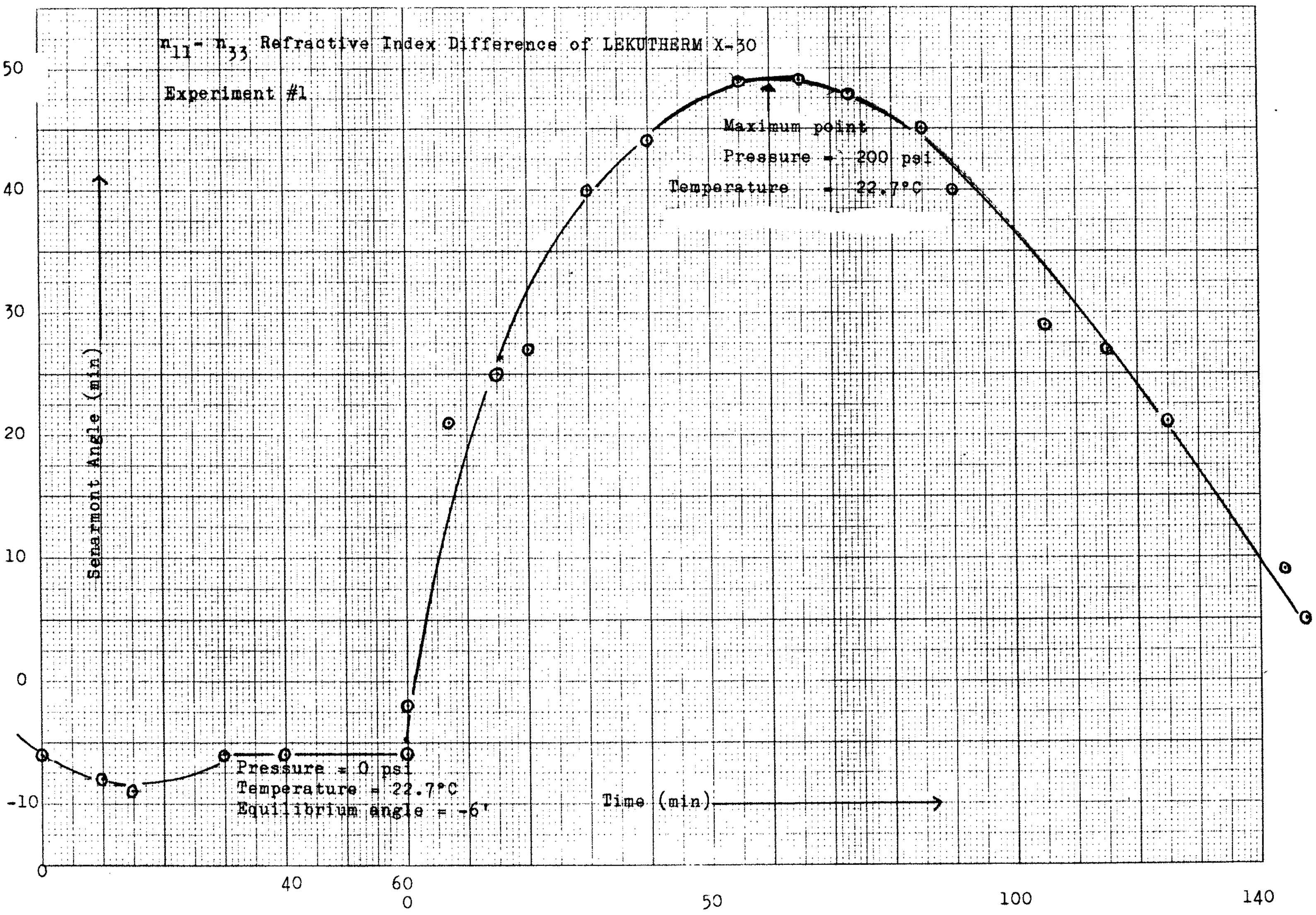
For C_{br} - true value

$$\Delta n_{(1-2)} = 2 \times 348000 \times 680 \times 10^{-13}$$

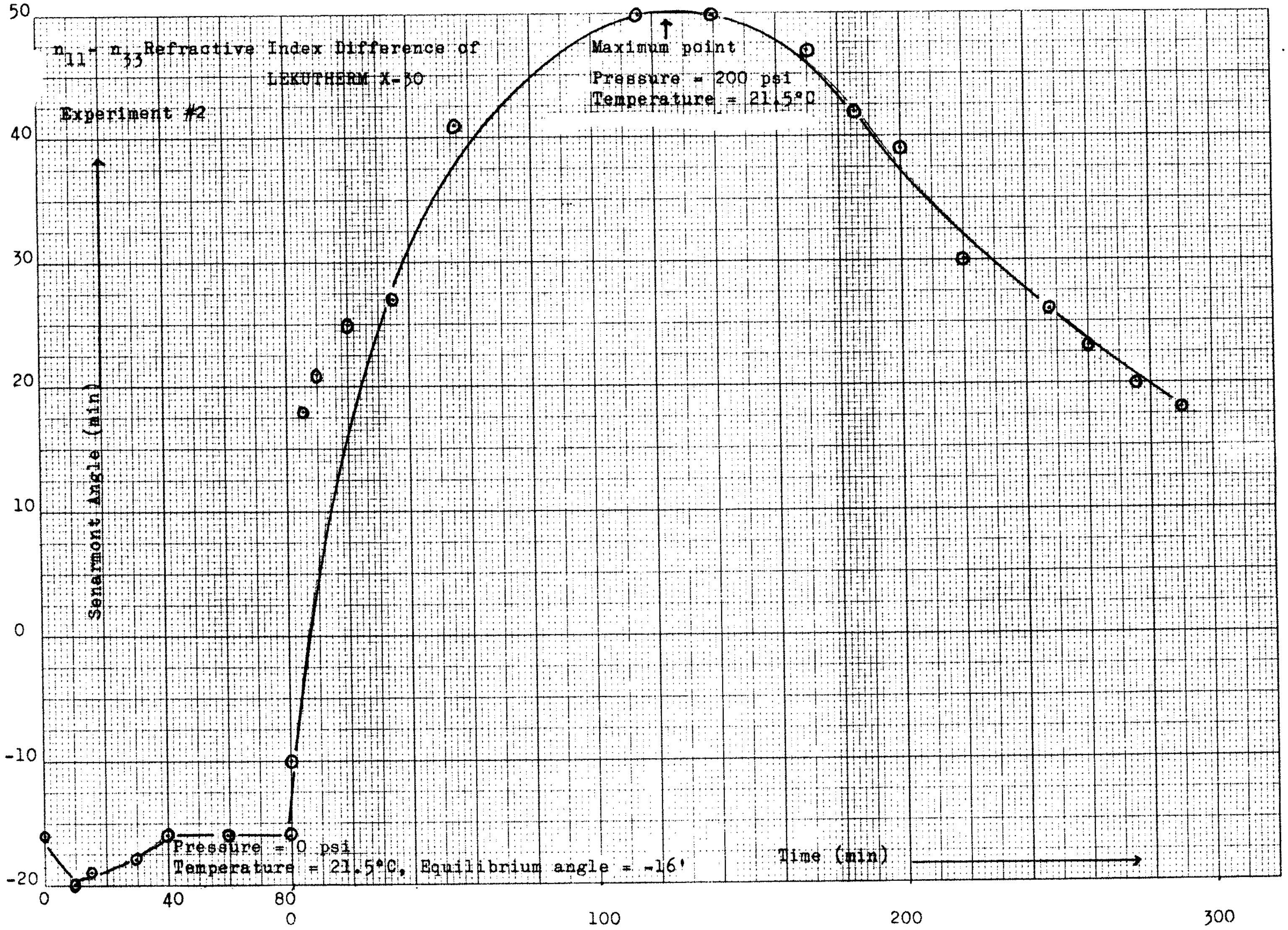
$$= 4733 \times 10^{-8}$$

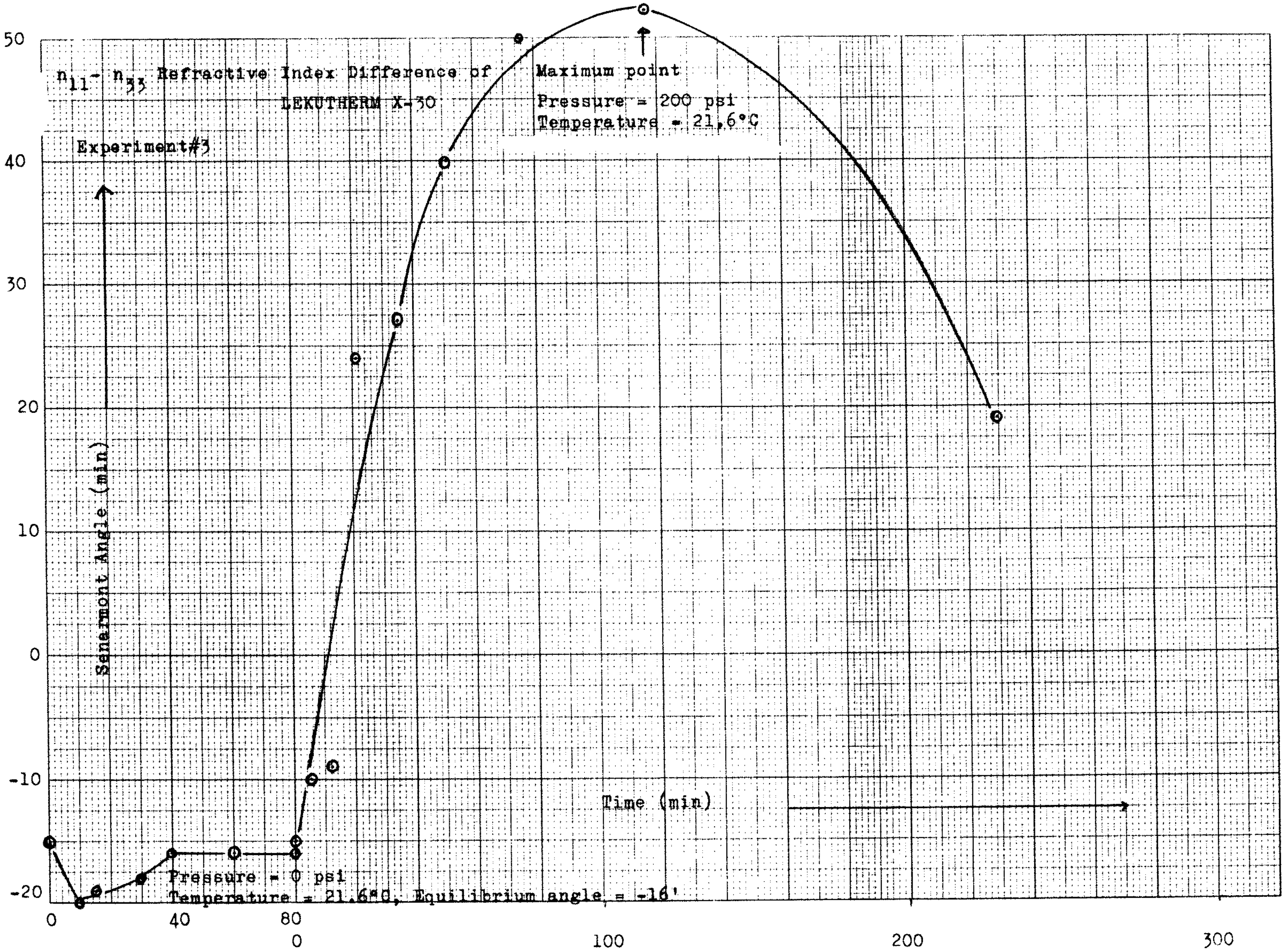
$$\%\ \text{ratio} = \frac{132 \times 10^{-8}}{4733 \times 10^{-8}} \times 100$$

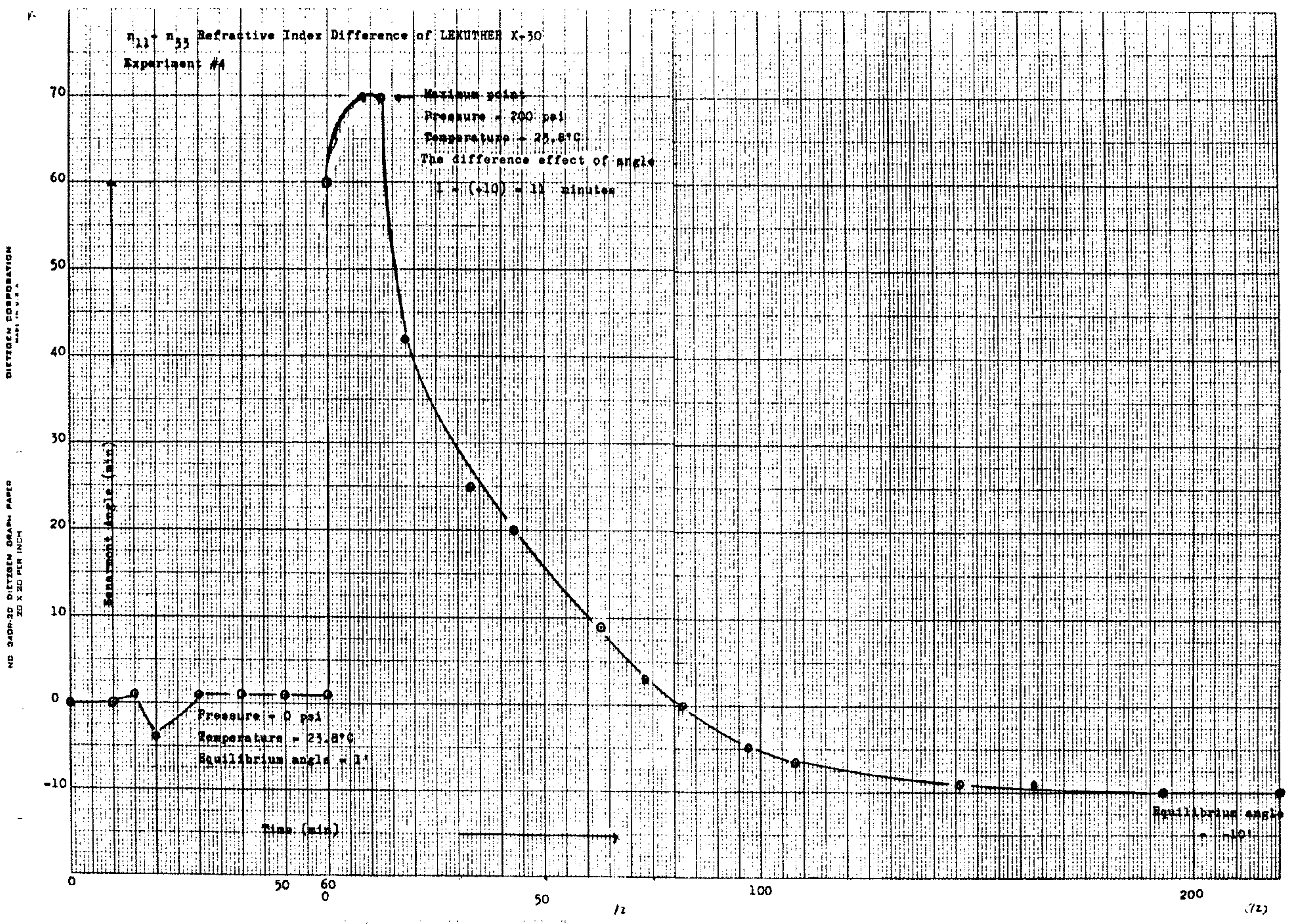
$$= 2.8\ \%$$


$n_{11} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

Experiment #1


$n_{11} - n_{33}$ Refractive Index Difference of
LEKUTHERM X-30
Experiment #2
Maximum point
Pressure = 200 psi
Temperature = 21.5°C
Senarmont Angle (min)
Pressure = 0 psi
Temperature = 21.5°C, Equilibrium angle = -16'
Time (min)
50
40
30
20
10
0
-10
-20
0
40
80
0
100
200
300


n11 - n33 Refractive Index Difference of
LEKUTHERM X-30
Experiment#3
Maximum point
Pressure = 200 psi
Temperature = 21.6°C
Pressure = 0 psi
Temperature = 21.6°C, Equilibrium angle = -16'
Senarmont Angle (min)
Time (min)
50
40
30
20
10
0
-10
-20
0
40
80
0
100
200
300


$n_{11} - n_{33}$ Refractive Index Difference of LEKUTHER X-30
Experiment #4
Maximum point
Pressure = 200 psi
Temperature = 23.8°C
The difference effect of angle
1 - (-10) = 11 minutes
Pressure = 0 psi
Temperature = 23.8°C
Equilibrium angle = 1'
Equilibrium angle
= -10'
Time (min)
Senarmont Angle (min)
70
60
50
40
30
20
10
0
-10
0
50
60
0
50
100
200
DIETZGEN CORPORATION
NO 340R-20 DIETZGEN GRAPH PAPER
20 X 20 PER INCH

C. $n_{11}- n_{33}$ Results and Discussion

Experiment#1, T = 22.7°C

pressure = 0, equilibrium angle = -6 min.

pressure = 200 psi, maximum angle = 49 min.

Experiment#2, T = 21.5°C

pressure = 0, equilibrium angle = -16 min.

pressure = 200 psi, maximum angle = 50 min.

Experiment#3, T = 21.6°C

pressure =0, equilibrium angle = -16 min.

pressure = 200 psi, maximum angle = 52 min.

Experiment#4, T = 23.8°C

pressure = 0, equilibrium angle = 1 min.

pressure = 200 psi, maximum angle = 70 min, and equilibrium angle =-10

For this experiment, one observes the stress that varia with time, which it is very dependent and sensitive with temperature as the results show above, and also see graph of angle (S'en) versus time in varable temperatures.

The temperature dependent for this particular material also shows in the equilibrium angle, as experiment#1,2 and 4 show different values.

For a positive value of the $n_{11}- n_{33}$ refractive index difference is refered as a newtonian liquid,which has the equation as follows:

$$(n_{11}- n_{33})_w = C\,\tau_w^2 / G$$

The values are derived from

$$(n_{11}- n_{33})_w = 3\lambda\, Sn^\circ / 180d$$

where λ is the wavelength of th light, 0.546×10^{-4} cm. Sn is the Senarmont angle in degree, and d is the gap. This equation can be reduced to the simple equation as follows:

$$n_{11}- n_{33} = K\ S'en$$

where S'en is the Senarmont angle in minutes, and $K = 23.9 \times 10^{-8}$ min^{-1} for small gap, 0.025 in., and 11.95×10^{-8} min^{-1} for large gap, 0.050 in.

There is only one calculation of $\Delta n_{(1-3)}$ of Lekutherm x-30 from the experiment #4 where the equilibrium angles were obtained. The viscosity was lowest at the higher temperature allowing an equilibrium in observable time. For the room temperature at 23.8°C and the pressure at zero, psi the equilibrium angle was 1 minute, and the pressure at 200 psi the equilibrium angle was -10 minutes. The $n_{11} - n_{33}$ refractive index was 132×10^{-8}. The percentage ratio were 4.5% and 2.8%, where the 2.8% was calculated from C_{br}-true value. For this particular value, one can see that $\Delta n_{(1-2)}$ value is much larger than $\Delta n_{(1-3)}$ value. Theoretically, $P_{11} - P_{22} = N_1$ and $P_{11} - P_{33} = N_1$ and the values which were measured by J. L. S. Wales and W. Philippoff with the material LDPE, found that the values of $\Delta n_{(1-2)}$ with the cone-and-plate agreed with $\Delta n_{(1-3)}$ values of the measurements obtained from slits.[67] But there was still doubt about the accuracy of these experimental values which I measured because the temperature was lower than 32°C and the viscosity could not be measured accurately. This especially applies to Lekutherm x-30 resin which was highly temperature dependant and the material had a very high viscosity at low temperatures. $\Delta n_{(1-2)}$ and $\Delta n_{(1-3)}$ obtained values from the extrapolated values of both viscosity and C_{br}. Therefore the accuracy of the values for this experiment are in doubt. These reasons could possibly cause the values of $\Delta n_{(1-3)}$ and $\Delta n_{(1-2)}$ to have such large differences among them.

CHECK VALUES FOR MODULUS

Shear stress (τ) = 348,000 dynes/cm^2

From 1-3 Plane

$$\frac{\Delta n_{(1-3)}}{\Delta n_{(1-2)}} = 0.028 \qquad \text{(True value of } C_{br}\text{)}$$

At 23°C

$$S = 2 \times 0.028 = 0.056$$

$$G = \frac{\tau}{S} = \frac{348000}{0.056} = 6.2 \times 10^6 \quad \text{dynes/cm}^2$$

τ_{max} in ROTATIONAL INSTRUMENT BRF = 24,000 dynes/cm^2

$$S_{max} = \frac{24000}{6.2\text{x}10^6} = 0.387\text{x}10^{-2}$$

$$= 0.00387$$

$$2 \cot 2x = 0.00387$$

$$\cot 2x = 0.00193$$

$$\tan 2x = 518$$

$$2x = 89.98°$$

$$x = 44.94°$$

x = 44° 56' -------- ± 30' accuracy (below sensitivity)

At 40°C, G = 1.0x10^6 -------- from recoil measurement

$$S_{max} = \frac{24000}{1\text{x}10^6} = 0.024$$

$$\cot 2x = 0.012$$

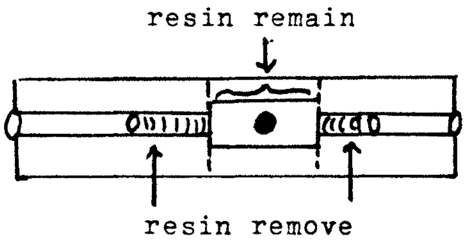
$\tan 2x$ = 83.33 ---- $2x$ = 89.31° --- x = 44.66°

x = 44° 39' (±30') -- Immeasurable at 30°C due to difficulty of measurement

One cannot measure an extinction angle accurately because it is beyond the sensitivity of an instrument. But the order and magnitude is shown to be corrected.

Recommendations

I had to change to a new resin because bubbles appeared on the window. It is probably caused by leaving the pressure on over the weekend. The pressure pushed the resin out. It is quite difficult to fill the device with resin. The best way to do this is to heat the resin for half an hour to about 200°C. The large and small bubbles will come to the surface of the resin and then some will disappear. Next, cool the resin for 10 minutes. This helps to remove some bubbles, and allows some dirt in the resin to sink to the bottom of the container. After this is done, pour the resin into the device; be carefull to avoid getting bubbies into the window glass area. Pour the resin a little above the content, excluding the removal area. The result is the removal of resin from both sides of the middle section. This is done because all the pressure should be concentrated on the middle area where the measurement is taken. If resin remains in both sides the pressure will include these areas causing a lose of pressure. The device needs to be completely full for the liquid material.



After pouring the resin into the device, heat the device for a few minutes and close the device by putting the top on it. Be sure that both windows of the device are clean. Measurement takes place when the resin and the device cools to room temperature.

Be as carefull as possible in filling the device with resin. I still get unhomogeneous material. There are still some dark areas at the window. This is due to the window not being clean enough and the material being unhomogeneous. If this has occured the material can be refilled again or the experiment can continue by ignoring those dark areas while reading the values.

X. $n_{22} - n_{33}$ REFRACTIVE INDEX DIFFERENCE

A. Refractive index difference n_{22} - n_{33} Apparatus:

A simple slit arrangement is constructed for a device used in the refractive index difference $n_{22} - n_{33}$. In this experiment the direction of flow corresponds exactly with the light beam. The apparatus consists of a 2.54 centimeter diameter stainless steel cylinder with a length of 4.36 centimeters. The measurement of the slit is 2.54 centimeters in length, 0.8 centimeters in width and 0.0735 centimeters in thickness. Two glass windows of 0.37 centimeters thickness are located on either end of the cylinder. They are mounted within a brass holder and this is in turn clamped to the cylinder. Very high shear stresses can be conducted, which depends on the thickness of the windows and the limitations of the pressure vessel.

B. Refractive Index Difference $n_{22} - n_{33}$ Procedure:

The epoxy resin (LEKUTHERM X-30) was employed for measuring the refractive index difference $n_{22} - n_{33}$. The variation of temperature and pressures were applied. The evaluation of the temperature dependent which performs by stress varies with time upon the refractive index difference $n_{22} - n_{33}$ were obtained.

The procedure for obtaining the flow rate calibrations and the pressure shear stress relationship for the $n_{22} - n_{33}$ device is identical to that of the $n_{11} - n_{33}$ device. In this situation the refractive index difference $n_{22} - n_{33}$ was derived from the equation as follows:

$$n_{22} - n_{33} = \frac{\lambda\ S}{180 \times l}$$

where l equals the length of the slit of 2.54 centimeters. The final equation is reduced to

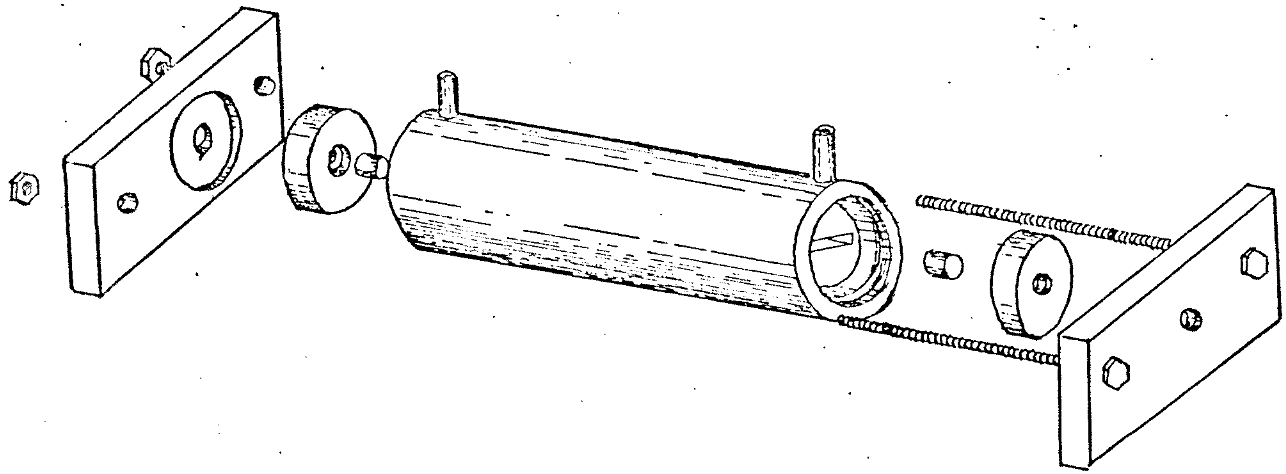
$$n_{22} - n_{33} = K\ S'n$$

where $K = 1.99 \times 10^{-9}\ \text{min}^{-1}$. In this case the shear stress ranges from 0 to 250,000 dynes/cm^2.

$$n_{22} - n_{33} = \frac{S' \cdot \lambda}{180 \times 60 \times 2.54} = 1.99 \times 10^{-9}(\text{min } Se'n)$$

68

n_{22}-n_{33} BIREFRINGENCE DEVICE



Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

Experiment 1

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
24.44	0	0	40	0
			40	5
			40	10
			40	20
24.44	200000	200	- 130	5
			- 200	30
	250000	250	- 200	35
			- 200	40
	0	0	40After release the pressure	
$\eta = 0.25 \times 10^{10}$ P				
Experiment 2				
22.9	0	0	40	0
			40	10
			40	30
			40	40
22.9	250000	250	150	0
			240	7
			245	12.5
$\eta = 0.63 \times 10^{10}$ P			249	15
			270	35
			278	45
			300	60
			280	84
			280	98
			280	106
23.0	150000	150	200	0
			210	5

Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

Experiment 3

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
23.0	0	0	600	0
$\eta = 0.63 \times 10^{10}$ P			540	15
			480	20
			540	30
			570	35
Experiment 4				
23.0	0	0	940	0
			940	10
			945	20
23.65	200000	200	- 20	0
$\eta = 0.60 \times 10^{10}$ P			- 90	10
			-120	20
			- 70	35
			- 30	45
			0	65
Experiment 5				
22.75	0	0	280	0
$\eta = 0.67 \times 10^{10}$ P			325	6
			300	15
			310	25
			280	35
23.1	0	0	270	40
			243	48
			224	60
			170	93
			170	110
			170	120
			167	140

Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

Experiment 6

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
23.7	0	0	120	0
$\eta = 0.60 \times 10^{10}$ P			86	4
			80	11
			80	33
			160	60
			167	73
			150	83
			140	100
			110	114
			110	140
			110	160
Experiment 7				
22.8	0	0	140	18 hrs
22.8	200000	200	- 90	0
$\eta = 0.63 \times 10^{10}$ P			- 220	4
			- 250	7
			- 292	20
			- 330	38
			- 318	50
			- 296	60
			- 276	70
			- 250	90
			- 230	105
			- 170	130
			- 70	170
			- 20	185
			- 25	200
			40	210

Data of $n_{22}- n_{33}$ Refractive Index Difference of LEKUTHERM X-30

Experiment 7 (continue)

T (°C)	$\frac{dynes}{cm^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
23.4	200000	200	66	220
$\eta = 0.80 \times 10^{10}$ P			80	230
			100	240
			120	250
			130	260
			140	275
			150	290
			155	300
			160	310
			160	325
			160	335
			160	350
Experiment 8				
23.0	200000	200	160	350 + 18 hrs
$\eta = 0.67 \times 10^{10}$ P			160	355 + " "
			160	365 + " "
			160	380 + " "
			160	400 + " "

Turn off the pressure and release nitrogen out of the device, and start reading the angle immediate.

T (°C)	$\frac{dynes}{cm^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
23.0	0	0	390	0
			520	5
			440	10
			360	25
			340	35
			320	45
			310	55
			300	65

Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30
Experiment 8 (continue)

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
23.5	0	0	290	90
			290	100
			290	115
			290	135
23.8	0	0	290	150
Close the valve and put pressure on				
23.8	200000	200	30	0
$\eta = 0.40 \times 10^{10}$			- 70	2
			- 10	5
			60	14
			80	20
			110	30
			140	48
			150	60
			160	80
			160	90
			160	100
			160	125
24.0	0	0	410	0
			740	2
			520	4
			486	8
			445	18
			390	40
			367	60
			360	68
			335	100

Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

Experiment 8 (continue)

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
24.0	0	0	305	200
			298	250
			290	325
			290	350
			290	400
27.5	0	0	290	400 + 66 hrs
$\eta = 0.05 \times 10^{10}$ P			290	410 + " "
			290	430 + " "
			290	450 + " "

Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30 Difference pressures are applied to investigate that there is any pressure effect.

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
Experiment #9				
27.5	150,000	150	- 20	0
$\eta = 0.05 \times 10^{10}$ P			10	2
			110	5
			170	10
			190	17
			190	23
			190	40
			190	50
			190	75
27.4	0	0	530	0
			380	2
			330	8
			300	15
			290	25
			280	35
			280	50
			280	75
			280	100

T = 27.5°C, P = 150 PSI, Equilibrium angle = 190 min.

T = 27.4°C, P = 0 PSI, Equilibrium angle = 280 min.

The difference of effect = 280 - 190 = 90 min.

Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
Experiment #10				
24.6	100,000	100	- 110	0
$\eta = 0.25 \times 10^{10}$ P			- 80	2
			- 10	5
			20	10
			80	15
			90	20
			115	30
			140	40
			150	60
			150	70
			150	80
24.75	0	0	320	0
			280	3
			230	6
			210	10
			200	20
			190	30
			190	40
			190	50

T = 24.6°C, P = 100 PSI, Equilibrium angle = 150 min.

T = 24.75°C, P = 0 PSI, Equilibrium angle = 190 min.

The difference of effect = 190 - 150 = 40 min.

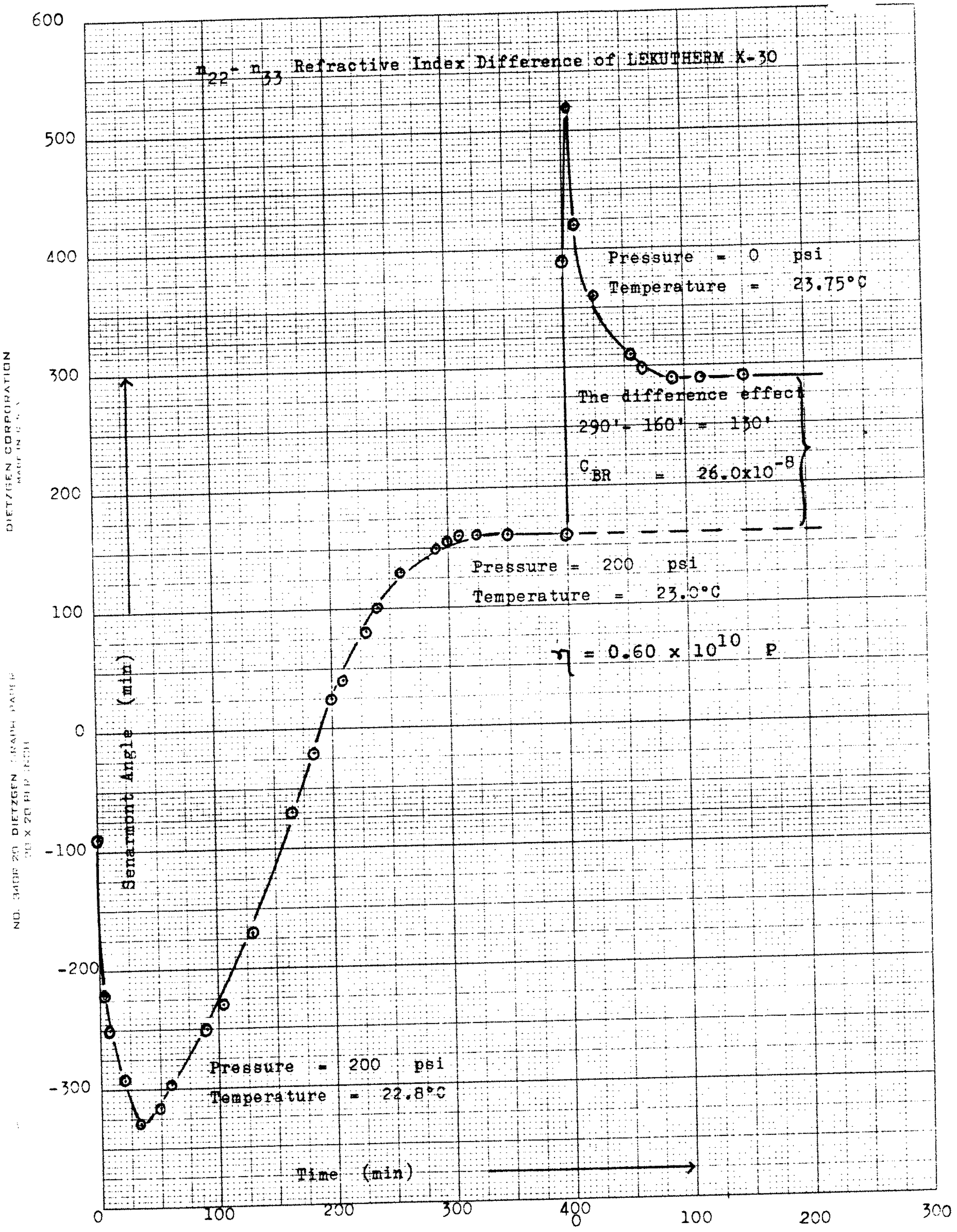
Data of $n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30

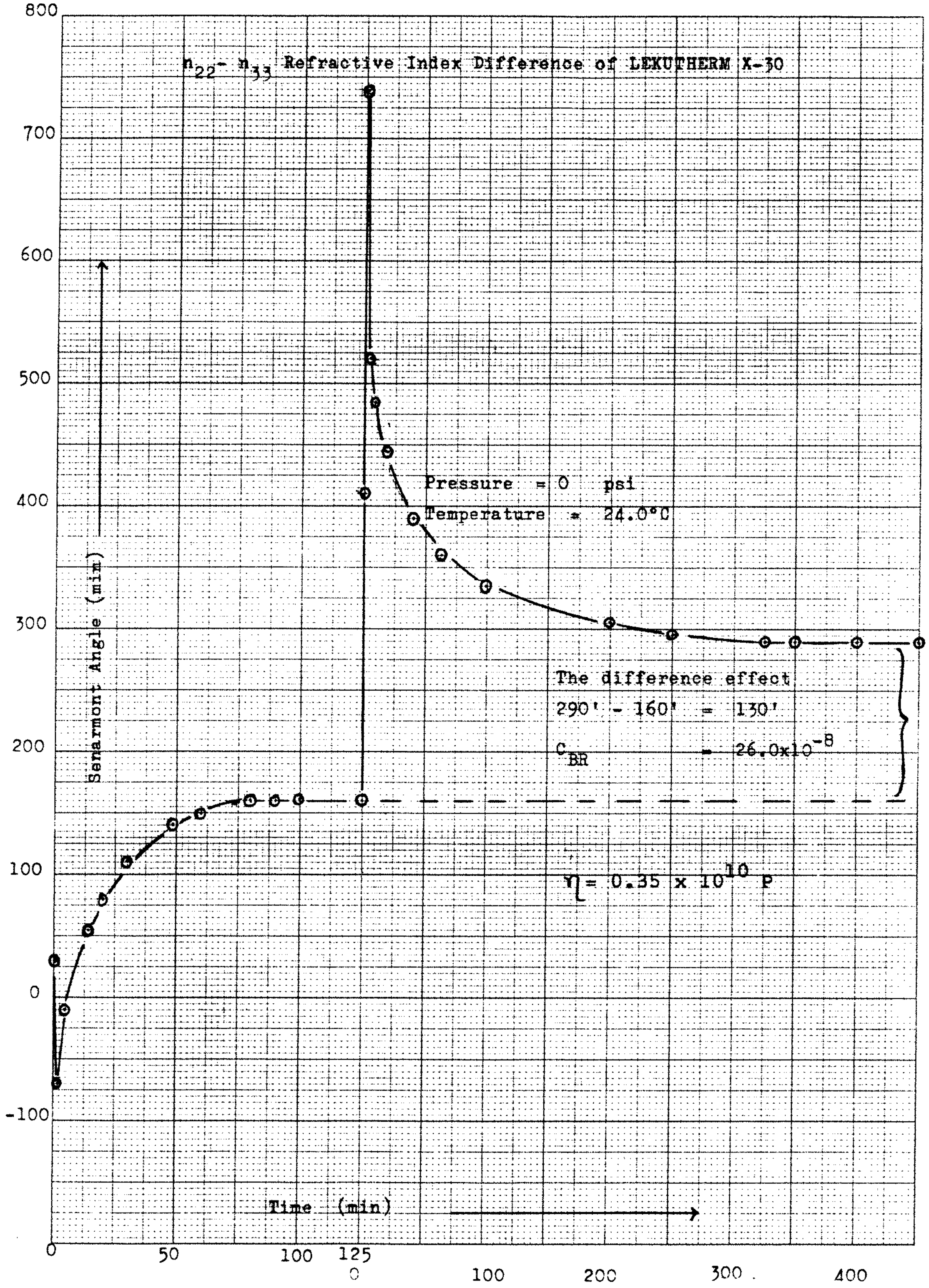
T (°C)	τ $\frac{\text{dynes}}{\text{cm}^2}$	Pressure (PSI)	Senarmont Angle(min)	Time (min)
<u>Experiment #11</u>				
24.9	0	0	520	0
			570	2
			410	5
			340	8
			300	15
			290	20
			260	30
			250	40
			250	70
			250	80
25.2	250,000	250	- 180	0
$\eta = 0.20 \times 10^{10}$ P			- 240	2
			- 80	5
			- 10	8
			20	15
			30	20
			50	30
			65	40
			80	50
			80	60
			80	70

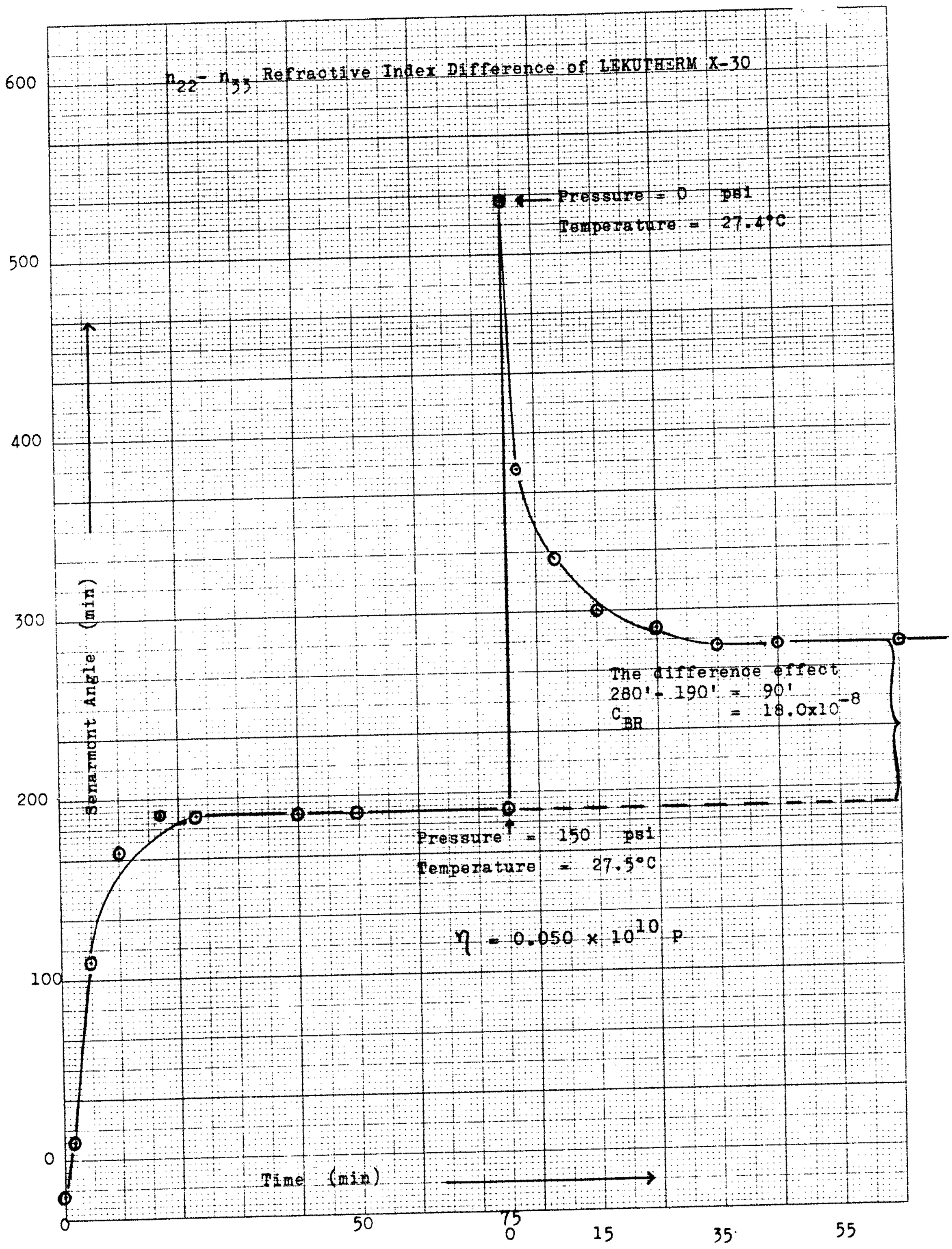
T = 24.9°C, P = 0 PSI, Equilibrium angle = 250 min.

T = 25.2°C, P = 250 PSI, Equilibrium angle = 80 min.

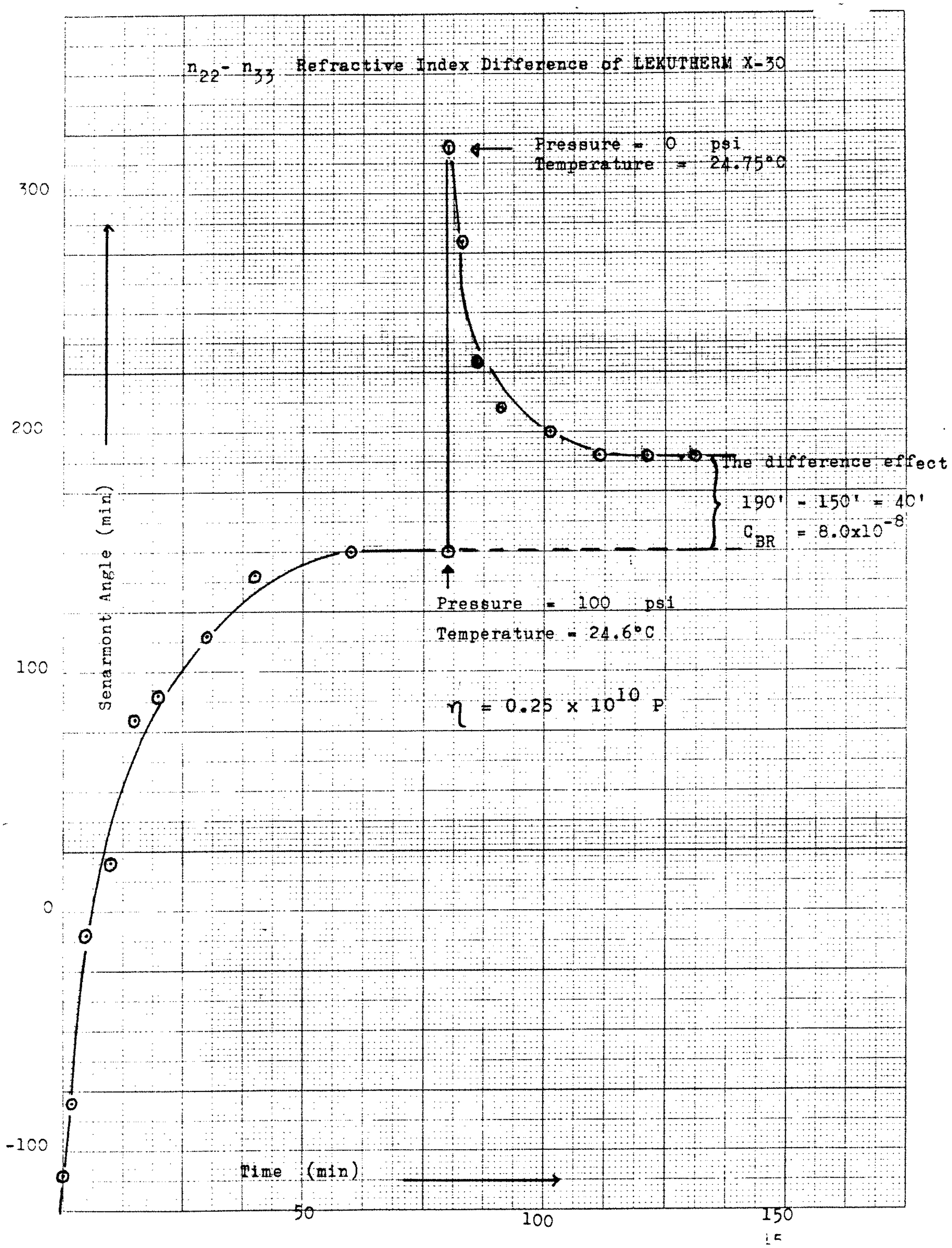
The difference of effect = 250 - 80 = 170 min.

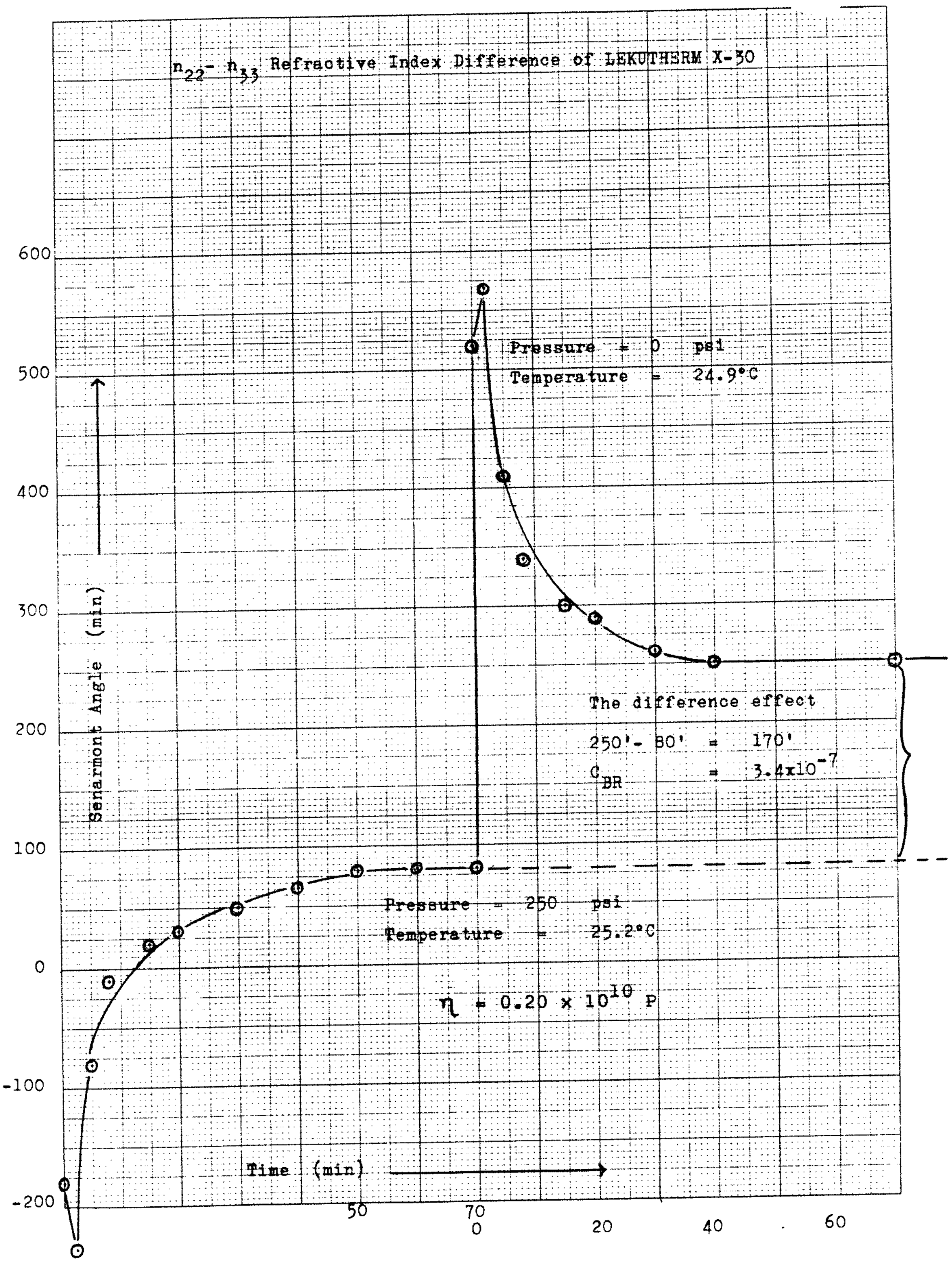

$n_{22}-n_{33}$ Refractive Index Difference of LEKUTHERM X-30
Pressure = 0 psi
Temperature = 23.75°C
The difference effect
290' - 160' = 130'
C_{BR} = 26.0x10^{-8}
Pressure = 200 psi
Temperature = 23.0°C
η = 0.60 x 10^{10} P
Pressure = 200 psi
Temperature = 22.8°C
Senarmont Angle (min)
Time (min)
600
500
400
300
200
100
0
-100
-200
-300
0
100
200
300
400
0
100
200
300
DIETZGEN CORPORATION
MADE IN U.S.A.
NO. 340R-20 DIETZGEN GRAPH PAPER
20 X 20 PER INCH


$n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30
Senarmont Angle (min)
Time (min)
Pressure = 0 psi
Temperature = 24.0°C
The difference effect
290' - 160' = 130'
C_{BR} = 26.0×10^{-8}
$\eta = 0.35 \times 10^{10}$ P
800
700
600
500
400
300
200
100
0
-100
0
50
100
125
0
100
200
300
400



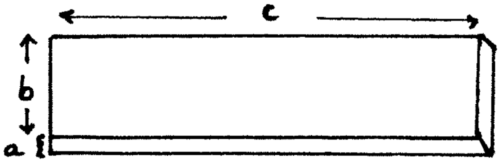
n22 - n33 Refractive Index Difference of LEKUTHERM X-30
600
500
400
300
200
100
0
Senarmont Angle (min)
Pressure = 0 psi
Temperature = 27.4°C
The difference effect
280' - 190' = 90'
CBR = 18.0x10-8
Pressure = 150 psi
Temperature = 27.5°C
η = 0.050 x 10^10 P
Time (min)
0
50
75
0
15
35
55


n_{22}- n_{33} Refractive Index Difference of LEKUTHERM X-30
Pressure = 0 psi
Temperature = 24.75°C
The difference effect
190' - 150' = 40'
C_{BR} = 8.0x10^{-8}
Pressure = 100 psi
Temperature = 24.6°C
η = 0.25 x 10^{10} P
Senarmont Angle (min)
300
200
100
0
-100
Time (min)
50
100
150


$n_{22} - n_{33}$ Refractive Index Difference of LEKUTHERM X-30
Pressure = 0 psi
Temperature = 24.9°C
The difference effect
250' - 80' = 170'
C_{BR} = 3.4×10^{-7}
Pressure = 250 psi
Temperature = 25.2°C
$\eta = 0.20 \times 10^{10}$ P
Senarmont Angle (min)
Time (min)
600
500
400
300
200
100
0
-100
-200
50
70
0
20
40
60

C. Results

Slit for 2-3 Plane



$a = 0.735$ mm.

$b = 8.000$ mm.

$c = 2.54$ mm.

$b/a = 10.9$

$\tau = 193\ h_{H_a}$ in $\frac{\text{dynes}}{\text{cm}^2}$

$\tau = 13.6 \times 981 \times h \times \frac{0.0735}{5.080}$ for Hg

$= 193\ h$

PSI $= 5.715$ cm Hg

$\tau = 193 \times 5.1715$

1000 PSI $= 69{,}000 \times \frac{a}{2c} = 69{,}000 \times \frac{0.0735}{5.080} = 998.33 \sim 1000$

100 PSI; $\tau = 100{,}000$ dynes/cm^2

150 PSI; $\tau = 150{,}000$ "

200 PSI; $\tau = 200{,}000$ "

250 PSI; $\tau = 250{,}000$ "

Calculations:

For P = 250 PSI, The difference effect = 170 min.

$\Delta n_{(2-3)} = 0.200 \times S'en \times 10^{-8}$

$= 0.200 \times 170 \times 10^{-8} = 34 \times 10^{-8}$

$= 3.4 \times 10^{-7}$

At T = 25.2°C; C_{br} from 1:4 slit

$C_{br} = 765$ cm^2/dynes, Viscosity = 0.20×10^{10} P

$\Delta n_{(1-2)} = 2 \times \tau \times C_{br} \times 10^{-13}$

$= 2 \times 250{,}000 \times 765.00 \times 10^{-13}$

$= 1.53 \times 10^{-5}$

% ratio $= \frac{34 \times 10^{-8}}{1.53 \times 10^{-5}} \times (100)$

$= 0.52\%$

At 24°C; $C_{br} = 750\ \mathrm{cm}^2/\mathrm{dynes}$ (from 1:4 slit), Viscosity $\eta = 0.35\mathrm{x}10^{10}\mathrm{P}$

$$\Delta n_{(1-2)} = 2 \times 200{,}000 \times 750.0 \times 10^{-13}$$
$$= 3.0\mathrm{x}10^{-5}$$

For P = 200 PSI; The difference effect = 130 min.

$$\Delta n_{(2-3)} = 0.200 \times 130 \times 10^{-8}$$
$$= 26.0 \times 10^{-8}$$
$$\%\ \text{ratio} = \frac{26.0 \times 10^{-8}}{3.0 \times 10^{-5}}(100)$$
$$= 0.87\%$$

At 27.4°C; $C_{br} = 865\ \mathrm{cm}^2/\mathrm{dynes}$ (from 1:4 slit), Viscosity $\eta = 0.05\mathrm{x}10^{10}\mathrm{P}$

$$\Delta n_{(1-2)} = 2 \times 150{,}000 \times 865.0 \times 10^{-13}$$
$$= 2.60\mathrm{x}10^{-5}$$

For P = 150; The difference effect = 90 min.

$$\Delta n_{(2-3)} = 0.200 \times 90 \times 10^{-8}$$
$$= 18 \times 10^{-8}$$
$$\%\ \text{ratio} = \frac{18 \times 10^{-8}}{2.6 \times 10^{-5}}(100)$$
$$= 0.69\%$$

At 24.75°C; $C_{br} = 765\ \mathrm{cm}^2/\mathrm{dynes}$ (from 1:4 slit), Viscosity $\eta = 0.25\mathrm{x}10^{10}\mathrm{P}$

$$\Delta n_{(1-2)} = 2 \times 100{,}000 \times 765.0 \times 10^{-13}$$
$$= 1.53\mathrm{x}10^{-5}$$

For P = 100; The difference effect = 40 min.

$$\Delta n_{(2-3)} = 0.200 \times 40 \times 10^{-8}$$
$$= 8.0 \times 10^{-8}$$
$$\%\ \text{ratio} = \frac{8.0 \times 10^{-8}}{1.53 \times 10^{-5}}(100)$$
$$= 0.52\%$$

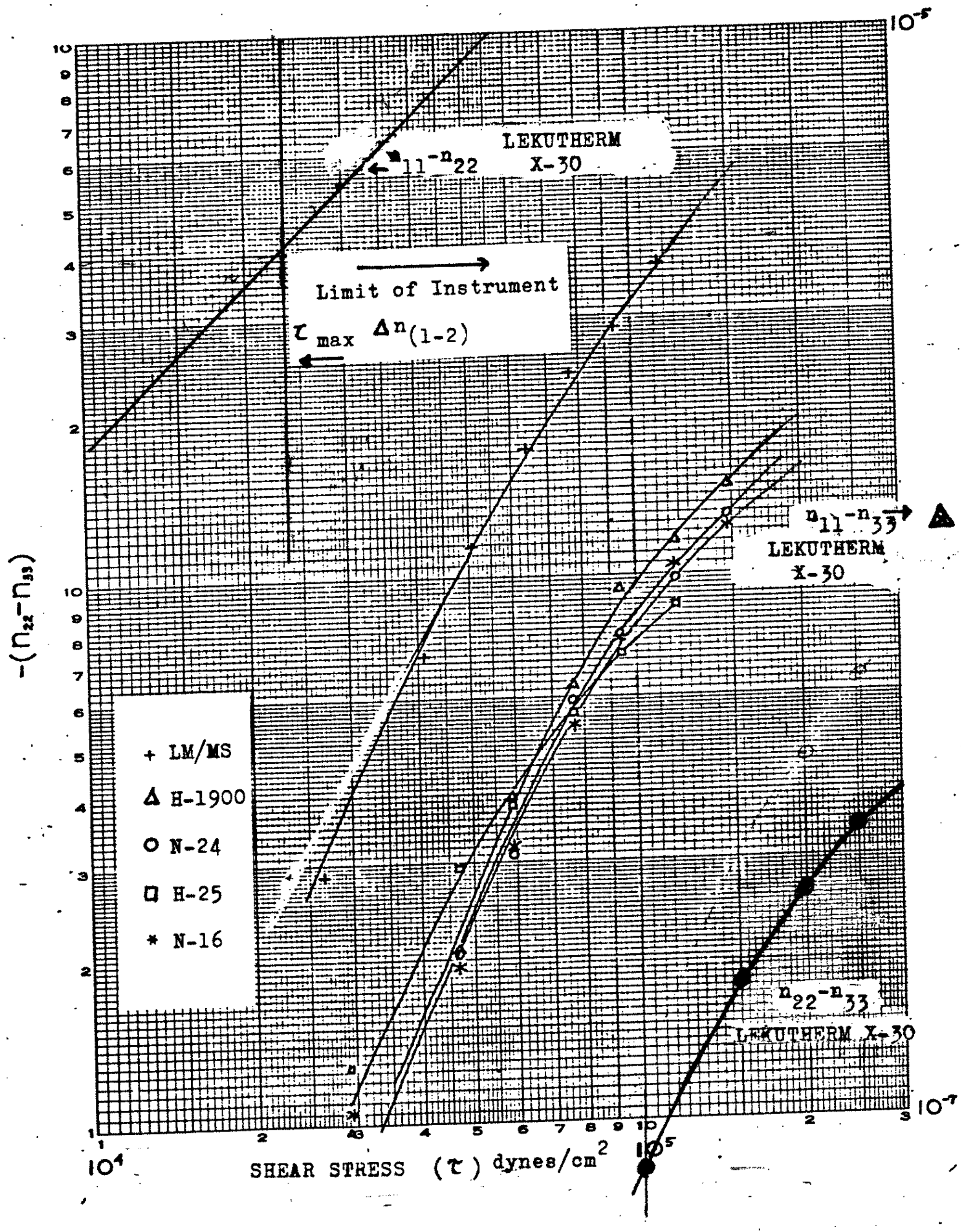
Some of the experiments were not in equilibrium , and the maximun angles were very sensitive to temperature change, for example:

* T = 23.65°C, P = 200 PSI
Maximum angle = - 120 min.
* T = 22.00°C; P = 200 PSI
Maximum angle = - 330 min.
* T = 23.8°C, P = 200 PSI
Maximum angle = - 70 min.
* T = 23.0°C, P = 0
Maximum angle = 520 min.
* T = 24.0°C P = 0
Maximum angle = 740 min.

For graph #1 ---- T = 22.8°C, P =200 PSI, Equilibrium angle = 160 min.
T = 23.75°C, P= 0 PSI, Equilibrium angle = 290 min.
The difference of effect = 290 - 160 = 130 min.
For graph #2 ---- T = 23.8°C, P = 200 PSI, Equilibrium angle = 160 min.
T = 24.0°C, P = 0 PSI, Equilibrium angle = 290 min.
The difference of effect = 290 - 160 = 130 min.
Graph #1 and #2 have the same effect, 130 min.

Notice that at low temperature, for example at temperature 22.8°C and 23.6°C when put pressure on the shape of maximum point is broad, but at higher temperature, for example at the temperature 23.8°C, the maximum point is sharp.

τ_w (dynes/cm^2)	Pressure (PSI)	$\Delta n_{(1-2)}$	$\Delta n_{(2-3)}$	% $\frac{\Delta n_{(2-3)}}{\Delta n_{(1-2)}}$
100000	100	1.53×10^{-5}	8.0×10^{-8}	0.52
150000	150	2.60×10^{-5}	18.0×10^{-8}	0.69
200000	200	3.00×10^{-5}	26.0×10^{-8}	0.87
250000	250	3.88×10^{-5}	3.4×10^{-7}	0.86


$n_{11}-n_{22}$ LEKUTHERM X-30
Limit of Instrument
τ_{max} $\Delta n_{(1-2)}$
$n_{11}-n_{33}$ LEKUTHERM X-30
$n_{22}-n_{33}$ LEKUTHERM X-30
+ LM/MS
Δ H-1900
O N-24
◻ H-25
* N-16
$-(n_{22}-n_{33})$
SHEAR STRESS (τ) dynes/cm^2
10^4
10^5
10^{-6}
10^{-7}
1
2
3
4
5
6
7
8
9
10

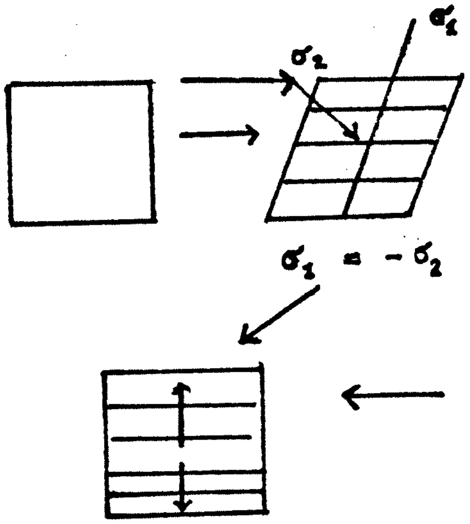
Disscussion

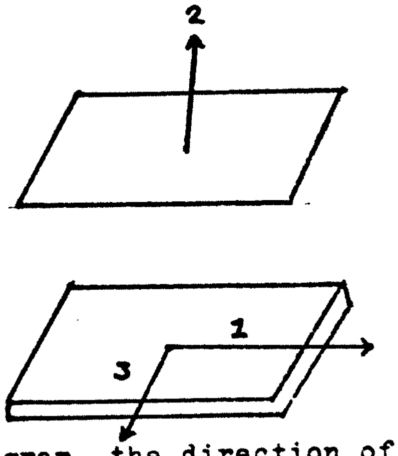
From this experiment one can see that the birefringence is in the 2-3 planes are very small, less than one percent of $\Delta n_{(1-2)}$. Percent ratio is high at higher pressure and lower at lower pressure.

Graph of $n_{22} - n_{33}$ refractive index difference, birefringence versus shear stres is slightly curved, it is not a straight line. But the shape of the curve is the same as the experiment from other materials, as Biss had done in (see page 186). It is roughly proportional to τ^2. This proves that there is a definite effect of birefringence in 2-3 plane.

In general $P_{11} - P_{22} = N_1$, $P_{22} - P_{33} = 0$. But for the Newtonian liquid $P_{22} - P_{33}$ is not zero, there is some effect.

The diagram of 3 plane 1, 2, and 3 and when the pressure is applied:





For this diagram, the direction of two arrows will cancel out, which give the result zero. But in the reality is not zero. There is some effect as the results show in this experiment.

From these birefringence experiments, one can see that the polymer melts in steady lamina flow occuring not only in the usual refractive index difference, $\Delta n_{(1-2)}$, but also in normal refractive index differences, $\Delta n_{(i-i)}$ in three directions in space. There is an extensive research that has been done on birefringence in the 1-2 and 1-3 planes, but very little is known about birefringence in the 2-3 plane. "The Anisotropy of Simple Shearing Flow", was investigated by J. L. S. Wales and W. Philippoff.[69] Their research on birefringence in plane 2-3 of various materials discovered that the effect of $\Delta n_{(2-3)}$ is 5 to 10% of $\Delta n_{(1-2)}$. It is exhibited in Newtonian fluids more than in non-Newtonian fluids. There was also an investigation that proved the effect of $\Delta n_{(2-3)}$ takes place only at high shear stresses and not necessarily at high Δn values. These results from different investigations haae shown to be in contradiction to the general stress-optical theories. However it is not known what causes the effect of birefringence in the 2-3 plane.

D. Recommedations

If the zero point angle shows the reading to fluctuate greatly, this indicates that the point of equilibrium was not yet reached. However, if one tries to put 40 PSI of pressure into the device the angle can then be read. If there is no change in angle, this implies that at low pressure there is no effect. For the device used in this experiment, a higher pressure is needed. The pressure should be 250 PSI in order to get the effect.

Another problem in doing this type of experiment is achieving a homogeneous material. If the material is not homogeneous then one cannot get the correct values or read the angle. If it is a minor problem, the device can be heated with a low flame, then cooled to room temperature before reading the angle. If the entire area of light from which the reading value is taken is slightly cloudy, it means that most of the material is not homogeneous. Therefore, the resin must be removed and new resin substituted.

The bubbles in the device cause a similar problem to that of cloudiness in an unhomogeneous material. When there are lots of bubbles at the window, it makes it very difficult to read the value. It should therefore be refilled. If only a few bubbles appear, heating the resin will solve the problem. Filling the n_{22} - n_{22} device with resin is much more difficult than filling the n_{11} - n_{33} device, and it takes a longer time to operate.

An additional problem with this apparatus was the effect of internal strain on the windows because they are much thicker. The windows can be positioned so that the effects cancel one another out. The orientation can be checked by applying pressure to the chamber without flow, hence the effects can be recorded. This value can then be used to subtract from the measurement of birefringence.

XI. CONCLUSION

Lekutherm x-30 was proven to have transient properties as follows:

1. It behaves like Newtonian liquid at low temperatures and at high temperatures it has some non-Newtonian characteristics.
2. The viscosity of Lekutherm x-30 is very dependent on temperature. It has a wide range of viscosity and has the highest viscosity measurement ever taken.
3. The stress-optical coefficients of Lekutherm x-30 were evaluated and found to be very sensitive at low temperatures but it almost became independent at high temperatures.
4. Lekutherm x-30 had an effect on birefringence in all three planes.
5. The glass-transition temperature of Lekutherm x-30 is about $284^{o}K$.
6. The composition of the compound is not known as it is a manufacturing secret.
7. Over all the experiment values are quite accurate considering the wide range of measurements up to millions or 10^6 scale.

REFERENCES

1. Billmeyer, Jr., Fred W., *Textbook of Polymer Science*, New York: John Wiley and Sons, Inc., 1971 p. 185, 186, 187, 188.

2. Ibid., p. 191.

3. Ibid., p. 185.

3. Eirich, Frederick R., Rheology: *Theory and Application*, New York: Academic Press Inc., 1956. p. 2.

4. Op. cit., Billmeyer, Jr., Fred W., p. 199

6. Ibid., p. 202, 203.

7. Ibid., p. 207, 208.

8. Severs, Edward T., *Rheology of Polymers*, New York: Reinhold Publishing Corporation. 1962. p. 1.

9. Philippoff, W., Gaskins, F. H. and Brodnyn, J. G., *Flow Birefringence and Stress V. Correlation or Recoverable Shear Strains With Other Rheological Propperties of Polymer Solutions,* Journal of Applied Physics, Vol. 28, No. 10. 1957.

10. Vinogradov, G. V. and Belkin, I. M., *Elastic, Strength, and Viscous Properties of Polymer Melts*, Journal of Polymer Science, Part A Vol. e. 1965. p. 917-932

11. Huppler, J. D., MacDonald, I. F., Ashare, E., Springgs T. W., Bird, R. B. and Holmes, L. A. *Rheological Properties of Three Solutions, Part II. Relaxation and Growth of Shear and Normal Stresses. Transactions of the Society of Rheology*, Vol. 11: 12. 1967 p. 181-204.

12. Trapeznikov, A. A. and Pylaeva, A. T. *Structural Changes In Concentrated Solutions of Polyisobutene*. Vysokomol Soedin., Ser. A, 12 (6). 1970 p. 294-370

13. Chen, I-Jen and Bogue, D. C., *Time Dependent Stress In Polymer Melts and Review of Viscoelastic Theory*. Transactions of the Society of Rheology, Vol. 16:1, 1972. p. 59-78.

14. Goldstein, G., *Transient and Steady Shear Behavior of SBR Polymers*, Vol. 18, Issue 3. 1974 p. 347-369

15. Zwetkow, Nikolans., Transient Phenomena of Polymer Solution. Masters Thesis of Science in Chemical Engineering, New Jersey Institute of Technology, Newark, New Jersey. 1975. p. 14, 18.

16. Lodge, A. S., Elastic Liquids, London: Academic Press Inc. 1964. p. 202.

17. Op. cit., Zwetkow, Nikolans. p. 19

18. Ibid., p. 17

19. Ibid., p. 15

20. Ibid., p. 16

21. Ibid., p. 18, 20

22. Ibid., p. 25, 27

23. Ibid., p. 26

24. Ibid., p. 27, 28

25. Ibid., p. 29

26. Ibid., p. 30, 32, 33

27. Ibid., p. 31

28. Ibid., p. 37

29. Ibid., p. 36, 38, 39

30. Dentsch, K., Hoff, E. A. W. and Reddish, W., Journal of Polymer Science, Vol. 13. 1954. p. 165.

31. Heyboer, J., Dekking, P., Staverman, A. J., Proc. 2nd Intern. Congress Rheology. London: Butterworth's Ltd. 1954. p. 123

32. Tobolsky, A. V. and McLoughlin, J. R., Journal of Polymer Science, Vol. 8. 1952. p. 543.

33. Ferry, J. D., THIS JOURNAL, 72, 3746 (1959); Ferry, J. D., Grandine, L. D. Jr., and Fitzgerald, E. R., Journal of Applied Physic, Vol. 24. 1953. p. 911.

34. Leaderman, H., Smith, R. G. and Jones, W. W., Journal of Polymer Science., Vol. 14. 1954. p. 47.

35. Ferry, J. D., Fitzgerald, E. R., Journal of Colloid Science, 8, 224 (1953); Ferry, J. D., Williams, M. L. and Fitzgerald, E. R., Journal of Physical

Chemistry, Vol. 59. 1955. p. 403.

36. Rouse, P. E. Jr., Journal of Chemistry Physic, Vol. 21. 1953. p. 1272

37. Bueche, F., Journal of Chemistry Physic, Vol. 22. 1954. p. 603

38. Vogel, H., Physik Z., Vol. 22. 1921. p. 645.

39. Tammann, G. and Hesse, W., Z. anorg. allgem. Chem., Vol. 156. 1926. p. 499

40. Conant, F. S., Hall, G. L. and Lyons, W. J., Journal of Applied Physic, Vol. 21. 1950. p. 245.

41. Williams, M. L., Landel, R. F. and Ferry, J. D., Journal of Applied Physic, Vol. 22. 1951. p. 717.

42. Op. cit., Zwetkow, Nikolans. p. 22.

43. Ibid., p. 23.

44. Ibid., p. 24.

45. Op. cit., Zwetkow, Nikolans. p. 35, 59, 60.

46. Davison, D. W. and Cole, R. H., Journal of Chemistry Physic, Vol. 19. 1951. p. 1484.

47. Op. cit., Zwetkow, Nikolans.

48. Mooney, M and Ewart, R. H., The conicylindrical Viscometer, Physic. Vol. 5. 1934. p. 350

49. Philippoff, W. and Gaskins, F. H., Instrumentation for the Rheological Investigation of Viscoelastic Materials, Journal of Applied Polymer Science. Vol. 2. 1959. p. 143.

50. Ferry John D., Viscoelastic Properties of Polymers, New York: John Wiley and Sons, Inc., 1961, p. 213.

51. Fesko D. G. and Tschoegl N. W., Time-Temperature Superposition in Styrene/Butadiene/Styrene Block Copolymers, Intern. J. Polymeric Mater., 1974 Vol. 3, p. 59

52. Ibid., p. 75.

53. Ibid., p. 65.

54. Philippoff, W., "Present State of Rheology Theory", Esso Research and Engineering Co., Linden, 1970.

55. Wayland "Streaming Birefringence as a Rheological Research Tool" Rheo-optics of Polymers, ed. R. Stein, New York: Inter-science Pub., 1964

56. Kundt, A., Wied. Ann. 13 (1881) P. 110

57. Philippoff, W., "Determination of the Anisotropy of Bond Polarizability of Liquids Using Flow Birefringence Measurements", Journal of Applied Physics, Vol. 31, No. 11, Nov. 1960, p. 1899-1906.

58. Jerrard, H. G., "Theories of Streaming Double Refraction" Chemical Reviews, 59 (1959) p. 355.

59. Signer, R. and Gross, H., Z. Pysik Chemistry, (A) 165 161 (1933)

60. Kuhn, W. and Grun, F., Journal of Polymer Science, Vol. 1 No. 3 (1946) p. 183-199.

61. Lodge A. S., "Variation of Flow Birefringence with Stress", Nature, 176, (1955) p. 838.

62. Lodge A. S., "A Network Theory of Flow Birefringence and and Stress in Concentrated Polymer Solutions", Trans. Faraday Soc. 52, (1956) p. 120.

63. Biss, Russel B. Rheo-Optical Properties of Polyisobutynene, Master Thesis of Science in Chemical Engineering, New Jersey Institute of Technology, 1974. p. 14.

64. Ibid., p. 16.

65. Op. cit., Philippoff, W., Gaskins, Frederick H. and Brodnyan, John G., p. 1118.

66. Op. cit., Biss, Russel B., p. 19.

67. Philippoff, W., and Wales, J. L. S., The Anistotropy of Simple Shearing Flow, Rheol. Acta 12, 1973. p. 29.

68. Op. cite., Biss, Russel B., p. 19.

69. Op. cite., Philippoff, W., and Wales, J. L. S., p. 30.

ABSTRACT (PART II)

Aniline-formaldehyde, and aniline-phenol-formaldehyde (copolymer) resins were made by condensation polymerizations. These resins are formed as linear polymers for the purpose of drawing fibers by melt spinning. Then these fibers were cured in a specific curing liquor to form crosslinked fibers.

Aniline-formaldehyde fiber is of a primary interest for research. It is made by the reaction of aniline and formaldehyde in a proportion of 3:2 with about 8% of oxalic acid as a catalyst. For the curing liquor, it was discovered that ammonium hydroxide is the best catalyst for crosslinking the aniline-formaldehyde fiber. The best proportion of formaldehyde is about 89% and ammonuim hydroxide is about 11% which is about 8:1 by volume.

Aniline-phenol-formaldehyde resin, copolymer ratio is 2:1 (two moles of aniline and one mole phenol). 2/3 mole of aniline and 1/3 mole of phenol react with 0.8 moles of formaldehyde with about 4% of oxalic acid. The curing solution contains 20% ammonium hydroxide solution and 80% formaldehyde solution by volume. The solubility properties of uncared and cured aniline-formaldehyde fibers were determined.

The resins and crosslinked fibers were examined by IR and NMR. The most important part of this study is the tensile strengths test. Each step of the crosslink reaction was determined. The improved curing solution and procedure

was predicted. A device to measure the fiber strength was built by the author.

TABLE OF CONTENTS

I. INTRODUCTION

Historical Development of Synthetic Fibers and Their Chemical Reactions

Synthetic fibers are fibers made from combinations of many simple chemical units forming large molecules whose physical properties permit them to be drawn into a fiber or filament. They are different from man-made fibers which are derived from cellulose such as rayons and acetates, or protein origin. In fiber made by man, the chemical nature of cellulose or protein has been changed only slightly.

The significance of synthetic fiber lies in the physical shape of the fiber and the molecular size of the polymer. Various general types of research must be carried out in order to make commercially successful textile material from a new form of polymer fiber.

Some Examples of Synthetic Fibers

Nylon

Forming substance is any long chain synthetic polyamide having recurring amide groups as an integral part of the polymer chain. Nylon was the first of the synthetic fibers. In 1928, Dr. Wallace H. Carothers researched the fundamentals of the polymerization processes.

The principal type of nylon in the United States is designated as Nylon 66 and is so described because both the dibasic acid (adipic acid) and diamine (hexamethylene diamine) contains six carbon atoms.

$HOOC(CH_2)_4COOH+H_2N(CH_2)_6NH_2 \longrightarrow HOOC(CH_2)_4COHN(CH_2)_6NH_2+H_2O$

adipic acid hexamethylene diamine

Then two molecules of the dimer would give:

$HOOC(CH_2)_4COHN(CH_2)_6NHOC(CH_2)_4OCNH(CH_2)_6NH_2$

One of the many chemical by-products which can be made from coal is this adipic acid. During the process, ammonia is used, and one of the ways of making ammonia is by a combination of nitrogen of the air and hydrogen which one might consider as being produced from water. Thus the coal, air and water concept is a rather general and inexact statement of origin. The diamine may also be synthesized from corn husks, bran, and other cereal waste.

Manufacturers of Nylon

Company	Fiber Generic Name	Trade Name	Type Available
Allied Chemical Corp.	Nylon (6)	Caprolan	F
American Enka Corp.	Nylon (6)		F M
Beaunit Fibers, Div. Beaunit Mills, Inc.	Nylon (6)		F
Chemstrand Co.	Nylon (66)	Cumuloft	F M
		Cadon	F
			F
Dawbarn Brother, Inc.	Nylon (66)		F M
E. I. Du Pont De Nemours & Co.	Nylon (66)		F S T M
		Antron	F
Firestone Synthetic Fibers Co.	Nylon (6) & (66)		F M
National Wire & Plastic Co.	Nylon (6)		M

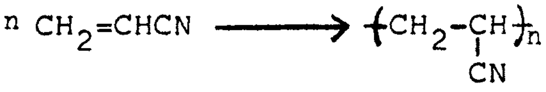
Acrylic Fibers

An acrylic is defined by the Federal Trade Commission for Textile Fiber Products Identification Act, as "A manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85 percent by weight of acrylonitrile units $\left(CH_2-\underset{\displaystyle CN}{\underset{|}{C}}H\right)$".

Acrylonitrile is a basic monomer also for another group of fibers. These are the modacrylics and differ from acrylics in the amount of acrylonitrile contained therein.

Orlon

The chemical reaction of this addition polymerization reaction takes place as follows:



$$n\ CH_2{=}CHCN \longrightarrow \left(CH_2-\underset{\displaystyle CN}{\underset{|}{C}}H\right)_n$$

acrylonitrile orlon acrylic polymer

Similar to orlon are two fibers produced in Germany and widely used throughout the new Common Market area. These are Pam and Dralon.

Modacrylics

Several interesting fibers with unique uses are classified under the generic name of modacrylics. The federal Trade Commission Rules defined the modacrylic as, "a manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of less than 85, but at least 35 percent by weight of acrylonitrile units $(-CH_2-\underset{CN}{CH}-)$". These, then, are copolymers in which acrylonitrile cōpolymers in which acrylonitrile may be the minor instead of the major monomer component.

Dynel

In 1949, Dynel came on the market in considerable quantities two years later, and is a product of the Union Carbide Chemical company, a division of the Union carbide Corporation. It has been marketed only in staple yarn form.

The chemical nature of Dynel is fairly well established as a copolymer of vinyl chloride $(CH_2=CHCl)$ and acrylonitrile $(CH_2=\underset{CN}{CH})$. The proportions are roughly 60-40 and the polymerization is carried out in much the same manner as that of acrylics, with catalyst and actual polymerization conditions being trade secrets.

Polyester Fibers

A polyester has been defined by the FTC in its administration of the Textile Fiber Products Identification Act as "a manufactured fiber in which the fiber-forming substance is any long-chain synthetic polymer composed of at least 85 percent by weight of a dihydric alcohol and terephthalic acid $(HOOC-C_6H_4-COOH)$."

Dacron

Dacron is a polyester; an ester is formed by reacting an acid with an alcohol. The raw material of principle consequence is ethylene, which is obtained from petroleum. Ethylene is oxidized to a glycol - a dihydric - which is then heated with terephthalic acid in vacuum at a high temperature to produce polyethylene terephthalate.

Fortrel

Fortrel is a copolymer of ethylene glycol and dimethyl terephthalate. Thus, the reaction monomer, as in terylene, is methyl ester rather than the acid itself. In the condensation reaction, they are very similar to Dacron, both for filament and tow or staple.

Polyethylene and Polypropylene

Polyethylene is produced by the British firm, the ICI, Ltd. Velon LP by Firestone Plastics Company; Bolathene by General Tire and Rubber Company. Among the trademarked propylene fibers are: Courlene by Courtaulds, Ltd. of England; Beaunit polypropylene; Propylon by Canadian Celanese, Ltd.; Olane by Avi Sun; and Propylene by Industrial Rayon Corporation.

These polymers have been in consumer use for a long period of time as cast polymeric articles or films. The textile applications are relatively new.[1]

The Aim of This Research

Aniline-formaldehyde polymer has been selected in an attempt to produce a synthetic fiber for this research. Aniline-formaldehyde fibers were cured in a special curing liquor for further polymerization to form crosslinked fibers. The main aim of this research is to find a method to cure aniline-formaldehyde fiber.

History of Aniline-Formaldehyde Resins

Aniline-formaldehyde resins were made on a commercial scale from about 1928 to 1950, during and shortly after World War II. Aniline-formaldehyde resins are the only arylamino-formaldehyde resins which were produced on a commercial scale. Presently, aniline-formaldehyde resins are not produced. This is due to the growth of the newer and less expensive resins with far better electrical properties. In the 1930's and 1940's, aniline-formaldehyde resins were made in the United States by Continental Diamond Fiber Company. Their trade name was Dilectone and as aniline-formaldehyde-impregnated, vulcanized fiber, their trade name was Dilecto. In Europe, they were produced by I.G. Farbenindustrie A.G. and Ciba A.G. in the form of resin, called Cibanite in laminated sheet form, called Cibanite and cellulose-filled. Fibra Vulcanisata, Italy produced aniline-formaldehyde resin-impregnated vulcanized fiber named Fibra Etiopica.

Types of Aniline-Formaldehyde Resins

Aniline-formaldehyde resins produced for the molded articles are light to dark brown in color, slightly translucent in thin sections, and perfectly homogeneous. They are easily machined by turning, sawing, boring, etc., and very fine threads can be machined. Their electrical properties are better than phenolic resins. Aniline-formaldehyde resins have two insurmountable disadvantages.

The first is their low flow, and the consequent difficulty in molding them, demanding higher-than-usual pressures. The second is that their manufacturing cost is higher than of some of the newer thermoplastics, such as polystrene or polyethylene, which in addition, have uniform electrical properties.

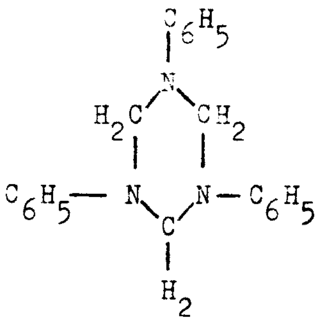
The best filler - containing a aniline-formaldehyde resin product is made by using cellulose fiber impregnation in a beater process right in the paper mill. An aniline-formaldehyde resin - containing paper is produced that can be molded satisfactorily but at higher than usual pressure, into laminated aniline-formaldehyde resin sheets.

Another application of aniline-formaldehyde resins was, for quite a number of years, impregnation of vulcanized fiberboard. Vulcanized fiber sheets are built up by superimposing pure cellulose paper sheets, previously swollen by soaking in concentrated zinc chloride solution. After removal of the bulk of the zinc chloride by coutercurrent washing, the sheets are steeped for a few days in an acid solution of aniline-formaldehyde resin prepared from 1 mole aniline, 1 mole HCl, and 1.2-1.3 moles formaldehyde. The swollen, vulcanized fiber sheets are thus impregnated with the red acid aniline-formaldehyde resin solution; this process is easily followed by watching the red color on the cross section of the fiber sheet. As soon as the desired degree of impregnation is reached, the sheets are immersed in a weak

NaOH solution (about 0.5-1.0%), until neutralization of the acidic aniline-formaldehyde resin solution is complete. This is easily seen on the cross section of the sheet as the red color turns yellowish.[2]

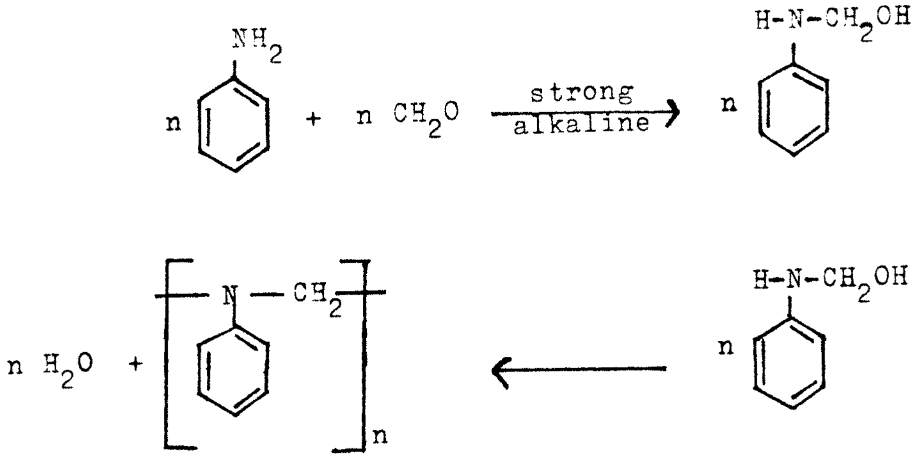
Aniline and Formaldehyde Reactions

The reaction of aniline with diluted formaldehyde gives a mixture of products at ordinary conditions. However, with proper control anhydroformaldehyde aniline may be obtained as the main product. It forms the trimer of the hypothetical Schiff's base, methylene aniline $(C_6H_5CH_2)_3$, probably has a cyclical structure analogous to that of the trialkyl trimethylenetriamines.

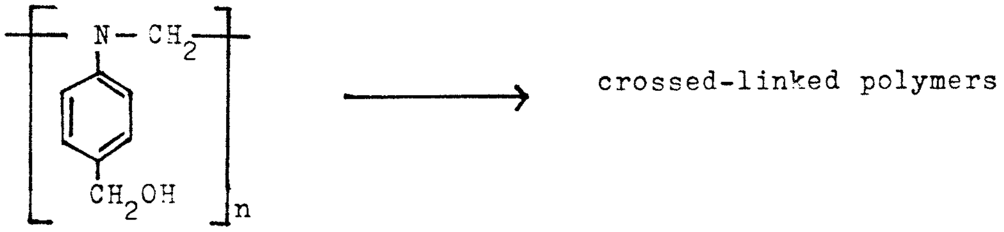


Anhydro-formaldehyde Aniline melts at 140° -140° C [3]

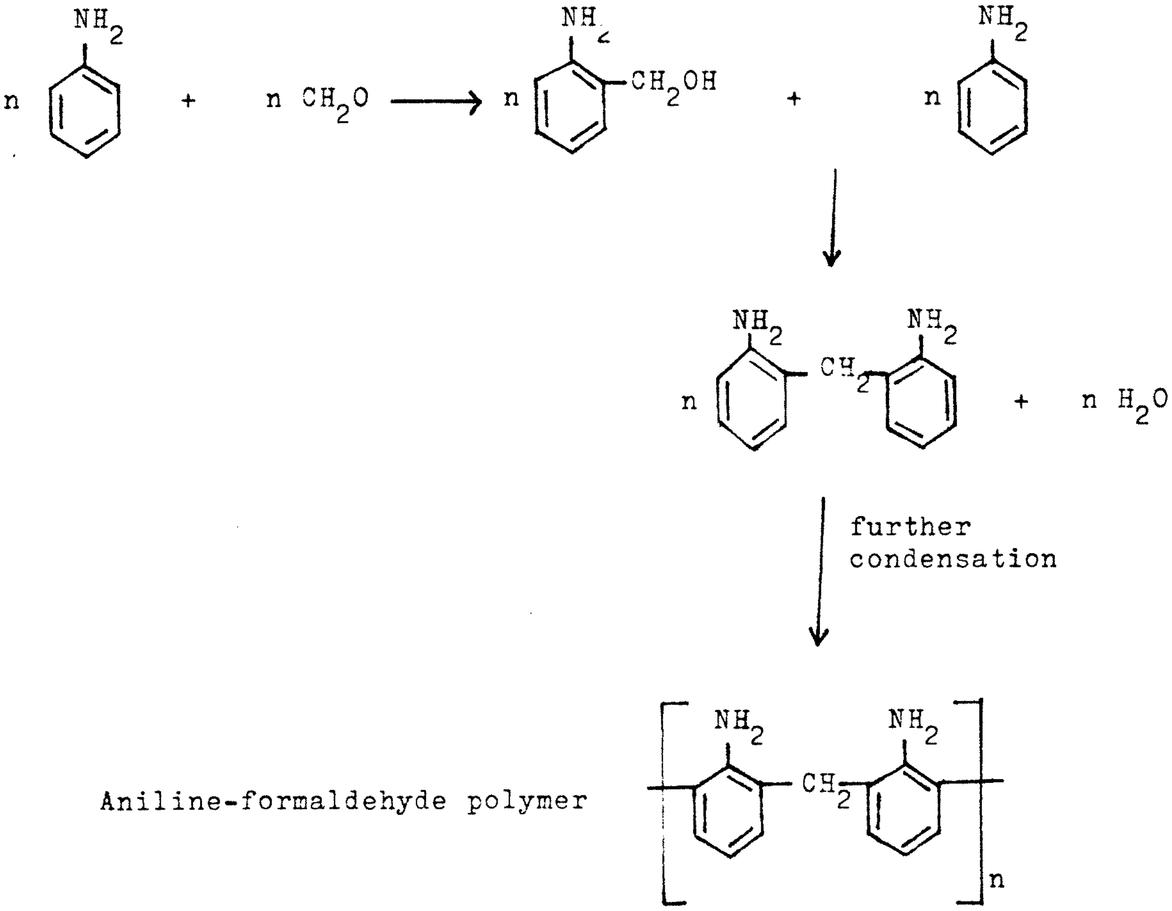
In strong alkaline solution, one mole of aniline and one mole of formaldehyde are allowed to react a soluble, fusible (thermoplastic) product is formed. In this condition, the resin is a linear polymer with no cross-linkages. The reaction may be formulated as follows:



If an excess of formaldehyde is used, the solubility fusibility decrease. This may be due to the introduction of crosslinkages. It is known that phenol and amine groups increase the reactivity of hydrogen atoms in the ortho and para positions of the benzene ring. The linear polymers first formed may react with formaldehyde to form reactive methylol groups. These methylol groups could then react with other chains to form complex branched or crosslinked polymers. The reaction is shown as follows:[4]



In acid solution aromatic amines form resins with formaldehyde. This reaction involves the formation of nuclear methylene linkages similar to those which occur in phenol-formaldehyde resins. The reaction type is characteristic of aromatic nucleus rather than of the activating amine group, whose presence merely facilitates reaction. The reaction shows as the following:[5]



Fire-Retardant Properties

The synthetic fiber generally has good properties. For example it is resistant to insects, mildew, bacteria, water, but some other synthetic fibers are very flammable. Therefore, it is dangerous to use them.

> "In 1953, the Flammable Fabrics Act (Public Law 88), which is administered by the Federal Trade Commission and applies specifically to wearing apparel and fabrics intended to be worn which are so flammable as to be hazardous. These materials are not to be introduced into interstate commerce nor moved between states. This act applies particularly to cellulose fibers, which in napped or raised surface fabrics and in extreme sheers, such as nets, contains sufficient air to provide a fast burning when they become ignited. Fabrics of this nature and some of the more flammable synthetic fibers intended for wearing apparel must be given a satisfactorily permanent fire-retardant finish so that when tested by the standard procedure under the AATCC test methods, the speed of burning will be reduced to a safer level."[6]

This act caused a lot of fabric companies to study fire-retardant or fireproof fibers. Fire-retardant textiles refers to a fabric which will not support combustion after the igniting flame is removed.

The method used to make the textile fire-retardant is saturation of the fabric by a chemical. The chemical usually used is an ammonium salt. This will cause the fabric to burn slowly and only while the flame remains in contact; the fabric will not support combustion and the cloth will no longer burn when the match or torch is removed.

Formaldehyde may in some instances be employed in the preparation of fireproofing compositions. Stellmacher, for example, uses a water-glass solution combined with hydrogen peroxide, sodium perborate or formaldehyde.[7] A mixture of ammonium sulfate, ammonium chloride, magnesium carbonate, zinc sulfate and sodium phosphate containing formaldehyde is claimed to have value as a flame-proofing agent.[8]

A resinous substance produced by reactions involving formaldehyde, dicyandiamide and ammonia is also reported to function as a fireproofing agent.[9] Ethylidene-urea gives resins with formaldehyde which produce a voluminous char on exposure to heat and show promise in the production of fire-retardant coatings.

The effect of cure is another important variable in the burning characteristics of thermosetting polymers. The degree of cure is the criteria for this purpose, increasing the degree of cure generally increases the fire-retardant property. It will decrease in the amount of volatile combustian products as the crosslinking density is increased. Because of the larger surface-to-volume ratio, polymer fabrics are more difficult to make fire-retardant. It requires more fire-retardant material per unit weight than a molded part.

Certain compounds, for example nitrocellulose, shows notoriously high flammability while others such as the phenolics burn only with great difficulty or not at all. This effect is caused by structural considerations, according to the nature and arrangement of the atoms present. For example a compound that contains a high proportion of chlorine in the molecule shows reduced flammability. Nylon 66, polycarbonate, polyurethane, polyvinyl chloride (rigid) and urea-formaldehyde resin, are compounds that have the ability of self-extinction, but ABS resin and polyester have slow flammability rates.[10] Cellulose fabrics, modacrylic fibers, polypropylene fabrics and phenolic fibers are the well known fire-retardant textiles.

Cured aniline-formaldehyde, and copolymer, aniline-phenol-formaldehyde fiber for this experiment have fire-retardant properties. For this research, aniline-phenol-formaldehyde fiber has a better cure than aniline-formaldehyde fiber. Phenolic fiber or phenol-formaldehyde fiber has already been developed by some companies but aniline-formaldehyde and aniline-phenol-formaldehyde fibers have not yet been developed in this particular procedure to the best of my knowledge. Therefore it has potential for production of new products. Aniline-formaldehyde fiber had developed a curing reaction for tensile strengths (see chapter II-4,p.37) hence it has a better chance of obtaining the best cure.

II. EXPERIMENTAL

1. Preparation of Polymer

Aniline-Formaldehyde Resin

A. Chemicals:

1. Aniline, reagent grade, Matheson Coleman & Bell Co.
2. Formaldehyde 37% solution, contains 10-15% of methyl alcohol as a preservative, technical grade, Matheson Coleman & Bell Co.
3. Oxalic acid dihydrate reagent grade, Mallinckrodt Co.
4. Acetic acid, reagent grade, Fisher Scientific Co.

B. Apparatus:

1. One liter four-necked reaction kettle
2. Glascol heating mantle
3. Glass stirrer
4. Electric motor with a speed control
5. Variable transformer
6. Thermometer
7. Condenser
8. Water trap
9. Cryostat
10. Vacuum gauge
11. Vacuum pump

C. Procedure:

1. Aniline, formaldehyde 37% solution and catalyst were placed in the reaction kettle which was

equipped with a condenser, thermometer, nitrogen inlet tube and stirrer.

2. Nitrogen gas was purged into the reaction mixture for five minutes, then it was heated slowly to its boiling point by a glascol mantle and under nitrogen blanket while stirring.
3. Reflux period (see Table on page 16)
4. Water was removed by vacuum distillation at 2 cm of Hg for 3-5 hours.
5. Resin was collected by pouring the molten resin into another container.
6. Resin was weighed and checked for its softening point.

D. COMPOSITION OF ANILINE-FORMALDEHYDE RESINS :

Experiment number	Aniline		Formaldehyde 37% solution		Catalyst		Reflux time	Result of resin		
	(g)	(mole)	(g)	(mole)		(g)	(hrs)	yield	softening point (°C)	Ability to draw fiber
1	90.0	0.97	24.0	0.30	acetic acid	20.5	13	yellow poor waxy resin	low	cannot
2	93.0	1.00	60.0	0.74	oxalic acid	6.0	3	good amber resin	80	can
3	139.5	1.50	90.0	1.24	oxalic acid	15.0	3	poor waxy resin	low	cannot
4	93.5	1.01	70.0	0.86	oxalic acid	10.0	4	poor waxy resin	low	cannot
5	95.0	1.02	65.0	0.80	oxalic acid	3.0	3	dark brown resin	low	cannot
6	139.25	1.50	90.0	1.11	oxalic acid	9.25	3	130 g amber resin	85 - 95	can
7	139.25	1.50	90.0	1.12	oxalic acid	10.0	3	135 g amber resin	85 - 95	can
8	140.0	1.51	90.0	1.12	oxalic acid	12.0	4	125 g amber resin	80 - 85	can

Preparation of Copolymers

p-Chlorophenol-Phenol-Formaldehyde and Aniline-Phenol-Formaldehyde Resins

A. Chemicals:

1. p-Chlorophenol, practical grade, Matheson Coleman & Bell Co.
2. p-Toluenesulfonic acid, reagent grade, mallinckrodt Co.
3. Phenol, reagent grade, J. T. Baker Co.
4. Formaldehyde 37% solution, containing 10-15% methyl alcohol as a preservative, technical grade, Matheson Coleman & Bell Co.
5. Oxalic acid dihydrate reagent grade, Mallinckrodt Co.
6. Aniline, reagent grade, Matheson Coleman & Bell Co.

B. Apparatus:

The same as the apparatus in the previous section

C. Procedure:

1. Aniline-phelol-formaldehyde resin proportion:

   Aniline 2/3 mole : Phenol 1/3 mole = 1 mole : 0.8 mole formaldehyde

   and 10.0 of oxalic acid

2. Added 35.0 g of aniline oil, 5 g of oxalic acid and 15 g of formaldehyde 37% solution in the reaction kettle which was equipped with a condenser, thermometer, nitrogen inlet tube and stirrer
3. Purged nitrogen gas into the reaction mixture for five minutes, then it was heated slowly to

its boiling point by a Glascol mantle and a nitrogen blanket while stirring

4. Reflux for 2 hours
5. Then added 11.75 g of phenol and 5 g of oxalic acid
6. Added 15 g of formaldehyde solution drop wise
7. Reflux for 3 hours
8. Water was removed by vacuum distillation at 2 cm of Hg for 4 hours (temperature reached 210°C)
9. Resin was collected by pouring the molten resin into another container.
10. Resin was weighed and checked for its softening point.

D. COMPOSITION OF p-CHLOROPHENOL-PHENOL-FORMALDEHYDE AND ANILINE-PHENOL-FORMALDEHYDE RESINS :

Experiment number	Phenol		p-Chlorophenol		Aniline		Formaldehyde 37% sol'n		Catalyst		Result	
	(g)	(mole)	(g)	(mole)	(g)	(mole)	(g)	(mole)	p-toluene-sulfonic acid (g)	oxalic acid (g)	yield	ability to drawn fiber
1	18.8	0.2	102.8	0.8	-	-	64.9	0.8	5	-	Dark brown resin.	can
2	47.0	0.5	-	-	46.5	0.499	60.0	0.74	-	10	Waxy resin.	cannot.
3	11.75	0.125	-	-	35.0	0.380	30.0	0.43	-	10	Amber resin, softening point range in between 145°C-160°C.	can

2. Formation of Fiber by Melt-Spinning

A. Apparatus:

1. Nitrogen gas tank
2. Stainless steel resin melter
3. Heating tape
4. Fiber collector or bobbin
5. Distance between pressure chamber and bobbin, 2-3 feet
6. Electric motor with a speed selector
7. Thermometer
8. o.75 mm diameter of orifice
9. Variable transformer
10. Thermo-watch

B. Procedure:

1. A stainless steel resin melter was wrapped with a heating tape and plugged into a variable transformer, and the variable transformer was connected to the nitrogen gas tank.
2. The shaft of a rotating electric motor with a variable speed control was attached to a bobbin which collected the spun fiber.
3. A suitable amount of pulverized polymer was placed in the stainless steel resin melter and gradually heated. For this resin, the fiber was drawn under optimume temperature. (between 150° -180° C)
4. Then nitrogen pressure of 3-5 psi was introduced into the melter.
5. A spinning rate of about 2500 ft/min, the higher the speed the finer fiber diameter is produced.
6. The distance between the resin melter and bobbin was about 2 to 3 feet

3. Curing

Curing of Aniline-Formaldehyde Fiber

A. Chemicals:

   1. Ammonium hydroxide 36% solution, Matheson Coleman & Bell Co.
   2. Aluminum chloride anhydrous, Mallinckrodt Co.
   3. Oxalic acid dihydrate reagent grade, Mallinckrodt Co.
   4. Hydrochloric acid 36.46% solution, Mallinckrodt Co.
   5. Methanol, anhydrous, Mallinckrodt Co.
   6. Hydrogen peroxide 3% solution, reagent grade, J. T. Baker Co.
   7. Sodium hydroxide, reagent grade, pellets, matheson Coleman & Bell Co.
   8. Formaldehyde 37% solution, contains 10-15% of methyl alcohol as a preservative, technical grade, Matheson Coleman & Bell Co.
   9. Paraformaldehyde, contains 93% formaldehyde, technical grade, Mallinckrodt Co.
   10. $FeSO_4 \cdot H_2O$ 1% aqueous, reagent grade, Fisher Scientific Co.

B. Apparatus:

   1. One liter four-necked reaction kettle
   2. Condenser
   3. Glascol heating mantle
   4. Glass stirrer
   5. Electric motor with a speed control

6. Variable transformer
7. Thermowatch
8. Thermometer

C. Procedure:

1. The curing liquor was prepared by adding formaldehyde solution, water, if any, and catalyst into a large beaker.
   The mixture is then allowed to cool to room temperature.
2. The curing liquor was then poured into a one liter four-necked reaction kettle and fiber which was prepared for curing was added. Note that the curing liquor should minimally cover the fiber.
3. After a condenser, thermometer and stirrer were connected, the curing liquor was heated slowly with a Glascol heating mantle.
4. The curing liquor temperature was raised very slowly, especially in the lower temperature range and the solution was stirred gently.
5. In general one can raise the temperature one degree every hour from room temperature to 35° C; from 35° C to 45° C the temperature was raised one degree every thirty minutes; from 45° C to 55° C the temperature was raised one degree every twenty minutes. For temperatures higher than 55° C one can allow the temperature to rise in less time.

6. In this particular curing liquor, the boiling point was 95° C. The liquor was allowed to boil for at least 24 hours and then it was cooled to room temperature.
7. The cured fiber was taken out of the kettle and rinsed with a large quantity of water a number of times and dried at room temperature.

D. COMPOSITION OF CURING LIQUORS :

Experiment number	Paraformaldehyde (g)	Formaldehyde sol'n (ml)	Distilled water (ml)	Catalyst					Result (final)
				HCl sol'n (ml)	NaOH (g)	NH_4OH sol'n (ml)	H_2O_2 aq. (ml)	$FeSO_4 \cdot H_2O$ aq.	
1	-	25	70	5	-	-	-	-	Fiber dissolved into curing liquor.
2	20	-	70	-	10	-	-	-	Fiber dissolved into curing liquor.
3	20	-	70	-	-	10	-	-	Fiber dissolved into curing liquor.
4	-	20	70	-	-	10	-	-	Fiber was cured, but not strong.
5	-	100	-	-	-	-	5	10 drops	Fiber broke down into small pieces, and partially dissolved.
6	-	95	-	-	-	5	5	10 drops	Fiber dissolved into curing liquor.
7	-	140	-	-	-	10	5	10 drops	Fiber was cured, but it broke easy.
8	-	80	-	-	-	20	5	10 drops	Some fiber was cured, but partially broken.
9	-	70	-	-	-	30	5	10 drops	Fiber dissolved when heat up.
10	-	60	-	-	-	40	-	-	Fiber dissolved when heat up.
11	-	100	-	-	-	50	5	10 drops	Fiber closed together, color change from yellow to orange, and dissolved at high temperature.

COMPOSITION OF CURING LIQUORS :

Experiment number	Formaldehyde sol'n (ml)	Distilled water (ml)	Methanol (ml)	Catalyst					Result (final)
				Acetic acid (ml)	NaOH sol'n (g)	NH_4OH sol'n (ml)	H_2O_2 aq. (ml)	$FeSO_4 \cdot H_2O$ aq.	
12 *	40	-	-	-	-	60	5	10 drops	Left fiber in the liquor at room temperature for 7 days. Some fibers were broken.
13	30	-	-	-	-	70	5	10 drops	Fiber dissolved into the curing liquor
14	95	-	-	-	-	5	-	-	Fiber dissolved into the curing liquor
15	70	-	-	-	-	30	-	-	Fiber was broken when heat up.
16	50	-	-	-	-	50	-	-	Fiber dissolved into the curing liquor
17	40	-	-	-	-	60	-	-	Fiber dissolved into the curing liquor
18	-	-	-	-	-	100	-	-	Fiber dissolved when heat up.
19	80	-	-	20	-	-	-	-	Fiber joined together in one piece.
20	80	-	-	-	-	20	-	-	Some fiber was cured but it broke easy
21	80	-	20	-	-	-	-	-	Fiber dissolved when heat up.
22	100	25	-	-	10	-	-	-	Fiber got brittle and hard in curing liquor.
23	185	-	-	-	-	27	15	15 ml	Fiber broke into small pieces.

* see procedure in APPENDIX

COMPOSTION OF CURING LIQUORS :

Experiment number	Formal-dehyde sol'n (ml)	Distilled water (ml)	Methanol (ml)	Catalyst			Result (final)
				NH_4OH sol'n (ml)	H_2O_2 aq. (drops)	$FeSO_4 \cdot H_2O$ aq. (drops)	
24*	225	-	-	25	5	5	Fiber was cured, but it broke easy.
25	25	-	-	75	5	5	Fiber was cured, but it broke easy.
26*	75	-	-	25	5	-	Fiber was broken into small pieces.
27*	75	-	-	25	-	-	Fiber was broken into small pieces.
28	75	-	-	25	5	5	Fiber was broken into small pieces.
29	100	-	-	-	15	15	Fiber was broken into small pieces.
30	150	-	-	-	7.5	7.5	Fiber was soft and broken easy.
31	150	-	-	-	3.75	3.75	Fiber was soft and broken easy.
32	40.54 g	101.13	-	58.33 g	-	-	Fiber jointed together and hard.
33	60.81 g	80.86	-	58.33 g	-	-	Fiber dissolved.
34	40.54 g	71.69	-	87.50 g	-	-	Fiber was broken into pieces.
35	54.05 g	67.78	-	78.17 g	-	-	Fiber was broken into pieces.
36	54.05 g	167.78	-	78.17 g	-	-	Fiber was broken.

*see procedures in APPENDIX

COMPOSITION OF CURING LIQUORS :

Experiment number	Formal-dehyde sol'n (ml)	Distilled water (ml)	Methanol (ml)	Catalyst		Result (final)
				NH_4OH sol'n (ml)	$AlCl_3$ (g)	
37*	80.0 g	100.00	20 g	20 g	-	Fiber was cured.
38*	80.0 g	100.00	30 g	20 g	-	Fiber was cured, but some fiber was defused, not uniform.
39*	54.05 g	25.95	-	20 g	-	Fiber was cured, and cured fiber was better than cured fiber of Expt.#37.
40	54.05 g	-	-	33.33 g	4.65 g of Aniline	Fiber got harder, brittle and joined together.
41	40.54 g	-	-	33.33 g	-	Fiber was similar to Expt.#40.
42*	80.00	55.00	21	15	-	Fiber was cured, but when heat up fiber was dissolved.
43*	80.00	60.00	10.5	10	1.0	Fiber was cured.
44*	80.00	65.00	21.0	5	1.5	Fiber was cured, but not strong as fiber (cured) of Expt.#43.
45	45 g	55.00	1.00	-	1.0	Fiber was soft and broken easy.
46	80	50.00	10.00	20	0.5	Fiber was cured, but not strong.

* see procedures in APPENDIX

E. Summary

Curing liquors from #1 through #31

1. Ammonium hydroxide solution of more than 20 ml (20%) is not good. The fiber becomes weak and dissolves. A solution lower than 20 ml still produces good results.
2. Formaldehyde 37% solution of more than 80 ml (80%) is not good because the fiber becoms weak and dissolves. A solution much lower than 80% e.g. 50-10% is not good either.
3. H_2O_2 and Fe $SO_4 \cdot H_2O$ 1% aq. were attempted as catalysts. They did not work. They caused fiber to become weaker and break easily. The curing liquor containing H_2O_2 and Fe $SO_4 \cdot H_2O$ 1% aq. appeared yellow, and this liquor did change the color of the fiber from light yellow to gold. (without H_2O_2 and $FeSO_4$ the liquor is clear)
4. Any acid is not good for this type of curing (fiber). Even very diluted acid or low (pH) acid will melt and partially dissolve the fiber.
5. The size of the condenser is very important in achieving good curing. A small condenser is not good (ass. CH_2O can evaporate) but a large condenser is.

6. NaOH is too strong for this type of fiber, it will dissolve the fiber. For example in the curing of experiment #2.
7. Paraformaldehyde reacts very rapidly with the NH_4OH solution, it did liberate heat to about 90°C and change the color to a dark brown (burn). It is not good for curing. The results of curing paraformaldehyde from curing liquors #2, #3 were not good.
8. Only one curing liquor is good, *#27. The moderately good ones are *#12, *#24, *#26, *#27, the rest of them are inadequate.
9. The curing liquor is made in the large flask because heat will be liberated. If made in a small flask the liquid will shoot out of the flask while the other kind of solution is being poured into the flask. For example if CH_2O solution is in the flask and NH_4OH solution is poured into the flask the proceeding will result.
10. Do not put the fiber into the flask and use this flask to mix the solution. The best method is to make the curing solution first and let it cool to R.T. and add the fiber later. The heat of the

(*see procedures in Appendix page 97)

solution liberated while mixing will be able to dissolve the uncured fiber.

11. Heating process - Increasing the temperature while curing is very important. If one increases the temperature too fast the fiber will dissolve before it has a chance to start curing and be strong enough to survive at high temperatures. This will be the effect even with a good curing solution. One has to increase the temperature very slowly by starting the heat at 25°-30° C, then increasing it 1° C every hour. This will take about 60 hours to boil. Boiling longer will not improve the fiber but weaken it. One should boil 2-3 days at the most.

Summary

Curing liquors from #32 through #46

12. Using the equivalent mole of CH_2O and NH_4OH did not work; e.g. in curing liquor #32, the result is poorer when NH_4OH has a higher mole proportion than CH_2O,e.g. in curing liquor #34.
13. Curing liquor #37 is good. The proportion of CH_2O and NH_4OH works well for curing fiber. After the curing liquor is boiling, CH_3OH is added. 10% of CH_3OH is good for fiber but higher than that is not good because the fiber weakens and breaks easily.

Formula:

80 g	of CH_2O solution
20 g	of NH_4OH solution
100 ml	of H_2O
20 ml	of CH_3OH

How to develop curing liquor #37

Former experiments (#1 - #31)
liquor #27 is the best one in the group.

Formula:

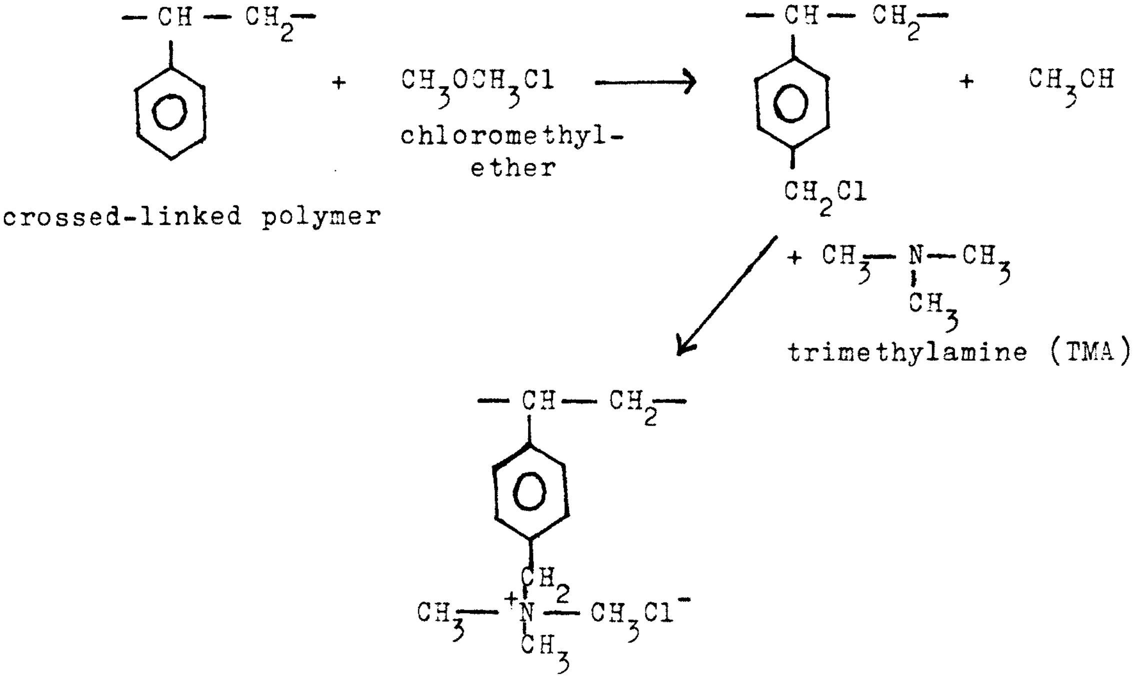
75 g	of CH_2O solution 37%	27.75 g	CH_2O
25 g	of NH_4OH solution 36%	9.0 g	NH_4OH
		H_2O 63.25 g	

For 75 g of CH_2O the solution is 27.75%; this is too high (should not use CH_2O higher than 20%) Hence it is a good idea to cut down CH_2O by adding more H_2O - (100 ml). For NH_4OH it has been shown, from the last experiment, that if one uses less than 25 g of solution it is still efficient enough to achieve a good curing, therefore NH_4OH is cut down to 20 g of NH_4OH solution.

CH_3OH is introduced as a swelling agent for the fiber. It is easier for the fiber to cure on the surface area than the inner-side of the fiber. Hence CH_3OH will help the fiber to swell and CH_2- from CH_2O will penetrate the fiber and form the crosslink causing the fiber to get a better cure. The fiber becomes stronger than the fiber which is cured only on the surface. One should be careful how much swelling agent is used in the curing liquor. Too much CH_3OH deteriorates the fiber and it becomes weak and easy to break.

14. Curing liquor #43 is much better than curing liquor #37.

    How to develop curing liquor #43.
    Curing liquor #37 is good; it can cure some of the fiber, but the strength of the fiber is not too good. If one pulls this cured fiber (#37) a little too hard it will break. Some other kinds of catalysts should give better results than NH_4OH, or one can use a co-catalyst.
    This idea led me to find other kinds of catalysts to test. $AlCl_3$ is used as the catalyst to make anionic exchange resin for polystyrene.



Hence $AlCl_3$ is introduced as formula #43 which shows as follows:

80 ml of CH_2O solution 37%
10 ml of NH_4OH solution 36%
60 ml of H_2O
0.6 g of $AlCl_3$ (0.1 + 0.2 + 0.3 g)
10.5 ml of CH_3OH

Curing of Copolymer, Aniline-Phenol-Formaldehyde Fiber

A. Chemicals:

1. Oxalic acid dihydrate reagent grade, Mallinckrodt Co.
2. Formaldehyde 37% solution, containing 10-15% methyl alcohol as preservative, technical grade, Matheson Coleman and Bell Co.
3. Ammonium hydroxide 36% solution, Matheson Coleman and Bell Co.
4. Sodium hydroxide, reagent grade, pellets, Matheson coleman and Bell Co.
5. Paraformaldehyde, containing 93% formaldehyde, technical grade, Mallinckrodt Co.
6. p-toluenesulfomic acid, reagent grade, Mallinckrodt Co.
7. Hydrochloric acid 36.46 % solution, Mallinckrodt Co.

B. Apparatus:

The same as the apparatus in the previous section

C. Procedure:

The general procedure is the same as the procedure in the previous section.

D. COMPOSITION OF CURING LIQUORS

Experiment number	Formaldehyde 37% solution (ml)	Paraformaldehyde (g)	Distilled water (ml)	Catalyst	Result (final)
1	80	-	5	15 g of oxalic acid.	Fiber got soft and weak.
2	80	-	-	20 ml of ammonium hydroxide solution.	Fiber was cured good and strong. Took cured fiber to test for the strength by putting fiber in conc. H_2SO_4, fiber changed color from dark gold to dark brown. Cured fiber sank but did not dissolve.
3	55	15	-	20 g of sodium hydroxide.	Fiber was partially cured but weak.
4	55	15	-	20 g of p-toluenesulfomic acid.	Fiber was partially dissolved and broken into small pieces.
5	55	15	-	20 ml of hydrochloric acid solution.	Fiber was partially dissolved.
6	100	-	30	10 g of sodium hydroxide.	Fiber was very weak.
7	55	20	5	10 g of p-toluenesulfomic acid.	Fiber was partially dissolved.

4. Tensile Strengths and Solubility Test

Tensile Strengths:

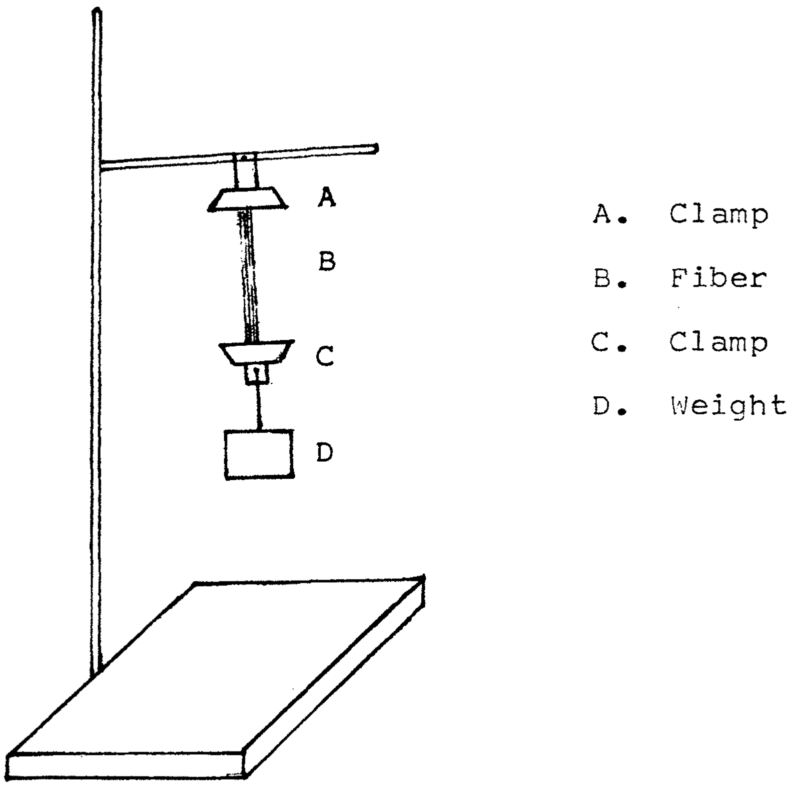
A. Introdiction and construction of a device for Measurement of the strength of fiber

I have done about fifty curings so far. For the curing liquor I had no previous knowledge of what kind of catalyst would work. I experimented with different kinds of acids, e.g., hydrochloric acid, sulfuric acid, oxalic acid, p - toluene sulfomic acid, etc., which gave negative results. Some of the acids dissolved the fiber, some just weakened and partially dissolved the fiber. Then I tried bases, e.g., sodium hydroxide, ammonium hydroxide, etc. Fortunately, ammonium hydroxide showed good signs of catalysis for this particular aniline-formaldehyde fiber that I developed. I followed this with large numbers of experiments to find the best proportion of catalyst in the curing liquor. The curing liquor from Experiment # 43 is the best proportion curing liquor. This curing liquor had some $AlCl_3$ as cocatalyst and CH_3OH as a swelling agent to help improve the curing. The curing liquor from Experiment # 43 was the best curing liquor over all, but it was still not good enough.

There are a few ways to improve the quality of the reaction. First of all, find the optimum amount of cocatalyst to add to the curing liquor at the optimum temperature. Second, the right amount of swelling agent and the best temperature to add. Third, find the optimum temperature while the curing reaction is taking place. With these factors known, we then can adjust the amount of cocatalyst, swelling agent, and add them at the proper temperature. More importantly, we can maximize the time at the optimum curing temperature. Hence, if one knows the trend of the reaction, one can utilize it for improving the quality of the cured fiber.

In developing this project, I have observed that one can trace the reaction trend in the curing process by removing a portion of fiber at different temperatures and recording the amount of cocatalyst and swelling agent added, and recording the time of each step. Then one can graph the trend of the curing reaction from the strength of fibers removed (by using stress on weight to break) versus the number of fibers which correspond to its strength.

One problem I had faced is the equipment for strength testing. I had known that there is such an instrument on the market, but it would be difficult to get the money to but it. This problem forced me to make my own simple equipment for this experiment which the diagram shows below.



Schematic diagram of device for measurement of the strength of the fiber

This simple instrument for measuring the strength of fiber by using the stress on fiber until the fiber breaks might not have been 100 percent accurate, but it will give enough accuracy for the experiment. In fact, the accuracy of the results (data) is not dependent on the equipment, but rather on the exact weight and length of the fiber, including good, even, fine strands of fiber in each length. Anyway, this type of operation on this equipment will give a high degree of accuracy.

The reason for constructing one's own equipment is not only due to a lack of money, but also because there are times and places when one has money, but there is no equipment available, as in technologically underdeveloped countries. Therefore, the making of one's own simple equipment should be a part of the successful scientific discovery, if it is possible.

B. Procedure of Curing Fiber for Tensile Strength Test

1. Uncared Aniline-formaldehyde fiber (which is called #1 fiber), from resin of Experiment #6.
2. Placed 7.0 g of uncured uniform fiber into 600 ml curing solution (containing 240 ml H_2O, 320 ml formaldehyde solution (37%) and 40 ml of ammonium hydroxide (36%) solution), closed container and left it at room temperature (25°C) for 24 hours. Then took some of fiber out and rinsed with a lot of water. Then left fiber in water for 12 hours, and dried fiber at room temperature. This fiber is called #2 fiber.
3. In 30 hours (after taking fiber #2 out), took out some of fiber, and cleaned and dried as fiber #2. This fiber is called fiber #3 (still at R.T., 25°C)
4. Added 0.5 g of $AlCl_3$ and 2½ ml of CH_3OH after taking fiber #3 out, then increased temperature slowly up to about 45°C - left temperature constant for 26½ hours then took some fiber out to clean and dry. This fiber is called fiber #4.
5. Added 0.1g of $AlCl_3$ and ½ ml of CH_3OH after taking fiber #4 out, and raised temperature slowly up to 50°C, - left temperature constant for 11½ hours, then took some fiber out to clean and dry. This fiber is called fiber #5.

6. Left temperature constant at 50°C for 6 hours -

later took out some of the fiber and called fiber #6.

7. Left temperature constant at 50° C for four hours; later took out some of the fiber and called fiber #7.
8. Left temperature constant at 50° C for three hours; later took out some of the fiber and called fiber #8.
9. Added 0.2 g of $AlCl_3$ and 1 ml of CH_3OH after took fiber #8 out, and increased temperature slowly to 63° C, then kept temperature constant for 11 hours. Took out some of he fiber and called fiber #9.
10. Added .1 g $AlCl_3$ and ½ ml of CH_3OH and raised temperature up slowly to 66° C and kept temperature constant for six hours; then took out some of the fiber and called fiber #10.
11. Added .1 g of $AlCl_3$ and ½ ml of CH_3OH and then raised temperature slowly to 73° C, kept temperature constant for 7½ hours; then took out some of the fiber and called fiber #11.
12. Added .1 g of $AlCl_3$ and ½ ml of CH_3OH, raised temperature slowly to 75° C, kept temperature constant for 9½ hours; then took out some of the fiber and called fiber #12.
13. Added 0.1 g of $AlCl_3$ and ½ ml of CH_3OH, raised temperature slowly to 78° C and kept temperature

constant for four hours; then took out some of the fiber and called fiber #13.

14. Added .1 g of $AlCl_3$ and ½ ml of CH_3OH, temperature kept constant at 78°C for three hours; then took out some of the fiber and called fiber #14.

15. Raised temperature up to 80°C and kept temperature constant for three hours; then took out some of fiber and called fiber #15.

16. Added .2 g of $AlCl_3$ and raised temperature up to 85°C, kept temperature constant for four hours; then took out some of thr fiber and called fiber #16

17. Added .2 g of $AlCl_3$ and kept temperature constant at 85°C for 3½ hours; then took some fiber out and called fiber #17.

18. Added .2 g of $AlCl_3$ and kept temperature constant at 85°C for 3½ hours; then took some of the fiber out and called fiber #18.

19. Added .2 g of $AlCl_3$ and kept temperature constant at 85°C for 3½ hours; then took some of the fiber out and called fiber #19.

20. Added 3 ml of CH_3OH and raised temperature slowly up to 89°C, kept temperature constant for three hours; then took some of the fiber out and called fiber #20.

21. Added 6 ml of CH_3OH and raised temperature slowly to 95°C, kept temperature constant for three hours;

then took some of the fiber out and called fiber #21.

22. Added 6 ml of CH_3OH and kept temperature constant at 95° C (boiling) for three hours; then took out some of the fiber and called fiber #22.

23. Added 6 ml of CH_3OH and kept it boiling for three hours; then took out some of the fiber and called fiber #23.

24. Kept temperature constant at 95° C for three hours; then took out some of the fiber and called fiber #24.

25. Kept temperature constant at 95°C for three hours; then took out some of the fiber and called fiber #25.

26. Kept temperature constant at 95° C for three hours; then took out some of the fiber, and called fiber #26.

27. Kept temperature constant at 95° C for 5½ hours; then took out some of the fiber and called fiber #27.

28. Added .2 g of $AlCl_3$ and kept temperature constant at 95° C for five hours; then took out some of the fiber, and called fiber #28.

29. Added 20 ml of CH_3OH and kept temperature constant at 95° C for 5½ hours; then took out some of the fiber and called fiber #29.

30. Kept temperature constant at 95° C for three hours;

then took some of the fiber out and called fiber #30.

Procedure for curing liquor:

1. Poured 240 ml of H_2O into a 1,000 ml flask
2. Added 320 ml of formaldehyde solution 37%
3. Added 40 ml of ammonium hydroxide of 36% solution
4. Closed container and kept solution at room temperature.

C. Results

Procedure for testing the strength of fibers

1. After fiber was dried at room temperature, each number of fiber sample was cut 3 inches long and each of them weighed 0.03 g (equal length and weight). Hence, each strip of fiber was approximately equal.
2. Cut small pieces of tape (the same length in each one) and attached it to the end of each fiber strip. The purpose was to protect the fiber from being cut by the clamps and allow a good grip by clamps.
3. Clamped both ends of fiber to the equipment and applied weight until the fiber broke.

The strength of fiber data shown as follows:

Number of fiber	Weight Applied to break (g)
1	65.0
2	74.0
3	75.2
4	8.6
5	78.5
6	92.3
7	103.4
8	106.3
9	107.6
10	111.9
11	358.35
12	469.3
13	534.6
14	592.6
15	765.0
16	894.2
17	1,043.2
18	1,100.0
19	1,122.9
20	979.8
21	489.9
22	431.8
23	563.5
24	512.7
25	636.9
26	680.6
27	904.1
28	869.0
29	354.5
30	518.3

D. Calculations for % cured of each fiber

Uncured fiber = 65.0 g

#19 is highest cured fiber = 1,122.0 g

Net cured took place in fiber = 1,122.0 - 65.0 g

Assume 100% cured increase in strength = Δ g = 1,057 g

#1 uncured fiber = 0% cured fiber

#2 strength of fiber = 74.0 g

∴ net cured (strength) = 74.0 - 65 = 9 g

% cured of fiber #2 = $\frac{9 \times 100}{1057} = 0.85$

#3 strength of fiber = 75.2 g

the increasing of strength = 75.2 - 74.0 = 1.2 g

% increase of curing = $\frac{1.2 \times 100}{1057} = .11$

#4 strength of fiber = 8.6 g

the fiber strength (decrease) = 8.6 - 75.2 = -66.6 g

% (decrease) cured of fiber = $\frac{-66.6 \times 100}{1057} = -6.30$

% cured of fiber #5 = $\underline{(78.5-8.6) \times 100} = 6.613$ (increase)

% cured of fiber #6 = $\frac{(92.3-78.5) \times 100}{1057} = 1.305$ (increase)

% cured of fiber #7 = $\frac{(103.4-92.3) \times 100}{1057} = 1.050$ (increase)

% cured of fiber #8 = $\frac{(106.3-103.4) \times 100}{1057} = 0.274$ (increase)

%cured of fiber #9 = $\frac{(107.6-106.3) \times 100}{1057} = 0.123$

% cured of fiber #10 $= \frac{(111.9-107.6) \times 100}{1057} = 0.406$

% cured of fiber #11 $= \frac{(358.35-111.9) \times 100}{1057} = 23.32$

% cured of fiber #12 $= \frac{(469.3-358.35) \times 100}{1057} = 10.50$

% cured of fiber #13 $= \frac{(534-469.3) \times 100}{1057} = 6.121$

% cured of fiber #14 = 5.544 increase

% cured of fiber #15 = 16.310 increase

% cured of fiber #16 = 12.233 increase

% cured of fiber #17 = 14.096 increase

% cured of fiber #18 = 5.374 increase

% cured of fiber #19 = 2.167 increase

% cured of fiber #20 = -13.538 decrease

% cured of fiber #21 = -46.348 decrease

% cured of fiber #22 = - 5.497 decrease

% cured of fiber #23 = 12.450 increase

% cured of fiber #24 = -4.806 decrease

% cured of fiber #25 = 11.750 increase

% cured of fiber #26 = 4.134 increase

% cured of fiber #27 = 21.145 increase

% cured of fiber #28 = -3.321 decrease

% cured of fiber #29 = -48.675 decrease

% cured of fiber #30 = 15.497 increase

E. THE CURING REACTION STRENGTH DATA OF ANILINE-FORMALDEHYDE FIBER

Number of fiber	Temperature (°C)	$AlCl_3$ added (g)	Total $AlCl_3$ added (g)	CH_3OH added (ml)	Total CH_3OH added (ml)	Times (hours)	Total of Times (hours)	Weight stress on fiber (g)	Increase or Decrease for each fiber (g)	% of Curing in each fiber.
1.	Uncured fiber (does not put in curing solution)									
	25	0.0	0.0	0.0	0.0	0.0	0.0	65.00	0.0	0.0
2.	25	0.0	0.0	0.0	0.0	24.0	24.0	74.0	+ 9.0	+ 0.85
3.	25	0.0	0.0	0.0	0.0	30.0	54.0	75.20	+ 1.2	+ 0.11
4.	49	0.5	0.5	2.5	2.5	26.5	80.5	8.60	- 66.6	- 6.30
5.	50	0.1	0.6	0.5	3.0	11.5	92.0	78.50	+ 69.9	+ 6.613
6.	50	0.0	0.6	0.0	3.0	6.0	98.0	92.30	+ 13.8	+ 1.305
7.	50	0.0	0.6	0.0	3.0	4.0	102.0	103.40	+ 11.1	+ 1.050
8.	50	0.0	0.6	0.0	3.0	3.0	105.0	106.30	+ 2.9	+ 0.274
9.	63	0.2	0.8	1.0	4.0	11.0	115.0	107.60	+ 1.3	+ 0.123
10.	66	0.1	0.9	0.5	4.5	6.0	121.0	111.90	+ 4.3	+ 0.406
11.	73	0.1	1.0	0.5	5.0	7.5	128.5	358.35	+ 246.45	+ 23.32
12.	75	0.1	1.1	0.5	5.5	9.5	138.0	469.30	+ 110.95	+ 10.50
13.	78	0.1	1.2	0.5	6.0	4.0	142.0	534.00	+ 64.70	+ 6.121
14.	78	0.1	1.3	0.5	6.5	3.0	145.0	592.60	+ 58.60	+ 5.544
15.	80	0.0	1.3	0.0	6.5	3.0	148.0	765.00	+ 172.4	+ 16.310
16.	85	0.2	1.5	0.0	6.5	4.0	152.0	894.20	+ 129.2	+ 12.223
17.	85	0.2	1.7	0.0	6.5	3.5	155.5	1,043.20	+ 149.0	+ 14.096
18.	85	0.2	1.9	0.0	6.5	3.5	159.0	1,100.00	+ 56.8	+ 5.374
19.	85	0.2	2.1	0.0	6.5	3.5	162.5	1,122.90	+ 22.9	+ 2.167
20.	89	0.0	2.1	3.0	9.5	3.0	165.5	979.80	- 143.1	- 13.583
21.	95	0.0	2.1	6.0	15.5	3.0	168.5	489.90	- 489.9	- 46.348
22.	95	0.0	2.1	6.0	21.5	3.0	171.5	431.80	- 58.1	- 5.497
23.	95	0.0	2.1	6.0	27.5	3.0	174.5	563.50	+ 131.7	+ 12.460
24	95	0.0	2.1	0.0	27.5	3.0	177.5	512.70	- 50.8	- 4.806
25	95	0.0	2.1	0.0	27.5	3.0	180.5	636.90	+ 124.2	+ 11.750
26	95	0.0	2.1	0.0	27.5	3.0	183.5	680.60	+ 43.7	+ 4.134
27	95	0.0	2.1	0.0	27.5	5.5	186.0	904.10	+ 223.5	+ 21.145
28	95	0.2	2.3	0.0	27.5	5.0	191.0	869.00	- 35.1	- 3.321
29	95	0.0	2.3	20.0	47.5	5.5	196.5	354.50	- 514.5	- 48.675
30	95	0.0	2.3	0.0	47.5	3.0	199.5	518.30	+ 163.8	+ 15.497

95°C ⟶ biol
\+ ⟶ increase
\- ⟶ decrease

F. Graphical Analysis of the Curing Reaction

After the experiment ended, I constructed the chart for the curing reaction strength data. The chart contains the number of fibers, temperature at which each fiber had been taken out of the reaction, etc., and includes the percent that was obtained from curing of each fiber. Analysis of the overall experiment by plotting the graph is as follows:

Graph #1

Plot stress on fiber by weight vs. number of fibers from #1 to #30, temperature at which each fiber is taken out. The curve shows area of increase and decrease at certain temperatures. It would be easier if one could break down the graph into sections and analyze them along with the chart which gives details of each number of fiber.

Graph #2

Plot stress on fiber by weight vs. number of fibers from #1 to #10

fiber #1 is uncured fiber; fiber is not placed in the curing and the stress which is able to break fiber is 65.0 g

fiber #2 is placed in curing at room temperature (25°C) for 24 hours. The stress which is able to break the fiber is 74.0 g Fiber is increased in strength by 9.0 g, the calculation of percent curing of this fiber is 0.85.

fiber #3 was left in curing at room temperature for 54 hours (30 hours longer than #1). There is only a very small portion of curing; the increase is only 0.11%. In this particular case, one can conclude that there is very little curing taking place at room temperature (25°C)

fiber #4 became much weaker than fiber #3. The reason could be that the temperature jumped too fast 25°— 49°C. $AlCl_3$ and CH_3OH can cause the weakening of the fiber. The percent curing decrease is 6.30.

fiber #5 recovered from Fiber #4 -- the percent increase, 6.613.

fiber #6, #7 and #8 are at the same temperature, 50°C constantly. But each of them is taken out at different times. Fiber #6 was taken out at 98 hours; #7 at 102 hours; #8 at 105 hours. No other ingredients were added. Primary focus of this part of the reaction was the study of the time effect on curing. If one increases only the time and keeps the other things constant, one can see how much curing will occur. Apparently, for this case (50° C), there is very little effect on the curing. Percent increase of curing in each fiber is very small, 1.305%, 1.05% and 0.274% respectively.

fiber #9 was taken out at 63° C, 0.2 g $AlCl_3$ and 1 ml CH_3OH were added to the curing liquor before being taken out for 11 hours. The result being that this fiber still gained very little curing -- 0.123%.

fiber #10 was taken out at 66° C, 0.1 g $AlCl_3$ and ½ ml CH_3OH were added to the curing liquor. Fiber #10, was taken out 6 hours after fiber #9 -- percent of curing was only 0.406%.

Graph #3

Plot stress on fiber by weight vs. number of fiber from #10 to #19. This portion of the graph shows the best curing that took place compared to the overal reaction.

fiber #11 was taken out at 73° C, 0.1 g $AlCl_3$ and ½ ml CH_3OH were added to the curing liquor. It was taken out 7.5 hours after fiber #10. The total time of curing from the start of the reaction until then was 128.5 hours. A total $AlCl_3$ of 1.0 g and 5 ml of CH_3OH were added to the curing liquor. The percent of increase in curing of this fiber was 23.32 which was the highest increase in curing (see graph #6).

fiber #12 was taken out at 75° C, 0.1 g $AlCl_3$ and ½ ml CH_3OH were added to curing liquor. It was taken out 9.5 hours after fiber #11, percent increase of curing was 10.50.

fiber #13 and #14 were taken out at 78° C, 0.1 g $AlCl_3$ and ½ ml CH_3OH were added to each fiber. However, fiber #14 was in the solution 3 hours longer than fiber #13. Their percent increase of curing was 6.121 and 5.544 respectively.

fiber #15 had a pretty high percent increase of curing -- 16.310. It was taken out at 80° C, 3 hours after fiber #14.

fiber #16, #17, #18, and #19 are mainly to study how cocatalyst ($AlCl_3$) behaves with increasing amounts and times. The reaction shows good results, percent caring of each fiber was increased -- 12,223, 14.096, 5.374, and 2.167 respectively. All fibers were taken out at 85° C; the fibers were kept at a constant temperature. Time was increased constantly about 3½ hours after previous fiber.

There is no swelling agent (CH_3OH) added.

Graph #4

Plot stress on fiber by weight vs. number of fiber from #19 to #24. This portion of the reaction is primarily to study how the swelling agent affects the curing reaction.

fibers #20, #21, #22, and #23 have a constantly increasing amount of CH_3OH, 3 ml, 6 ml respectively as well as increased time of three hours after each previous fiber was taken out. The result of curing the fiber in each of them is very poor. Fibers are much weaker than the other ones before. Percent decrease of cured fiber is very high -- 13.538, 46.348 and 5.497 for fibers #20, #21, and #22 respectively. Fiber #23 increased in its curing but fiber #24 dropped down again. This result shows that the temperatures--85°C, 89°C and boiling point -- are not good for adding large amounts of swelling agent since the cured fiber at this state was not strong enough to cause swelling agent to penetrate the fiber.

Graph #5

Plot stress on fiber by weight vs. number of fiber from #24 to #30. This portion of graph recovered from the previous graph.

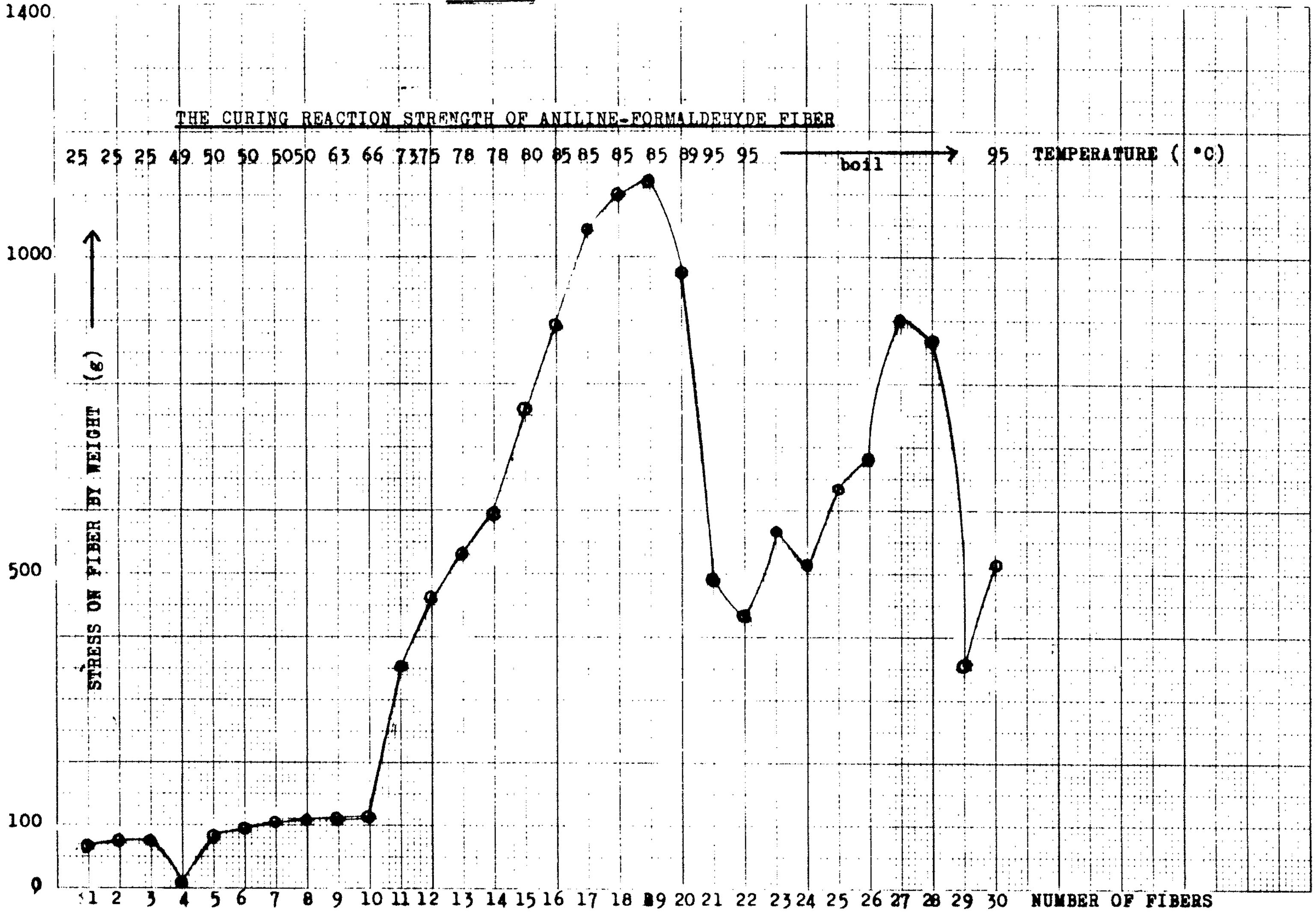
fibers #25, #26 and #27 were all taken out at 95°C (boiling) but time was increased every three hours for each fiber. There were no co-catalysts nor swelling agents added. The result is that curing increased nicely; percent increase of curing of each fiber was 11.75, 4.134 and 21.145 respectively. This result shows that at the boiling state, the curing reaction is increased with the increase in time.

fibers #28 and #29 decreaced. The result is affected by adding 0.2 $AlCl_3$ and 20 ml of CH_3OH. But fiber #30 had increased its curing by simply adding nothing and keeping it in the liquor for a longer period of time.

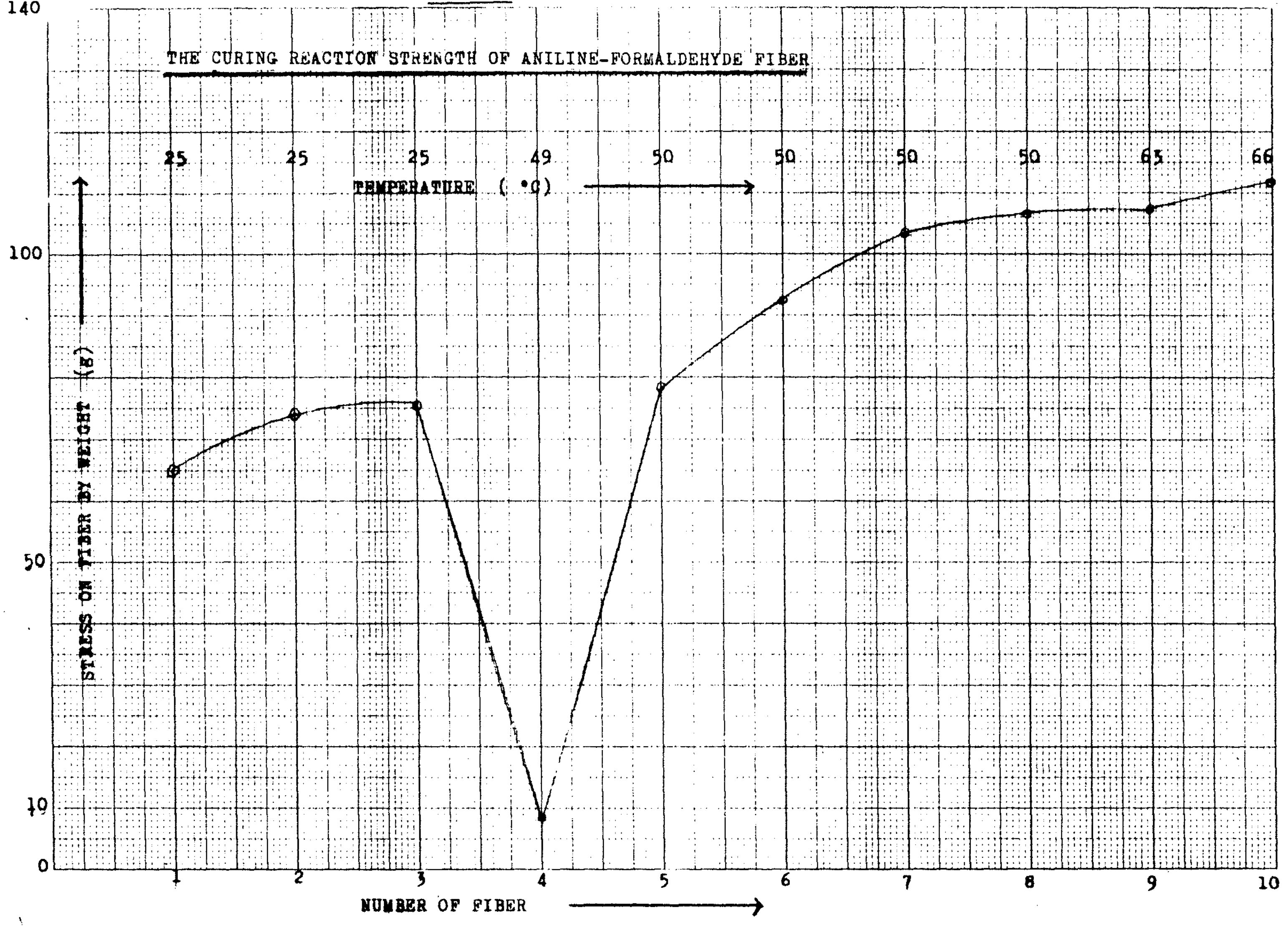
For the conclusion of the overall reaction, one can see graph #6, plot percent curing in each fiber vs. the number of fibers at each temperature. At high temperatures good curing took place at 70°C - 95°C (boiling), but curing was not good at the low temperatures. If one adds a very small amount of co-catalyst and swelling agent constantly, good curing occurs. Large amounts of cocatalyst and and swelling agent upset the curing reaction.

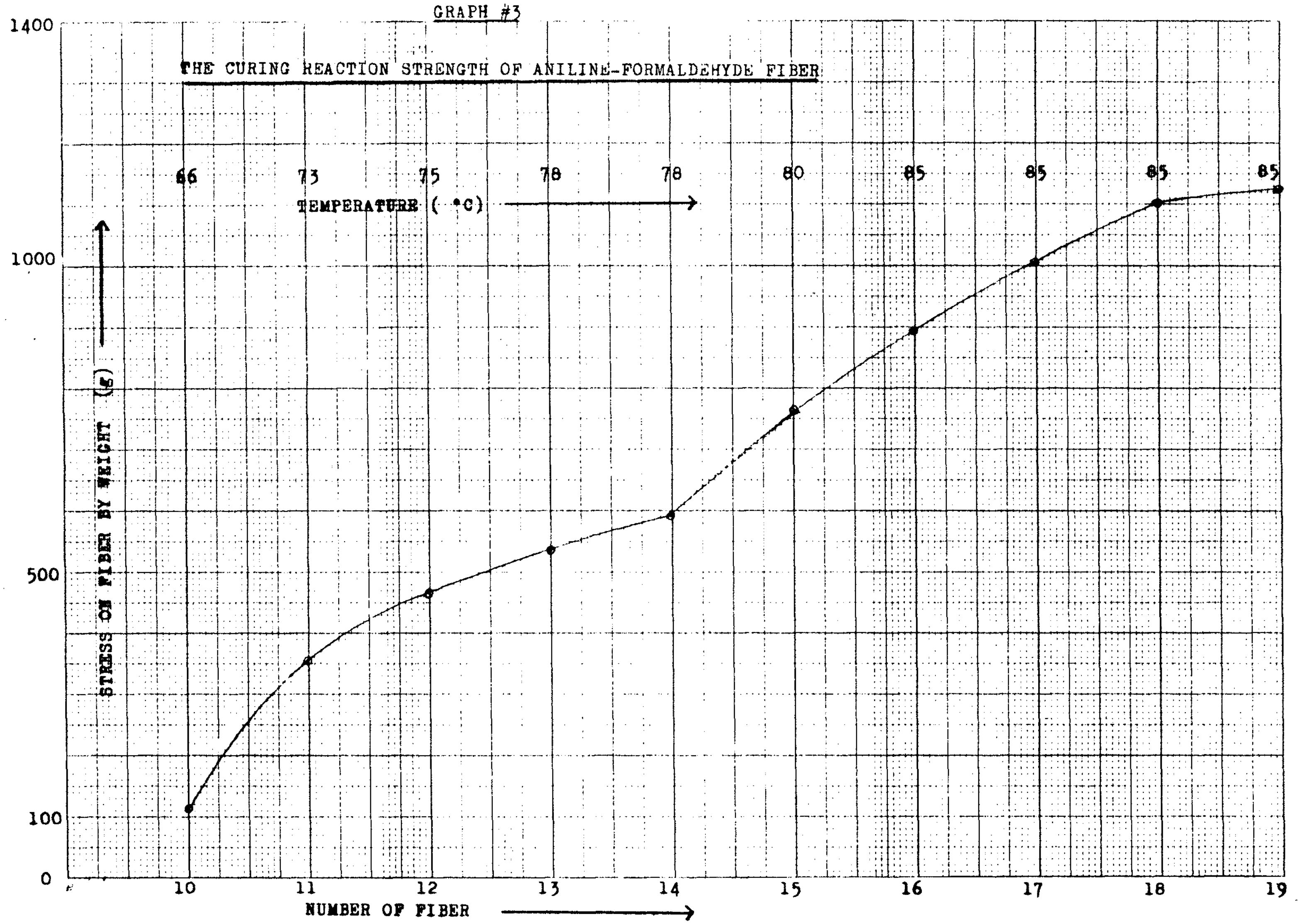
Overall curing of this reaction is not quite as successful since percentage of the decrease in curing is much larger than the percentage of increase in the curing. The result is that the curing was disturbed by adding too much $AlCl_3$ and CH_3OH, e.g., fibers #4, #21, and #29. Anyhow, the purpose of this experiment was not to obtain the best curing but rather to see how each of the components (co-catalyst, swelling agent, time and temperature) affected the curing reaction or observing the trend of the curing reaction.

GRAPH #1


THE CURING REACTION STRENGTH OF ANILINE-FORMALDEHYDE FIBER
25 25 25 49 50 50 5050 63 66 7375 78 78 80 85 85 85 85 89 95 95 boil 95
TEMPERATURE (°C)
STRESS ON FIBER BY WEIGHT (g)
1400
1000
500
100
0
1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30
NUMBER OF FIBERS

GRAPH #2

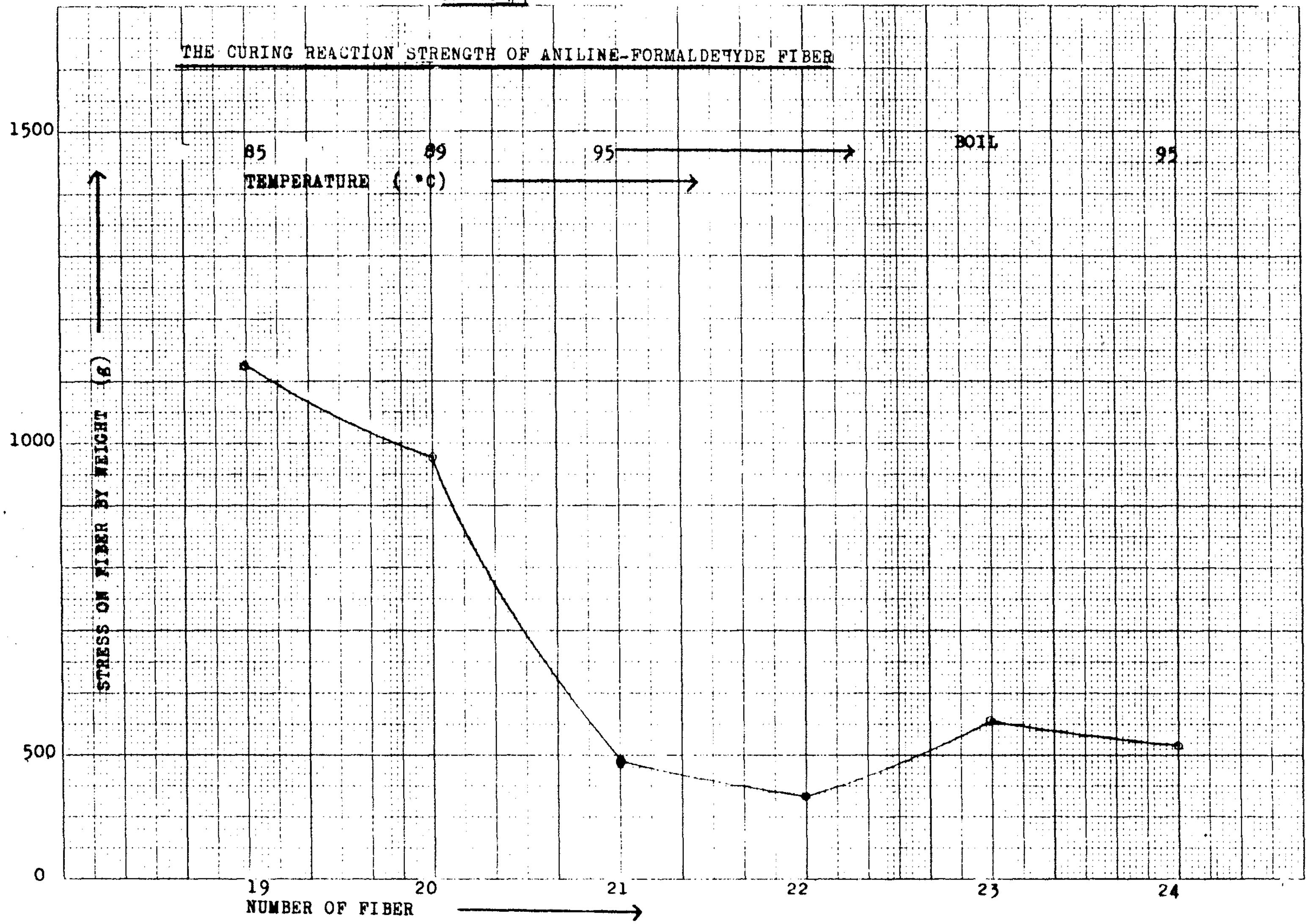

THE CURING REACTION STRENGTH OF ANILINE-FORMALDEHYDE FIBER
25
25
25
49
50
50
50
50
65
66
TEMPERATURE (°C)
STRESS ON FIBER BY WEIGHT (g)
140
100
50
10
0
1
2
3
4
5
6
7
8
9
10
NUMBER OF FIBER



GRAPH #3

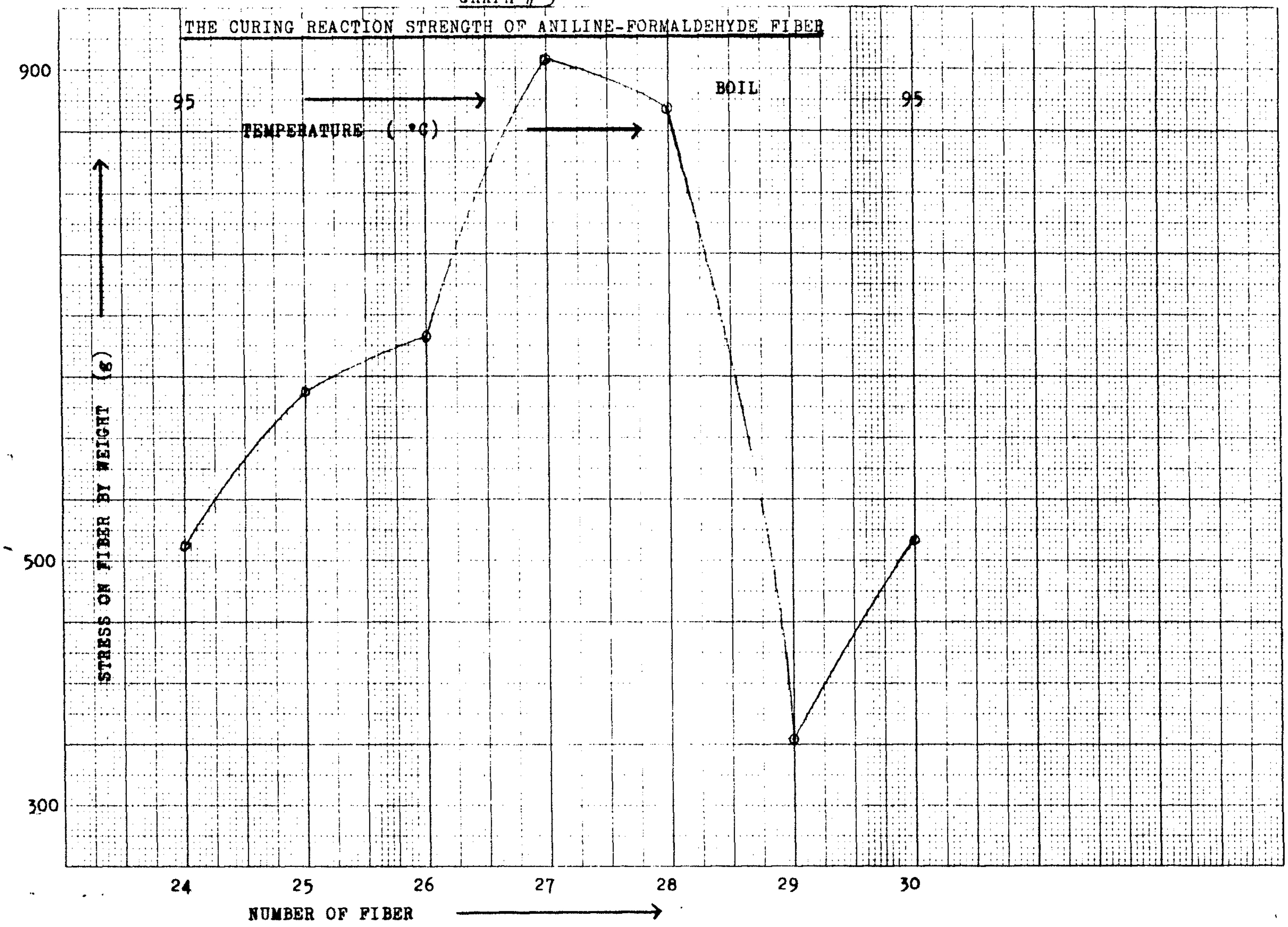
THE CURING REACTION STRENGTH OF ANILINE-FORMALDEHYDE FIBER

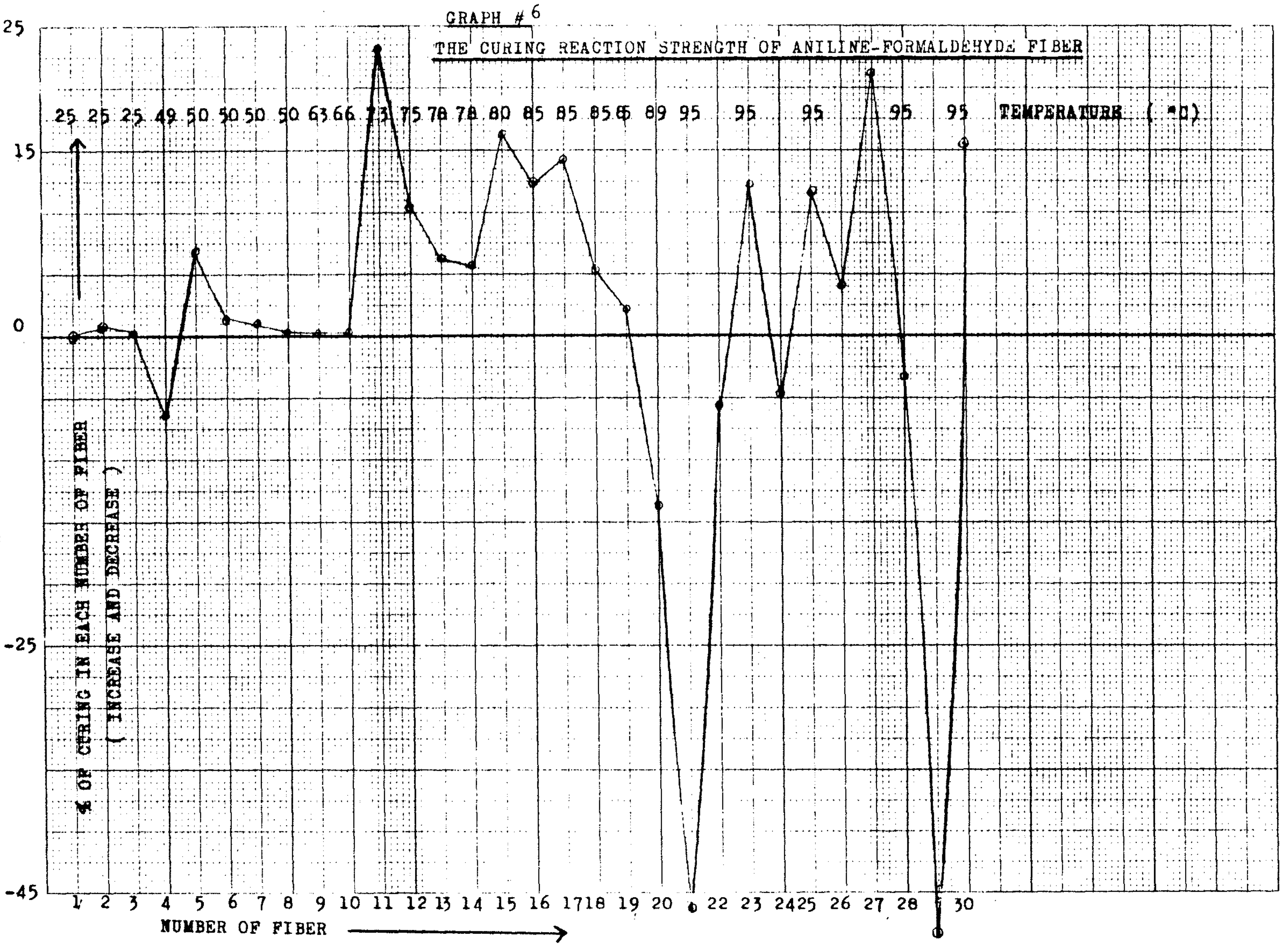
GRAPH #4


THE CURING REACTION STRENGTH OF ANILINE-FORMALDEHYDE FIBER
1500
1000
500
0
STRESS ON FIBER BY WEIGHT (g)
85
89
95
BOIL
95
TEMPERATURE (°C)
19
20
21
22
23
24
NUMBER OF FIBER

GRAPH # 5

THE CURING REACTION STRENGTH OF ANILINE-FORMALDEHYDE FIBER





GRAPH # 6

THE CURING REACTION STRENGTH OF ANILINE-FORMALDEHYDE FIBER

G. Suggested Curing Procedures

From the curing reaction strength of the former experiment I would suggest the folowing procedures for possibly better curing.

1. Place about 10 g of fiber (uncured) into 600 ml of curing liquor (320 ml of CH_2O, 37% solution + 240 ml of H_2O + 40 ml of NH_4OH, 36% solution and cool down at room temperature before use).
2. Close container and leave it for six hours at room temperature (25°C).
3. Then heat up slowly (one hour per 1°C) to 50°C (25 hours).
4. Add 0.1 g of $AlCl_3$ and ½ ml of CH_3OH after temperature reaches 50°C and raise temperature to 55°C (1 hour per 1°C) which takes five hours; keep temperature constant at 55°C for five hours.
5. Add 0.1 g of $AlCl_3$ and ½ ml of CH_3OH and raise temperature to 60°C (one hour per 1°C); keep temperature constant at 60°C for six hours.
6. Add 0.1 g of $AlCl_3$ and ½ ml of CH_3OH and raise temperature to 65°C (one hour per 1°C) and keep temperature constant at 65°C for 7 hours.
7. Add 0.1 g $AlCl_3$ and ½ ml of CH_3OH and raise temperature to 70°C (1 hour per 1°C) and keep temperature constant at 70°C for 8 hours.
8. Add 0.2 g of $AlCl_3$ and ½ ml of CH_3OH and raise

temperature to 75° C (1 hour per 1° C) and keep temperature constant at 75° C for 9 hours.

9. Add 0.2 g $AlCl_3$ and ½ ml CH_3OH and raise temperature to 80° C (1 hour per 1° C) and keep temperature constant at 80° C for 10 hours.
10. Add 0.2 g $AlCl_3$ and ½ ml CH_3OH and raise temperature to 85° C (1 hour per 1° C) and keep temperature constant at 85° C for 10 hours.
11. Add 0.2 g $AlCl_3$ and ½ ml CH_3OH and raise temperature to 90° C (1 hour 1° C) and keep temperature constant 90° C for 10 hours.
12. Add 0.2 g $AlCl_3$ and ½ ml CH_3OH and raise temperature to 95° C (1 hour per 1° C) and keep temperature constant at 95° C for 10 hours.
13. Add 0.2 g $AlCl_3$ and 2 ml CH_3OH and keep temperature constant (boil) 95° C for 5 hours.
14. Add 0.2 g $AlCl_3$ and 3 ml CH_3OH and keep temperature constant (boil) 95° C for 5 hours.
15. Add 0.2 $AlCl_3$ and 3 ml CH_3OH and keep temperature constant 95° C for 5 hours.
16. Add 0.2 g $AlCl_3$ and 3 ml CH_3OH and keep temperature constant 95° C for 24 hours.
17. Cool to room temperature, take out to clean and dry.

Solubility Test

A. Solubility of Aniline-formaldehyde fiber (uncured) from the resin of experiment #6

Solvents	Results			
	Dissolved completely	Partially dissolved	Did not dissolved	Others
Benzene	x	-	-	-
Ethylene glycol	x	-	-	-
Butyl alcohol	x	-	-	slowly
Nitric acid	x	-	-	-
Sulfuric acid	x	-	-	-
Hydrochloric acid	x	-	-	-
Acetone	x	-	-	-
Methyl alcohol	-	x	-	-
Ethyl acetate	-	x	-	-
Methyl ethyl ketone	-	x	-	-
N,N-Dimethyl-p-toluidine	-	-	x	-
Tetrahydrofuran	x	-	-	-
Bromotrichlorothane	x	-	-	-
Propolene glycol	-	-	x	broke into small pieces
A-Petroleum ether	x	-	-	slowly
Ethyl alcohol	-	-	x	became a resin
Glycerine	-	-	x	-
n-Butyl bromide	-	x	-	-
Toluene	-	x	-	-
Triethylene glycol	x	-	-	-
Chloroform	x	-	-	-
Acetic acid anhydride	-	x	-	-

B. Solubility of Cured Aniline-formaldehyde fiber

Solvents	Dissolved completely	Did not dissolved	Remained good fiber	Fiber dispersed
Benzene	-	x	x	-
Ethylene glycol	-	x	-	x
Butyl alcohol	-	x	-	x
A-Petroleum ether	-	x	x	-
Ethyl alcohol	-	x	x	-
Glycerine	-	x	-	x
n-Butyl bromide	-	x	-	x
Toluene		x	-	x
Nitric acid	x	-	-	-
Sulfuric acid	x	-	-	-
Hydrochloric acid	x	-	-	-
Acetone	-	x	x	-
Methyl alcohol	-	x	x	-
Ethyl acetate	-	x	-	x
Methyl ethyl ketone	-	x	-	x
Tetrahydrofuran	-	x	-	x
Bromotrichloromethane	-	x	-	x
Propolene glycol	-	x	-	x
N,N-Dimethyl-p-toluidine	-	x	x	-

5. Structural Analysis

Determination of functional groups of Aniline-Formaldehyde Fiber, Aniline-Phenol-Formaldehyde Fiber, Cured and Uncured by IR and NMR.

A. Characteristic Infrared Absorptions of Functional Groups and [11] Spectrum of Aniline — Formaldehyde Fiber (uncured)

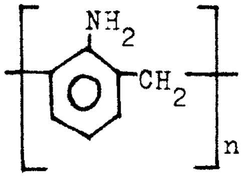
Group	Intensity (reference)	Range(cm^{-1}) (reference)	Spectra of Aniline — Formaldehyde Fiber (uncured)	Intensity Aniline — Formaldehyde Fiber (uncured)
Amines				
N — H Stretching vibrations	(m)	~ 3,500	3,500	(w)
Primary, free, two bands	(m)	~ 3,400	3,400	(m)
Secondary, free, one bands	(m)	3,500 ~ 3,310	3,420	(m)
N — H Bending vibrations				
Primary	(s — m)	1,650 — 1,590	1,650	(s-m)
Secondary	(w)	1,650 — 1,550		
C — N Vibrations				
Aromatic, primary	(s)	1,340 - 1,250	1,300	(m)
Aromatic, secondary	(s)	1,350 - 1,280		
Aromatic, tertiary	(s)	1,360 - 1,310		
C — H Stretching				
Aromatic	(v)	~ 3,030	3,080	(w)
C — H Bending				
Aromatic, substitution				
Three adjacent hydrogen atoms	(v,m)	~ 780	780	(m)
Two adjacent hydrogen atoms	(v,m)	~ 830	835	(m)
One hydrogen atoms	(v,m)	~ 880		
C—C Multiple Bond Stretching				
Aromatic	(v)	~ 1,600	1,625	(w)
	(v)	~ 1,580	1,540	(s)
	(m)	~ 1,500		
	(m)	~ 1,450	1,460	(w)
C—H Stretching, Alkane	(m-s)	2,962 — 2,853	2,965	(m)
C—H Bending, Alkane —CH$_2$	(m)	1,485 — 1,445	1,440	(w)

Discussion and Results

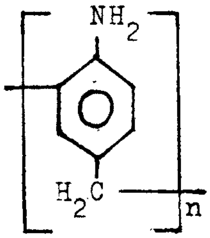
Primary amines[11]

1. Range 3,500 - 3,200 (cm^{-1})(m)
2. Range 1,645 - 1,555 (cm^{-1})(s)
3. Range 1,340 - 1,250 (cm^{-1})(s)
4. Range 800 - 640 (cm^{-1})(m)

Secondary amines and tertiary amines have a similar spectra in the range of 1, 2, 3. of primary amines. But neither of them have spectra in the range between 800 cm^{-1} -640 cm^{-1}(m). For the spectrum of aniline-formaldehyde fiber (uncured) shows the peak at 780 cm^{-1} (w) and 835 cm^{-1}(m). Therefore one can conclude that this aniline-formaldehyde fiber (uncured) did not have polymerization occur at NH_2 rather it occured at the benzene ring; formaldehyde will attach at the ring position form the methylene bridge. This structure is likely to occur for this type of polymer.



or

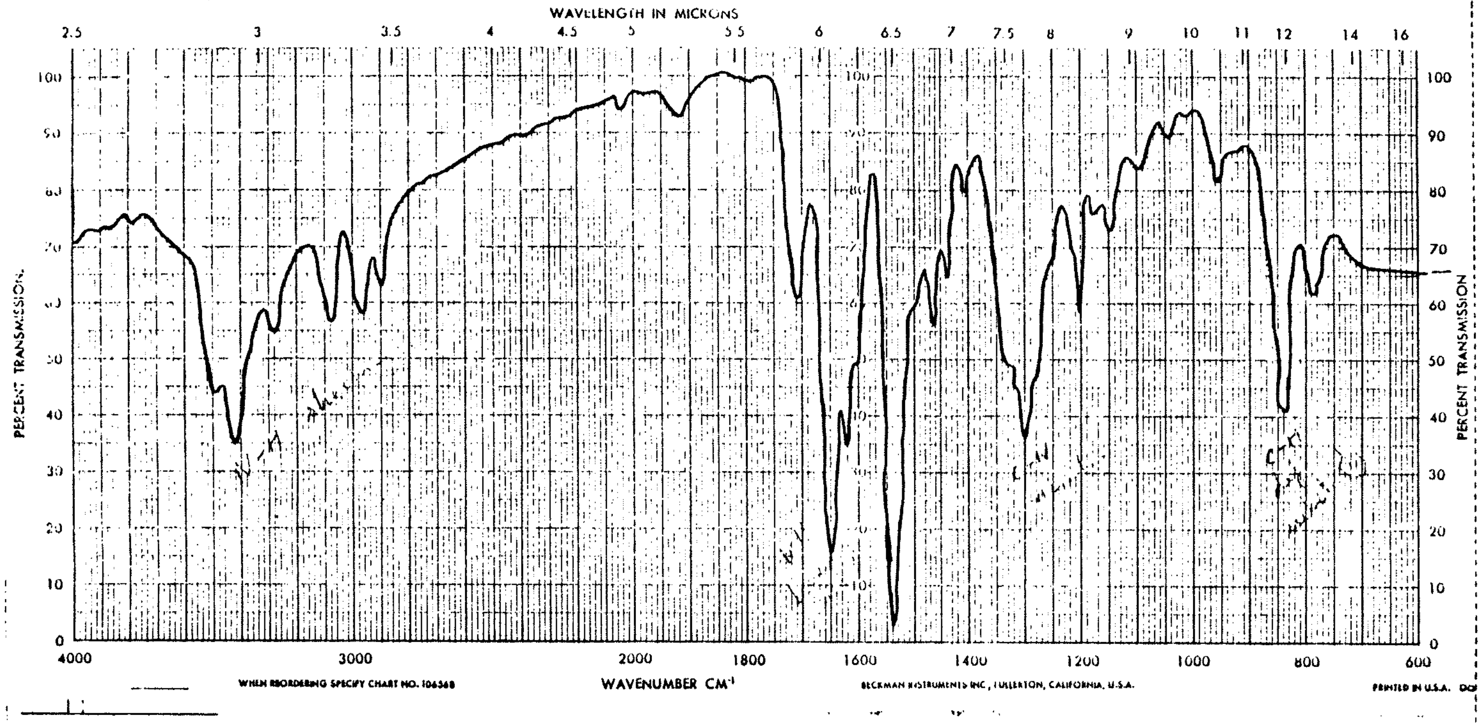


To prove that the methylene attaches at the benzene ring by investigation of aromatic substitutes. Vicinal trisubstitutes show spectra ranges at the following:

		Reference Values		Experimental Values
1.	Range	3,150 - 2,900 (cm^{-1})		3,800 and 2,970 & 2,900
2.	Range	1,620 - 1,540 (cm^{-1})		1,540 (cm^{-1})
3.	Range	1,500 - 1,450 (cm^{-1})		1,470 (cm^{-1})
4.	Range	1,180 - 1,140 (cm^{-1})		1,150 (cm^{-1})
5.	Range	1,100 - 1,070 (cm^{-1})		1,100 (cm^{-1})
6.	Range	1,050 - 960 (cm^{-1})		1,040 and 960 (cm^{-1})
7.	Range	800 - 760 (cm^{-1})	(s)	835 and 780 (cm^{-1})
8.	Range	750 - 680 (cm^{-1})	(w)	———
9.	No peak from	680 - 400 (cm^{-1})		No peak from 780 - 600 (cm^{-1}) (11)

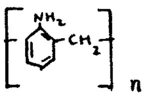
For aromatic, orth, meta and para disubstitute, unsymmetric →  symmetric →  have spectrum very similar to vicinal trisubstitute.[12] Therefore it is very difficult to decide specific positions. One can assume that this polymer probaby has a random position in the benzene ring rather than only one particular position.

C-H stretching, alkane (m-s) - range 2,962-2,853 for reference value and found for experimental value at 2,965 (m). -CH$_2$- appears at 1,440 and 1,465 (m) for experimental value, and for reference value C-H bending, alkane -CH$_2$- in the range of 1,485-1,445 (m).



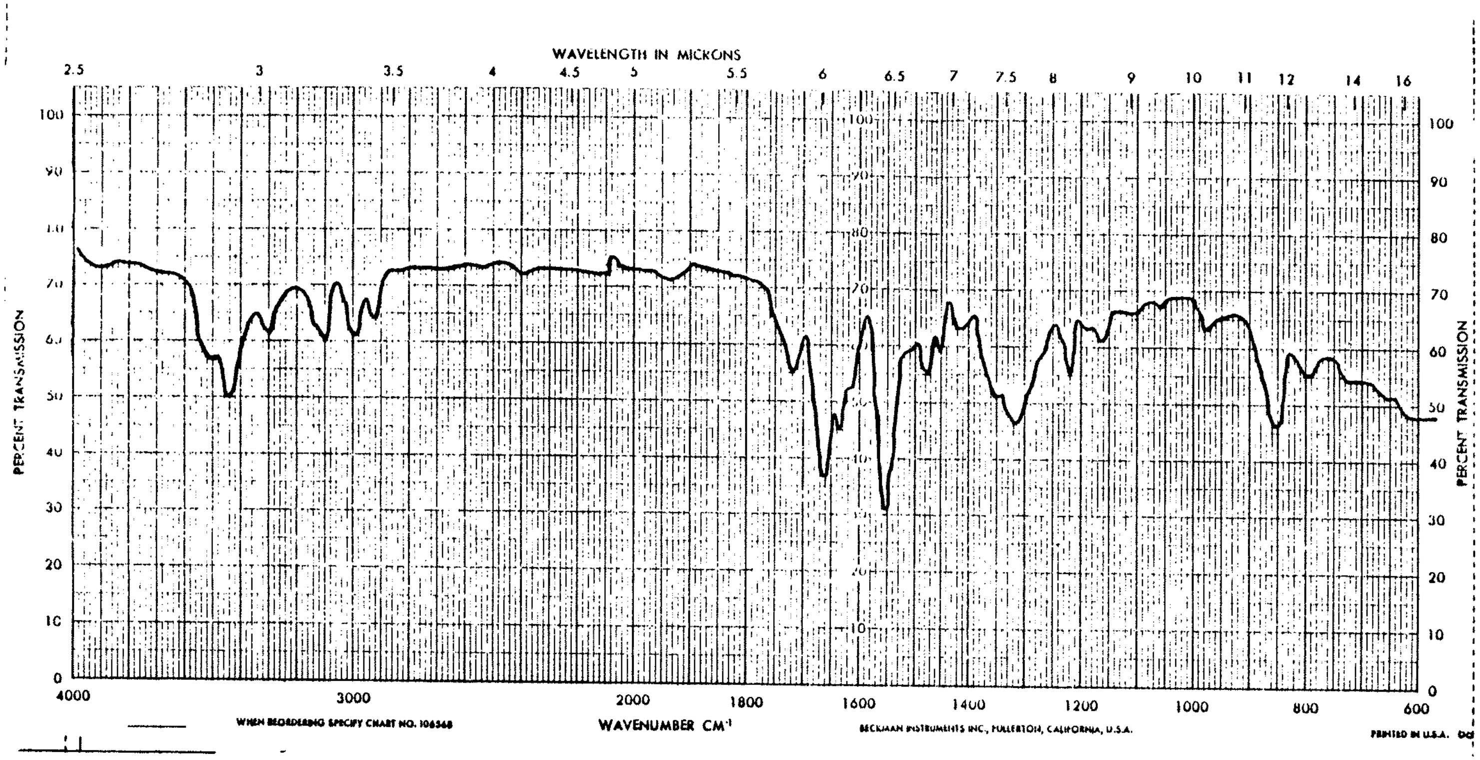
SAMPLE Uncured Aniline - Formaldehyde Fiber
(aniline - formaldehyde resin, linear polymer)

STRUCTURE



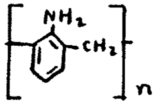
CONCENTRATION 20 mg of KBr
1 mg of sample

Preparation KBr



SAMPLE Uncured Aniline - Formaldehyde Fiber
(aniline - formaldehyde resin, linear polymer)

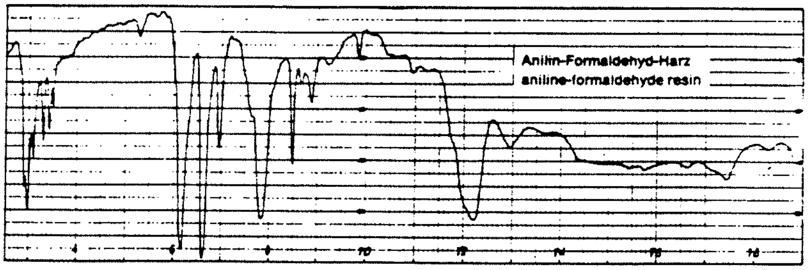
STRUCTURE



SOLVENT Acetone

Preparation NaCl, cell thickness $\frac{1}{4}$"

(13)



Hersteller:	**Dr. Beck & Co.**	Manufacturer:	**Dr. Beck & Co.**
Zusammensetzung:	**Anilin-Formaldehyd-Harz, schmelzbar**	Composition:	**aniline-formaldehyde resin, fusible**
Verwendung:	**Kombinationsharz für Elektroisolierlacke**	Use:	**combination resin for insulating varnishes**
Praparation:	**KBr (4/1000)**	Preparation:	**KBr (4/1000)**
Dezimalziffer:	**8.22**	Decimal No.:	**8.22**

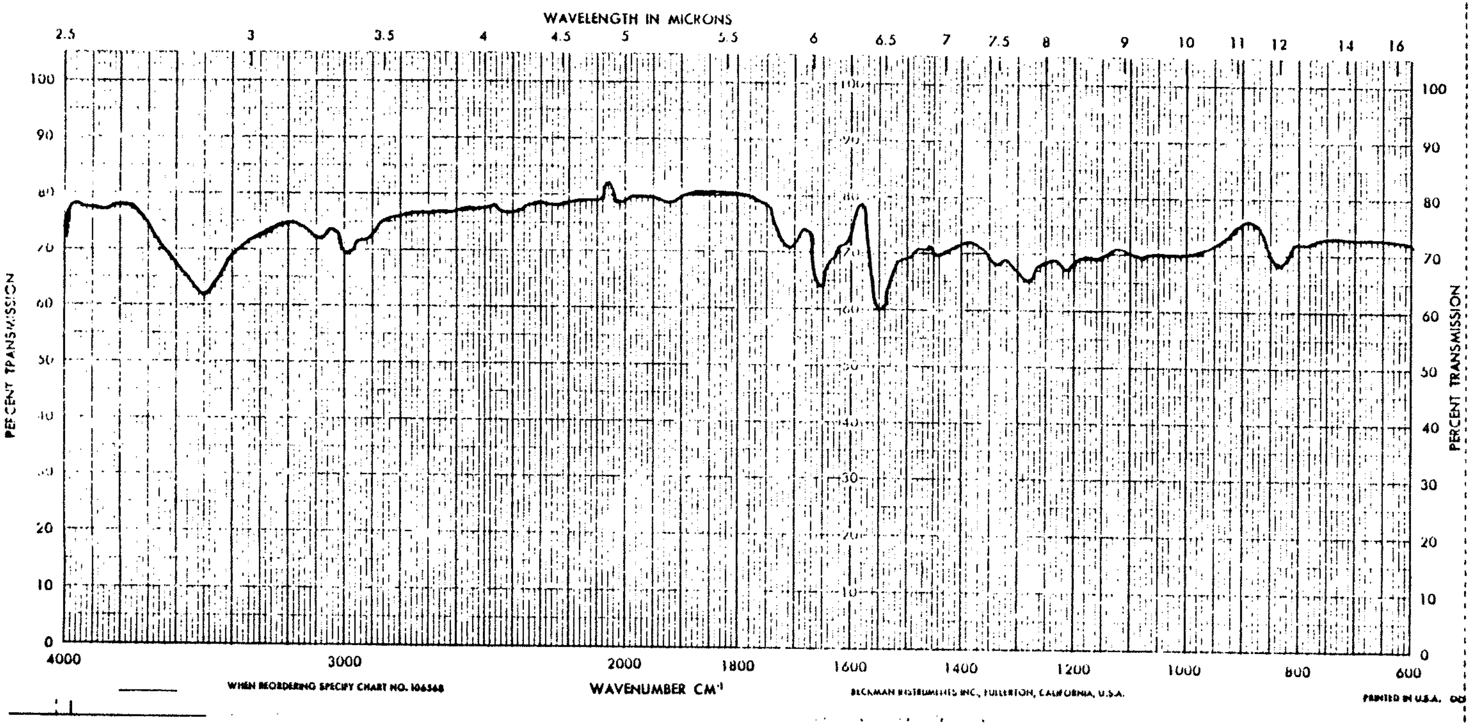
B. Results of Cured Aniline - Formaldehyde Fiber

Peak of uncured fiber (cm^{-1})	Intensity uncured fiber	Peak of cured fiber (cm^{-1})	Intensity cured fiber
3500	(w)	3500	(w)
3080	(w)	3100	(vw)
2970	(w)	3000	(vw)
2900	(w)	disappear	-
2050	(w)	disappear	-
1940	(w)	disappear	-
1650	(s-m)	1655	(w)
1540	(s)	1550	(w)
1460	(w)	disappear	-
1300	(m)	1280	(vw)
1200	(w)	1220	(vw)
1150	(w)	1150	(vw)
1100	(w)	disappear	-
1040	(w)	disappear	-
960	(w)	disappear	-
835	(m)	835	(w)
780	(w)	780	(vw)
3420	(m)	disappear	-
2965	(m)	disappear	-

s = strong
m = medium
w = weak
vw = very weak
s-m = strong-medium

Discussion of Aniline-formaldehyde fiber (cured)

The spectrum of cured aniline-formaldehyde fiber has peaks similar to the uncured one. Most of the peaks reduce their size to much smaller peaks and quite a few peaks disappear such as peaks at 3500, 2900, 2965, 2050, 1940, 1460, 1100, 1040 and 960. This evidence probably proves that the curing takes place in these specific areas.



SAMPLE Cured Aniline -Formaldehyde Fiber
Crosslink Polymer

CONCENTRATION 20 mg of KBr
1 mg of sample

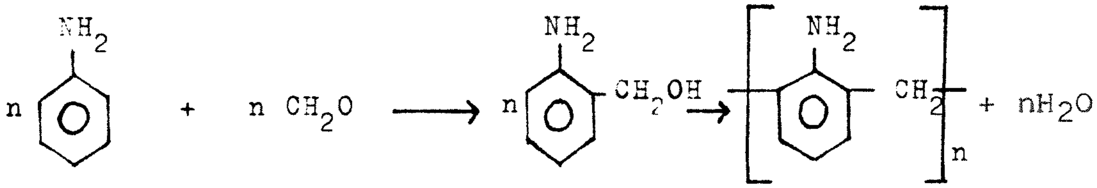
Preparation KBr

C. Characteristic Infrared Absorption of Functional Groups and[11] Spectra of Aniline — Phenol — Formaldehyde Fiber, Copolymer (Uncured)

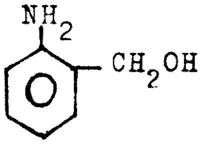
Group	Intensity (reference)	Range (cm^{-1}) (reference)	Spectra of Aniline — Phenol — Formaldehyde Fiber (uncured)	Intensity of Aniline — Phenol — Formaldehyde Fiber (uncured)
<u>Phenol</u>				
O—H Bending and	(s)	~ 1200	1200	(w)
C—O Stretching vib.	(s)	1410-1310	1290	(m, b)
O—H Polymeric association	(s, b)	3400-3200	3250	(w)
<u>Anline</u>. Primary				
N—H Stretching vib.	(m)	~ 3500	3500	(w)
two bands	(m)	~ 3400	3400	(w)
N—H Bending vib.	(w)	1650-1590	1640	(w)
C—N Vibrations, Aromatic	(5)	1340-1250	1290	(m, b)
<u>Aromatic</u>				
C—H Stretching	(v)	~ 3030	3050	(w)
C—H Bending vib.	(v, m)	~ 780	780	(m)
C—C Multiple Bond Stretching vib.	(v)	~ 1600	1620	(m)
	(v)	~ 1580	1540	(m)
	(m)	~ 1500	1480	(m)
	(m)	~ 1450	1440	(w)
<u>Alkane</u>				
C—H Stretching vib.	(m, s)	2962-2853	2950	(b, w)
C—H Bending —CH_2—	(m)	1485-1445	1480	(w)

Discussion of Uncured and Cured Aniline-Phenol-Formaldehyde Fiber

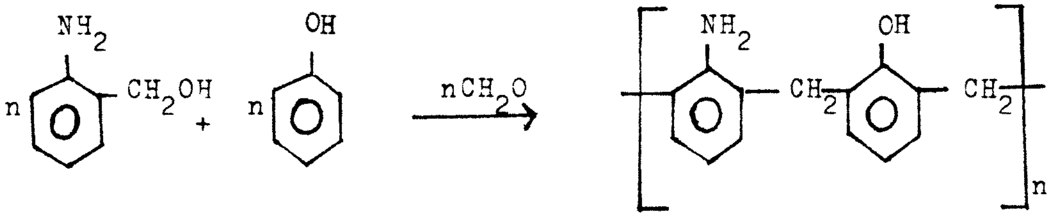
Spectrum of uncured aniline-phenol-formaldehyde fiber shows peaks of N-H and O-H, which proves that this fiber contains aniline and phenol. There are peaks shown at 3500 cm^{-1} for primary amine. O-H and C-O stretching of phenol shows 2 peaks distinctively at 1200 cm^{-1} and 1290 cm^{-1}. C-H stretching vib. and bending of alkane ($-CH_2-$)shows peaks at 2950 cm^{-1} and 1480 cm^{-1}. One can assume that the reaction of aniline-phenol-formaldehyde polymer (linear) can be written as the following:



some of



possible react with phenol later



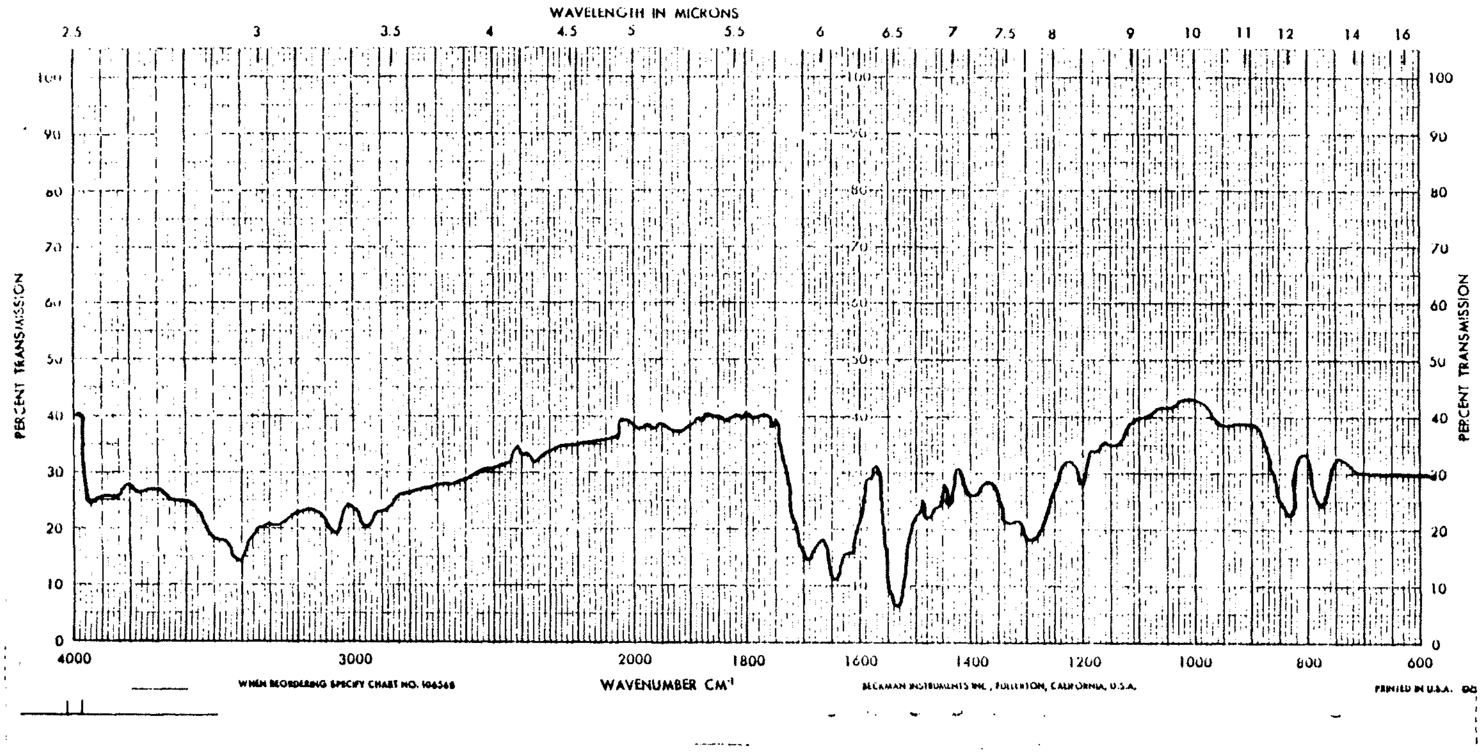
Linear polymer

+

2n H_2O

Since aniline was allowed to react with formaldehyde first, they formed methylol groups. Then some of them probably form a linear aniline-formaldehyde resin and some of the others will react further with phenol to form aniline-phenol-formaldehyde resin (linear polymer) by further condensation.
The processe of anilin-phenol-formaldehyde polymer is called condensation polymerization or step-reaction, which is formed by interunit functional groups.

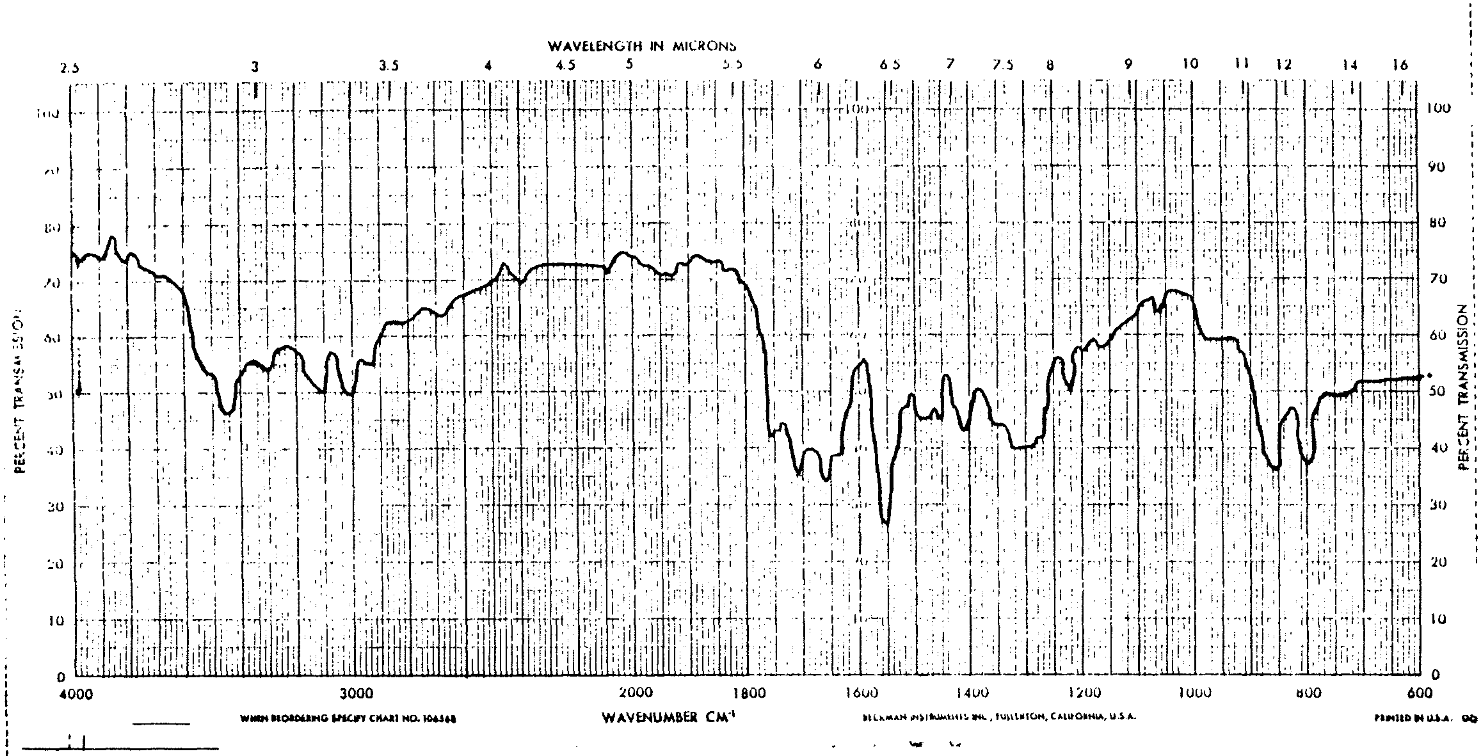
The spectrum of cured aniline-phenol-formaldehyde fiber shows a similarity to the spectrum of uncured fiber. But most of the peaks are shorter and smaller peaks at 780 cm^{-1} and 2900 cm^{-1} almost disappear, and other peaks have very weak absorption. It appears that curing changes the spectrum.



SAMPLE Uncured Aniline - Phenol - Formaldehyde Fiber
(aniline - phenol - formaldehyde resin, linear
copolymer) --- Ratio 2:1

CONCENTRATION 20 mg of KBr
1 mg of sample

Preparation KBr

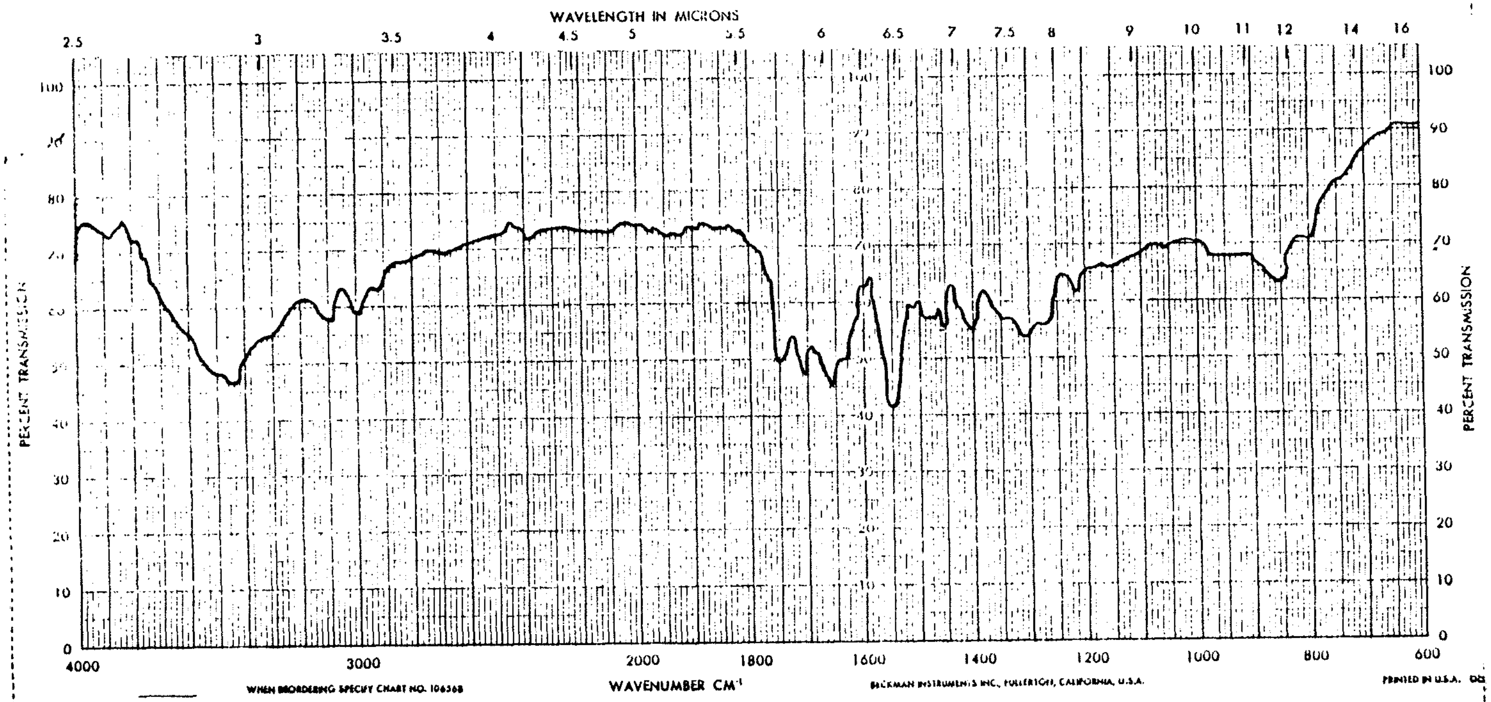


SAMPLE Uncured Aniline - Phenol - Formaldehyde Fiber
(aniline - phenol - formaldehyde resin,
copolymer) Ratio 2:1

SOLVENT Acetone

CONCENTRATION Large sample

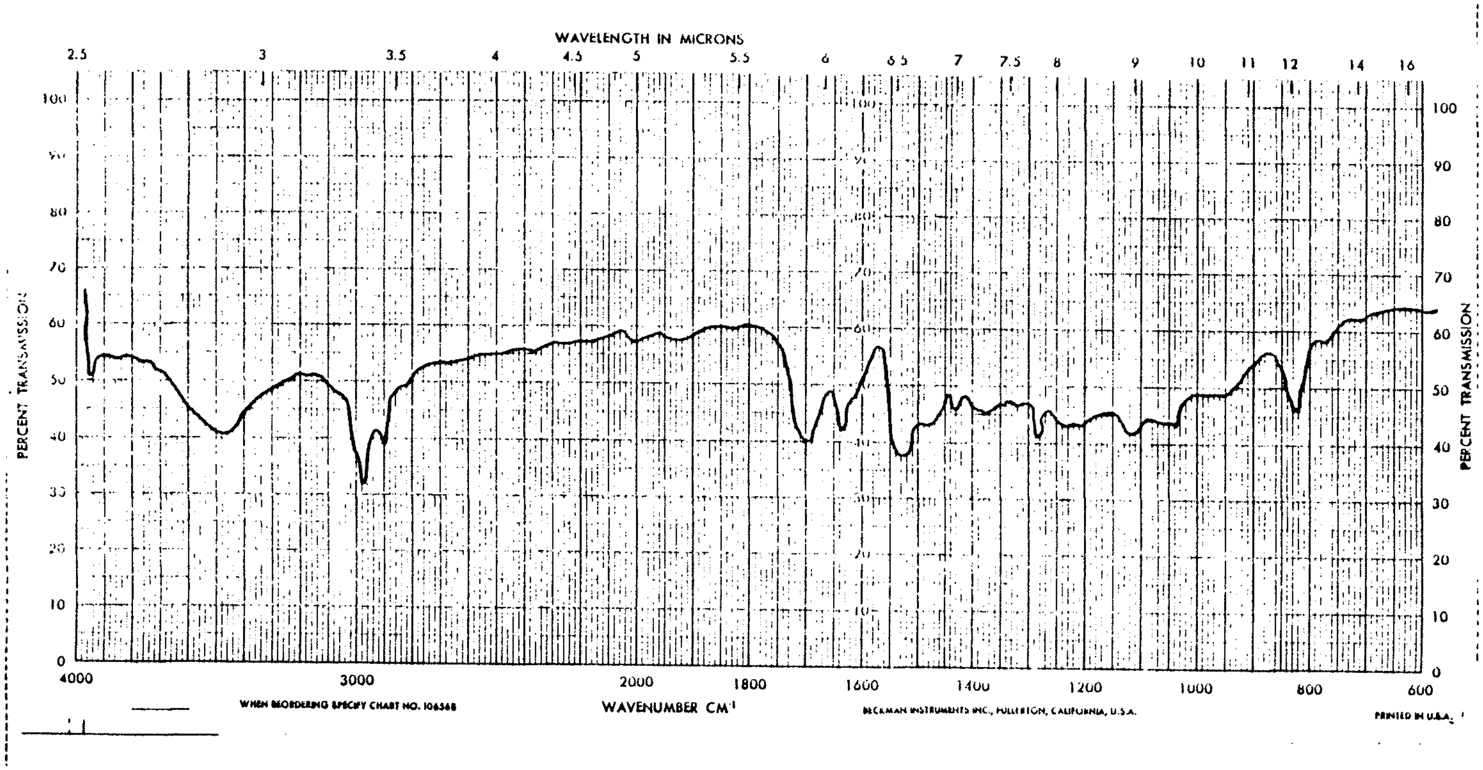
Preparation NaCl, cell thickness $\frac{1}{4}$"



SAMPLE Uncured Aniline - Phenol - Formaldehyde Fiber
(aniline - phenol - formaldehyde resin,
copolymer) ---- Ratio 2:1

SOLVENT Acetone
CONCENTRATION Small sample

Preparation NaCl, cell thickness $\frac{1}{4}$"



SAMPLE Cured Aniline - Phenol - Formaldehyde Fiber
Crosslink copolymer, Ratio 2:1

CONCENTRATION 20 mg of KBr
1 mg of sample

Preparation KBr

D. Results of Uncured Aniline-Formaldehyde Fiber (Resin) Spectrum by NMR

Aromatic protons appear between 6.8 - 8.0 δ

CH_2 overlapping with NH_2 appear between 3.5 - 4.2 δ

TMS appear at 0.0 δ

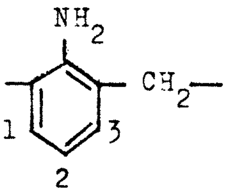
On the chart, data shows the following:

PPM	HEIGHT(%)
7.253	2.447
6.995	0.726
6.908	1.039
6.641	0.848
6.560	0.708
3.757	1.287
0.588	0.262
0.034	1.361
0.000	67.268 OVER FLOW
-0.593	0.469

Analysis and Discussion

Resins which are prepared by the reaction of formaldehyde with an excess of aniline will form a linear polymer in which aromatic rings are joined by methylene bridges. They can possibly form as ortho, meta and para isomers. This possible result will cause a complex aromatic spectrum in NMR for these possible isomers shows the following:

Ortho isomer

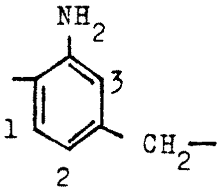


A. Hydrogen at position 1 spilt into two peaks, because it has one neighbor proton at position 2.

B. Hydrogen at position 2 spilt into three peaks, because it has two neighbor protons at position 1 and 3.

C. Hydrogen at position 3 spilt into two peaks from proton position 2.

Meta isomer

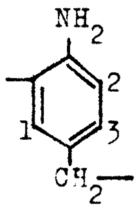


A. Hydrogen at position 1 will spilt into two peaks.

B. Hydrogen at position 2 will spilt into two peaks.

C. Hydrogen at position 3 will spilt into one peak.

Para isomer



A. Hydrogen at position 1 will spilt into one peak.

B. Hydrogen at position 2 will spilt into two peaks.

C. Hydrogen at position 3 will spilt into two peaks.

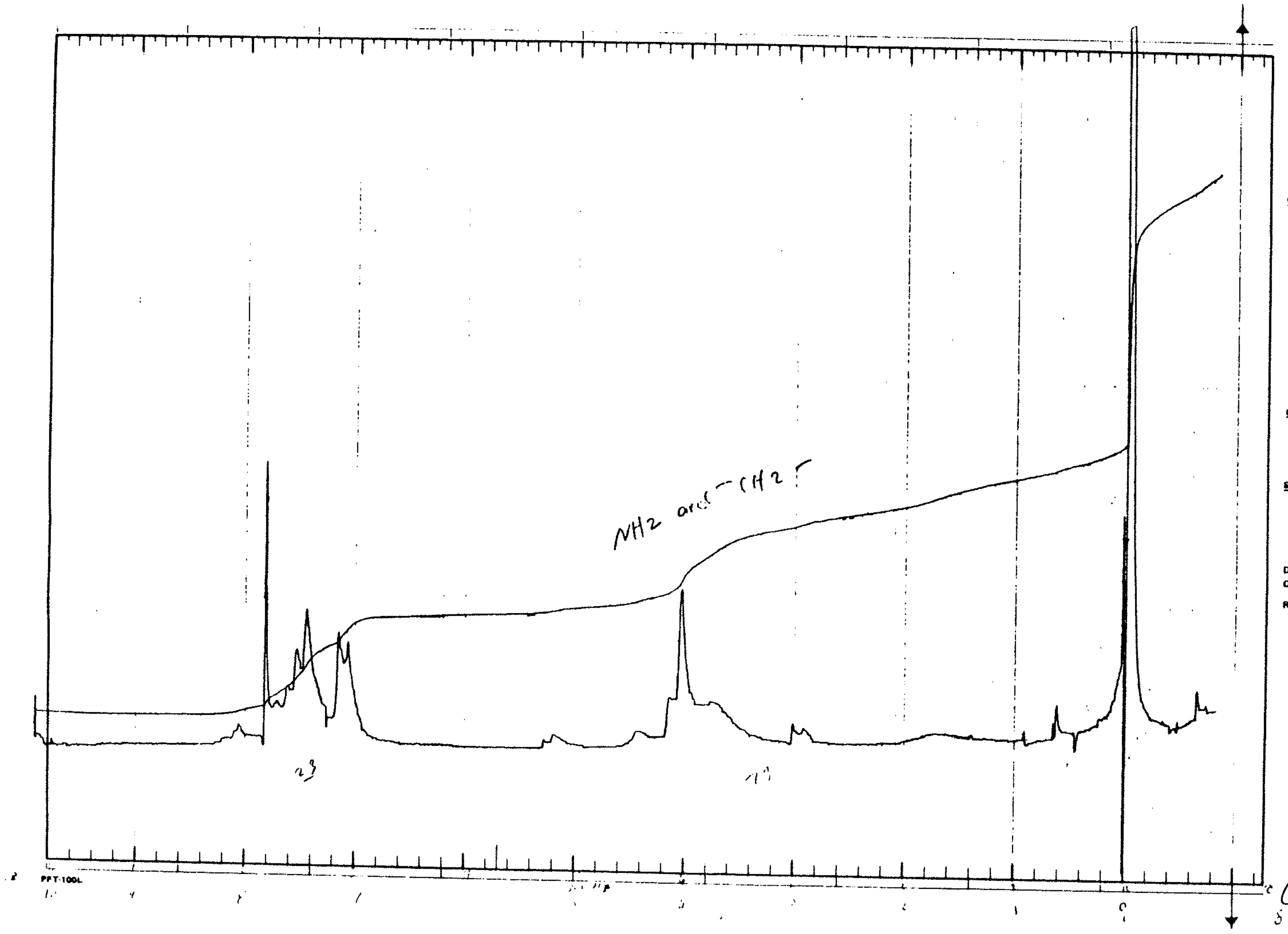
Most of the time the above theoretical peaks for hydrogen splitting are not clear on the spectrum, but multiple peaks did appear. These were caused by interference from neighboring hydrogens.

This analine-formaldehyde spectrum does not show hydrogen peaks clearly. This is possibly due to poor resolutions on spin - spin coupling. One literature source which supports above conclusion stated "The amine-formaldehyde resins usually produce poorly resolved NMR spectra. With the exception of modifying groups such as butylated urea, the main feature of their spectra arises from the isolated methylene groups which are formed. Since the type of substitution is variable (e.g. $-O-CH_2-O-$, $-O-CH_2-N-$, $-N-CH_2-N-$) as well as their position network, these bands resonate over a very broad region (4.0 - 5.0 ppm) and are poorly resolved. Little information concerning the actual structure of these resins is provided by NMR." [16]

John R. Dyer, author of, <u>Applications of Absorption Spectroscopy of Organic Compounds</u>, states that, "Aromatic protons of substuted benzenes generally absorb in the range 2.0 - 3.5 τ (8 - 7.5δ). Electron - withdrawing groups shift the absorption to a lower field, and electron - donating groups shift the absorption to a higher field because of the locul dimagnetic shielding effect. The effect on the ring proton chemical shifts caused by a substitute group is greatest for the ortho proton and least for the meta proton. Aniline shows at

3.49 τ (6.51δ), 1.08τ(8.92δ), meta at 2.93τ(7.07δ), 1.02τ(8.98δ) and para at 3.35τ(6.65δ), 1.06τ(8.94δ)." [17]

In order to support the agument about protons of CH_2 overlapping with NH_2, one can observe the spectrum of aniline (see page 89), protons of NH_2 appear singlet at 3.3δ and aromatic protons appear a range of 6.3 - 7.25δ.



SPECTRUM NO. ________
SAMPLE ________
SOLVENT ________
CONC. ________
REFERENCE ________
TEMP. ________ C°

OBSERVE
NUCLEUS ________
FREQ. ________ MHz
PULSE: ☐Sing. ☐Mult. ________
WIDTH ________ μ sec.
INTERVAL ________ SEC
REPETITION ________ SEC
DATA POINTS ________
WINDOW EXPONENTIAL T,C.= ________
MODE ________
SPECTRUM WIDTH ________ KHz
FILTER ________ KHz
AMPL. ________
NO. of SCANS ________

LOCK ☐INT. ☐EXT. ________
FREQ. ________ MHz (____)
SIGNAL ________
LEVEL RF ________ AF ________

SPIN DECOUPLER
FREQ. ________ HZ (____)
POWER ________ B.W. ________ KHz
MODULATION ________
☐CW ☐Noise ☐EXT. ________

DATE ________
OPERATOR ________

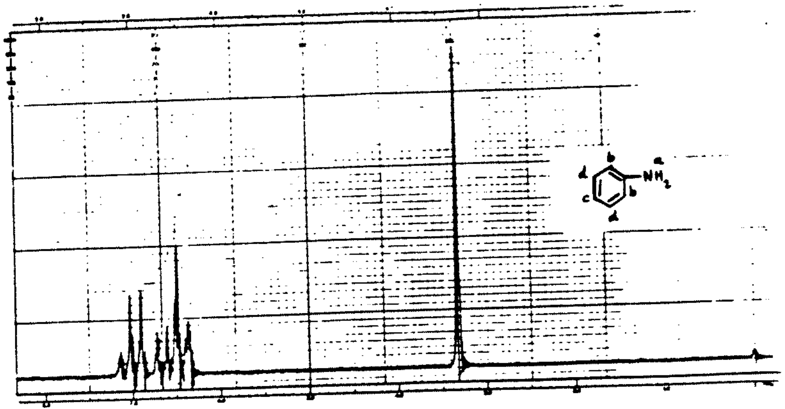
REMARKS:

```
•CONTROL DISP:IV
•CONTROL _?
•CONTROL ZERO•      4.09 SEC
•CONTROL CONST
 C1 =     50 SCANS : 5
 C_?
•CONTROL ZERO•      4.09 SEC
•CONTROL ACCUM END
•CONTROL DISP:D DISP:H
•CONTROL ZERO•      4.09 SEC
•CONTROL CONST
 C1 =      5 SCANS : 1
 CZ_?
•CONTROL ACCUM END
•CONTROL DISP:D DISP:H_?
•CONTROL ACCUM_?
•CONTROL ZERO•      4.09 SEC
•CONTROL ACCUM END
•CONTROL DISP:D DISP:H
•CONTROL CONST
 C1 =      1 SCANS : 200
 C_?
•CONTROL ZERO•      4.09 SEC
•CONTROL ACCUM END
•CONTROL DISP:D DISP:H
•CONTROL ZERO•      4.09 SEC
•CONTROL CONST
 C1 =    200 SCANS : 1
 C_?
•CONTROL ZERO•      4.09 SEC
•CONTROL ACCUM END
•CONTROL DISP:D DISP:H
•CONTROL ZERO•      4.09 SEC
•CONTROL CONST
 C1 =      1 SCANS : 1000
 C1 =   1000 SCANS : 100
 C_?
•CONTROL ZERO•      4.09 SEC
•CONTROL ACCUM END
•CONTROL DISP:D DISP:H$STOR_?
•CONTROL REDUC  NOISE(%)=      0.18  REFERENCE=
RESOLUTION=      0.24 HZ


   NO.    POSIT   FREQ(HZ)       PPM       HEIGHT(%)
     1     813     724.60       7.246      2.447  ••••••••••
     2     919     698.73       6.987      0.726  •••
     3     954     690.18       6.902      1.037  ••••
     4    1064     663.33       6.633      0.848  •••
     5    1097     655.27       6.553      0.708  ••
     6    2245     375.00       3.750      1.287  •••••
     7    3543      58.10       0.581      0.262  •
     8    3770       2.68       0.026      1.361  •••••
     9    3784      -0.73      -0.007     67.264   OVER FLOW
    10    4027     -60.05      -0.600      0.469  •
•CONTROL REDUC  NOISE(%)=      0.18  REFERENCE= 3784
RESOLUTION=      0.24 HZ


   NO.    POSIT   FREQ(HZ)       PPM       HEIGHT(%)
     1     813     725.34       7.253      2.447  ••••••••••
     2     919     699.46       6.995      0.726  •••
     3     954     690.91       6.909      1.037  ••••
     4    1064     664.06       6.641      0.848  •••
     5    1097     656.00       6.560      0.708  ••
     6    2245     375.73       3.757      1.287  •••••
     7    3543      58.83       0.588      0.262  •
     8    3770       3.41       0.034      1.361  •••••
     9    3784       0.00       0.000     67.264   OVER FLOW
    10    4027     -59.32      -0.593      0.469  •
•CONTROL DISP:H
•CONTROL DISP:IV
```

Fig 6.2



(18)

ANILINE

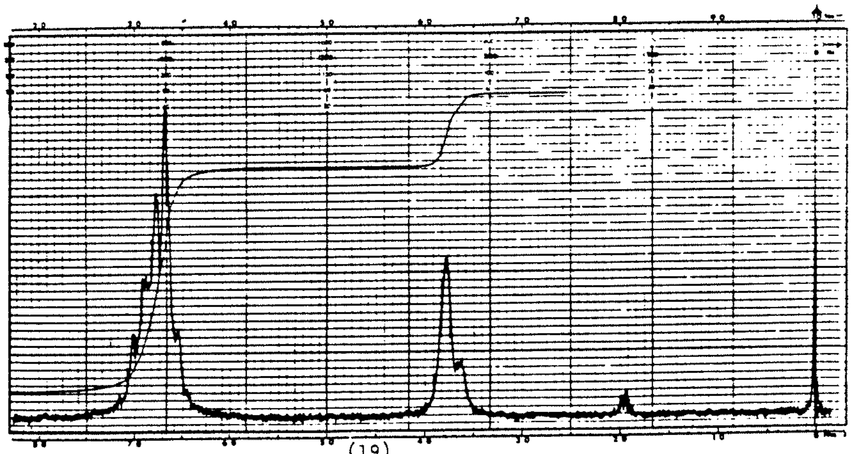
C_6H_7N Mol. Wt. 93.12 B. P. 184.4°C (lit.)

Source: Allied Chemical Corp., New York, N. Y.

Filter Bandwidth: 4 cps
Sweep time 250 sec
Sweep width 500 cps
Sweep offset - cps
Spectrum amp 5
Integral amp 80 (spec. amp. 2.5)
Conc. 30mg/0.5ml CCl_4

ASSIGNMENTS

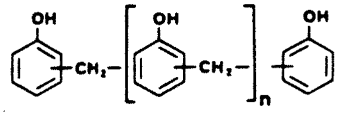
a 3.32
b 6.44
c ca 6.59
d 6.99
e
f
g
h
i
j



(19)

PHENOL-FORMALDEHYDE NOVOLAK

Solvent: Acetone-d6

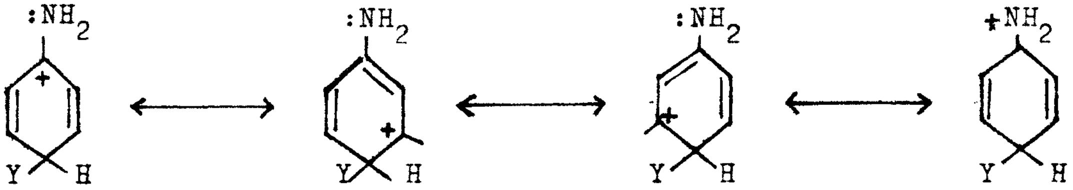


III DISCUSSION, RESULTS AND CONCLUSION

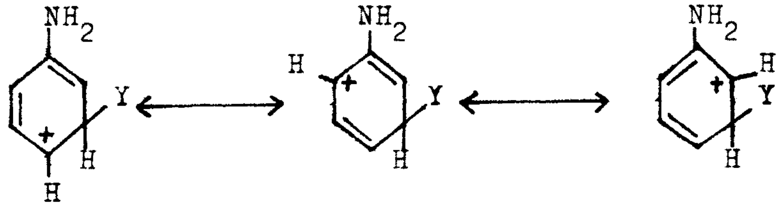
The aniline-formaldehyde resin structure is proved by IR. This shows that formaldehyde was attached at the aromatic ring to form a methylene group. The $-CH_2-$ peak appears at this region (1440 cm^{-1}) and two peaks in the region which indicate primary amine absorption (3500 + 3400 cm^{-1}). NMR gives spectrum which helps to confirm that methylene groups will possibly attach at the aromatic ring in the para and othro positions.

According to the spectrum and literature sources, the possible isomers will be ortho and para isomers. When aniline is attacked by an electrophil at the aromatic ring it will form resonance forms as follows:[14]

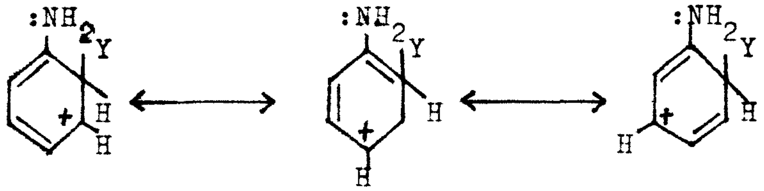
Para attack



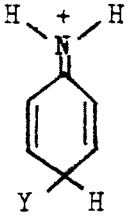
Meta attack



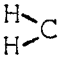
Ortho attack



The most important intermediate form is



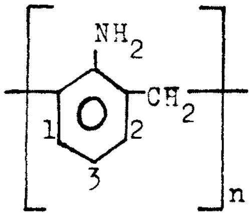
In this form and only this form, each of the atoms has a complete octet of electrons. A carbonium ion, with its sextet of electrons, tends to be highly unstable compared to an ammonium ion, into which the nitrogen has a complete octet. In this particular resonance form we essentially have an ammonium ion (actually an immonium ion), a much more stable sort of thing than the alternative carbonium ions. This resonance form can result only if the substitution into the ring has occurred at an ortho or para position. Thus aniline is a powerful ortho, para director, as a powerful activating group.

Aldehyde (formaldehyde →  $\mathrm{H_2C = 0}$) is a carbonyl group which acts as Lewis acid or electrophile (By the Lewis definition an acid species capable of accepting an electron pair, reagents which are electron - seeking, hence Lewis acids may be termed electrophiles or electron - loving).[15] Therefore formaldehyde will attach to the aniline aromatic ring at orth and para positions.

The cured fiber IR spectrums show shrinking peaks and some of the peaks disappear when compared to uncured fiber spectrums. Also checking physical properties of fibers by testing the solubility properties of uncured and cured fibers prove that cured fibers are not dissolved in some solvents in which uncured fibers will completely dissolve, for example benzene, ethylene glycol, acetone, etc. The fire-resistant quality also shows that the fiber is cured. I tested the flamability of the fiber by igniting the uncured fiber; after removing the ignition source, the flame continued but for the cured fiber the flame disappeared.

This is still a vague assumption about the positions of the curing that take place. In order to be specific and certain, more analyzation in both physical and chemical analysis is necessary. It is possible to be more specific by analyzing the uncured fiber structures.

For the methylene group attached at the ortho position, one can write the possible structure as follows:



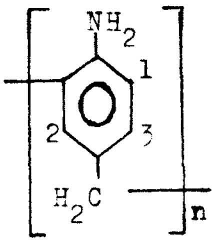
For curing to take place there are different positions that these methylene groups can attach.

1. At the amine groups, CH_2- can replace one or two hydrogens. According to the literature, if polymerization is present in a strong alkaline catalyst, then the CH_2- group will attach at the amine group to form secondary or tertiary amine. This specific curing liquor composition is the alkaline (NH_4OH) catalyst.
2. At the benzene ring the CH_2- group can attach at the 1,2 and 3 positions. It is possible that at position 3 it will be more favorable because it is easy to attach.

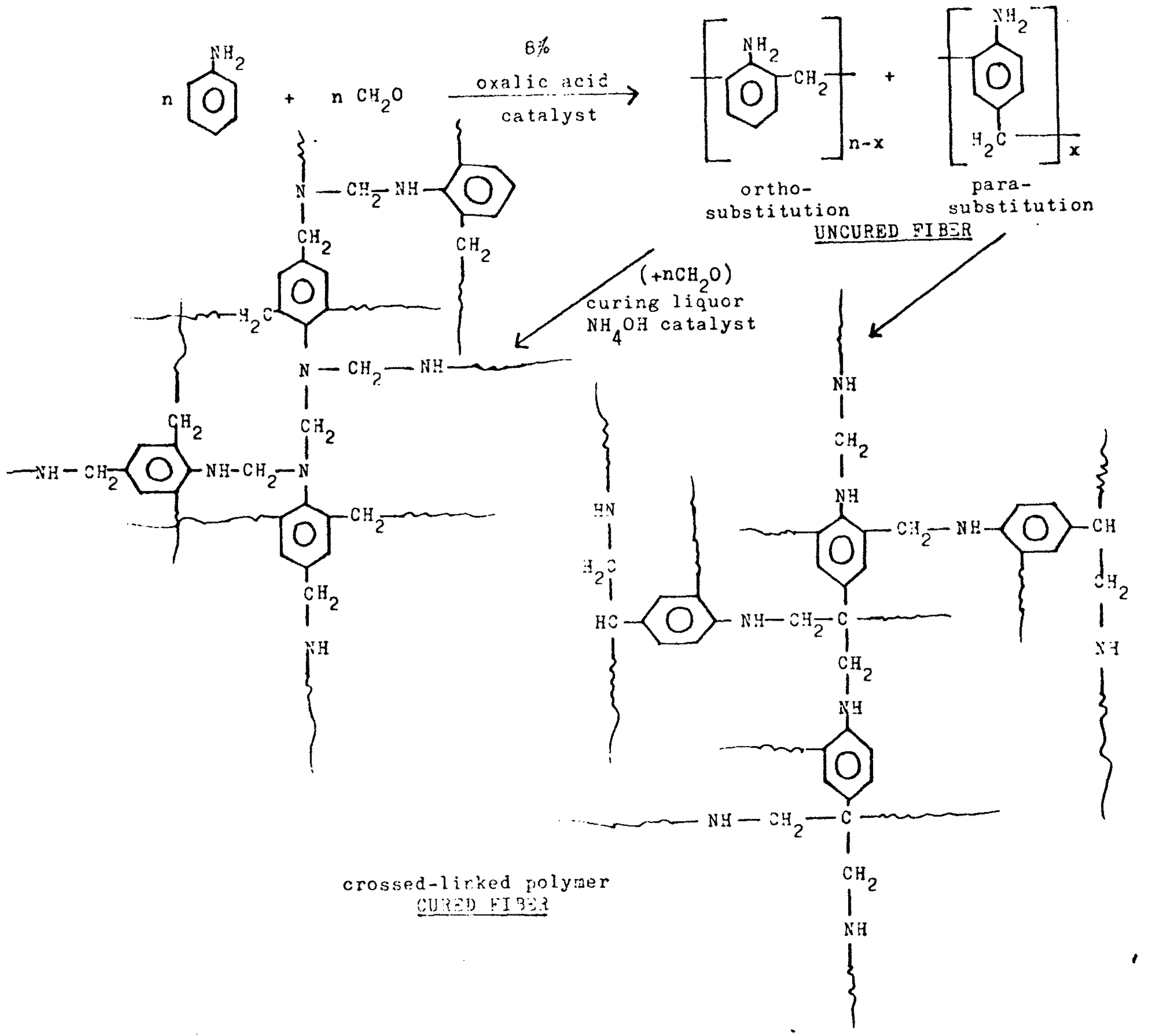
The position has more space for the other polymer chain to move freely.

3. At the CH_2- bridge, the methylene group can replace one or two hydrogens, but it is not likely to take place because the position of the position of the CH_2- bridge has no space for other polymers to move freely.

For the methylene group to attach at the para position it is possible to write the structure of uncured polymer as follows:



1. The CH_2- group can attach at the amine group for the same as the above reason.
2. The CH_2- group can attach at the aromatic ring on the 1,2 and 3 position but it is possible that position 1 will be more favorable.
3. At the CH_2- bridge the methylene group can replace one or two hydrogens.



The possible chemical reaction of uncured and cured aniline-formaldehyde fiber can be written as above:

The composition of aniline-formaldehyde resin which was adequate had about 3 moles of aniline and 2 moles of formaldehyde with 8% oxalic acid as a catalyst. The resin obtained was amber and it had a softening point in a range between 85°-95° C. This resin could draw fiber quite well.

The best curing liquor from the experiment, number 43, had a composition of 80 ml of formaldehyde 37% solution, 10 ml of ammonium hydroxide 36% solution, 60 ml of distilled water, 0.6 g aluminum chloride and 10.5 ml of methyl alcohol. The proportion of formaldehyde and ammonium hydroxide was about 8:1 by volume of their solution, about 40 percent of water. Aluminum chloride acted as cocatalyst. It helped to improve the curing liquor quality, but the percent added in the curing liquor is not completely accurate. There needs to be more experiments in order to achieve the best proportion. It is similar to methyl alcohol which acted as a swelling agent. One can do more tests to get the best proportion for better results.

p-Chlorophenol-phenol-formaldehyde resins were produced and they obtained good results, however, I did not continue to make cured fiber from them. I predict that the curing of p-Cholorophenol-phenol-formaldehyde will receive a good crosslinking. The fiber will possibly have a good fire-retardant property because of the presence of chlorine in the compound.

Proper fiber apparatus will produce a good thin fiber which will be better than the fiber I had drawn. The smaller diameter of the fiber will help the curing solution penetrate inside the fiber. Therefore smaller diameter fiber will improve curing. Also a good resin that has a high melting point will make it easier for a fiber to cure. To obtain a good resin also requires well functioning apparatus. Greasing the equipment well, will prevent formaldehyde leaking. The pump should be in good condition, and have sufficient suction to withdraw the water.

Many formulas and procedures for producing resins and curing received poor results and some of them did not work at all. I found that it was useful to report all the experiments both positive and negative because it will helpt others save time by not repeating the same experiments.

I found the literature sources very helpful in starting the experiment by searching out both chemical and physical properties of every chemical. Most of the chemicals I used have the potential for intoxication from inhalation. Oxalic acid fumes irritate the upper respiratory tract, methyl alcohol poisoning may occur from inhalation, etc.

APPENDIX

Procedures and composition of curing liquors of aniline-formaldehyde fiber

Experiment #12

1. 60 ml of ammonium hydroxide solution.
2. 50 ml of formaldehyde 37% solution.
3. 5 ml of hydrogen peroxide 3% solution.
4. 10 drops of ferrous sulfate 1% aqueous.

Experiment #24

1. Added 25 ml ammonium hydroxide and 75 ml formaldehyde 37% solution to a 250 ml beaker, left curing liquor to cool to room temperature.
2. Added fiber, 5 drops of H_2O_2 and 5 drops of $FeSO_4$ 1% aqueous and heated slowly.
3. 24 hours later added 50 ml of formaldehyde 37% solution and raised temperature, fiber became dark gold.
4. 48 hours later added 50 ml of formaldehyde 37% solution, and raised heat to 47°C.
5. 72 hours later added 50 ml of formaldehyde 37% solution, the fiber was good and the solution was clear, temperature was increased to boiling.
6. It was boiled for 5 days.
7. Took fiber out, cleaned and dried at 50°C.

Experiment #26

1. Added 25 ml ammonium hydroxide solution, 75 ml formaldehyde 37% solution and cooled to room

temperature.

2. Added fiber and raised temperature slowly.
3. 24 hours later fiber was light yellow, nothing had changed, continued to raise temperature slowly.
4. 48 hours later the fiber became light gold, continued to raise temperature slowly.
5. 72 hours later fiber became light gold, continued to raise temperature slowly to boiling.
6. Kept temperature constantly boiling for 5 days.
7. Took some fiber out to clean and dry, cured fairly well, but cured fiber was not too strong - left the rest of the fiber to boil.
8. Continued to boil for 3 more days.
9. Took some fiber out to clean and dry, checked fiber, it was not much better than the fiber that was removed the first time.
10. Continued to boil for 3 more days.
11. Took all of the fiber out, the fiber was not good, it brok into small pieces.

Experiment #27

1. 25 ml NH_4OH solution, added 75 ml CH_2O solution cooled to room temperature.
2. Added fiber and heated slowly.
3. 24 hours later fiber color was light yellow, nothing changed, continued to heat slowly.
4. 48 hours later fiber changed to light gold, continued to heat slowly.

5. 72 hours later nothing changed, continued to heat slowly.
6. 96 hours temperature reached 95°C (boiling), kept curing liquor constantly boiling for 5 days.
7. Took some fiber out to clean and dry, fiber cured fairly well but it was not too strong, left the rest of the fiber to boil.
8. Continued boiling for 48 hours more.
9. Took some fiber out to clean and dry, checked fiber, it was not much better than the first fiber removed.
10. Continued boiling for 3 more days.
11. Checked fiber it was weaker than the first fiber removed.
12. Took all of the fiber out, the fiber was not good, broke into small pieces.

Experiment #37

1. 0.99 mole, 29.6 parts, 29.6 grams equal to 80 grams of CH_2O (37% solution) 0.17 mole, 6.00 parts, 6 grams equal to 20 grams of NH_4OH (36% solution)
   (Added the above chemicals together and cooled to room temperature)
2. Added fiber, left at room temperature for 10 days.
3. Added 100 ml of H_2O and heated slowly.
4. 24 hours later checked fiber, color was light yellow, heated slowly and left it for 48 hours at 50°C.
5. Heated slowly to boiling and continued boiling for 72 more hours

6. Took some of the fiber out to clean and dry, checked fiber, it was cured and strong but still broke when pulled hard.
7. Added 20 ml of CH_3OH, about 10% of curing liquor, and boiled for 48 hours.
8. Checked some of the fiber, it was better than without CH_3OH.
9. Added 20 ml CH_3OH and boiled for 24 hours.
10. Checked all remaining fiber, it was weaker than before. Probably too much CH_3OH was added.

Experiment #38

1. 80 grams of CH_2O solution was added to 20 grams of NH_4OH solution, added 50 grams of H_2O and cooled curing liquor to room temperature, then added the fiber and left it at room temperature for 7 days.
2. Heated slowly
3. 24 hours later checked fiber spread out, color dark gold, heated slowly.
4. 24 hours later took some fiber out, fiber was good, heated slowly to 60° C.
5. Kept temperature constant for 3 days, then took some fiber out.
6. Fiber was good, uniform strands, heated slowly, increased temperature 1° C for every hour.
7. Heated to boil, 3 hours later added 10 ml of CH_3OH
8. 24 hours later checked some fiber, it was cured.
9. Added 50 ml H_2O and continued to boil for 3 hours

then check, fiber was better than before.

10. Added 20 ml CH_3OH and boiled for three more hours then checked the fiber, it was defused, spread out, not uniform strands, some fiber was good.

Experiment #39

1. 0.67 mole, 20.0 grams, 20.0 parts, 54.05 grams of CH_2O solution 0.17 mole, 6.0 grams, 6.0 parts 20.0 grams of NH_4OH solution and 25.95 grams of H_2O - added above chemicals into a beaker and left to cool to room temperature.
2. Added fiber and left at room temperature for seven days.
3. Heated slowly for 48 hours, checked fiber, it looked good, spread out, color was gold.
4. Heated to boiling, increased temperature 1° C for every hour, fiber looked good.
6. Kept solution boiling constantly for 3 days, checked some fiber, it was cured, but not strong, it was weaker than experiment #29 added 17 ml CH_3OH and continued to boil for 24 hours.
7. Checked fiber, better than before but some of the fiber was fused over the solution. (fiber was as good as Experiment #37 without CH_3OH)
8. Cooled solution to room temperature and added 40 ml of HCl solution (38%) - solution changed color from gold to dark orange and 30 minutes later some fiber started to dissolve and some fiber still remained.

Experiment #42

1. Added 80 ml of CH_2O solution, 15 ml of NH_4OH solution and 55 ml of H_2O into a beaker.
2. Added fiber and heated slowly.
3. Heated boiling, increasing temperature 1° C for every hour.
4. Added CH_3OH every 3 hours.
   (7.5 ml) 5% approximate 7.5 ml, (7.5 ml) 10%
   15 ml CH_3OH
   (3 ml) 12% approximate 18 ml, (3 ml) 14%
   21 ml CH_3OH 4 days later.
5. Took fiber out to clean and dry, fiber was cured but not too good, weaker than Experiment #37 - Assume too much CH_3OH
6. Put cured fiber in 40 ml CH_2O solution, added 60.00 H_2O and 1 ml HCl solution (38%) - fiber dissolved.

Experiment #43

1. 80 ml of CH_2O solution added 10 ml of NH_4OH solution added 60 ml of H_2O, cooled mixture solution to room temperature for 5 days.
2. Heated slowly to 30° C and added 0.1 gram $AlCl_3$, fiber looked good.
3. Heated slowly to 45° C, increasing temperature one degree every 2 hours.
4. Added 0 2 grams $AlCl_3$, increased temperature gradually to 65° C.
5. Added 1.5 ml of CH_3OH every 3 hours for 12 hours. (4 times)

6. Increased temperature to boiling and kept solution boiling constantly for 24 hours.
7. Added 1.5 ml of CH_3OH every 3 hours for 12 hours (4 times)
8. Checked some of the fiber, curing was good, stronger than the previous cured fiber.
9. Added 0.3 grams $AlCl_3$ and kept it boiling for 24 hours.
10. Checked some of the fiber, it had cured better than the first curing
11. Added 0.4 grams $AlCl_3$ and continued boiling.
12. Checked fiber 5 hours later, it was not as good as the previous one.

Experiment #44

1. 80 ml of CH_2O solution, added 5 ml of NH_4OH solution, 65 ml H_2O, and fiber and left at room temperature for five days.
2. Heated slowly, increasing temperature 1° C every 2 hours.
3. Added 6 ml CH_3OH and left it for 12 hours at 70° C.
4. Increased temperature slowly to 75° C then added 3 ml of CH_3OH.
5. Increased temperature slowly to 80° C then added 3 ml of CH_3OH.
6. Increased temperature slowly to 85° C then added 3 ml of CH_3OH.
7. Increased temperature slowly to 90° C then added 7 ml of CH_3OH, kept solution at 90° C for 12 hours.

8. Added 1 gram $AlCl_3$ and let it boil for 72 hours.
9. Checked fiber, it was not too strong.

V. REFERENCES

1. Labrathe, Jules, Textiles: Origins To Usage, New York: The Macmillan Co., 1968.

2. "Aniline-Formaldehyde Resins", Encyclopedia of Polymer Science and Technology, Vol. 2. New York: John Wiley and Sons Inc., p. 44, 45.

3. Walker, Frederic J., Formaldehyde, New York: Reinhold Publishing Corp., 1944, p. 203.

4. Mason, Philip J., The Technology of Plastics and Resins, New York: D. Van Nostrand Co., Inc., 1946, p. 208.

5. Op. cit. Walker, Frederic J. p. 204.

6. Op. cit. Labarthe, Jules. p. 109.

7. Kleeck, A. Van-Chemical Engineer, News 19, 1941. p. 626, 627, 628.

8. Almond, R., and Young, A.M., British Patent 487, 969, 1938; C.A., p. 33, 412.

9. Tramm, H., Clar, C., Kuhnel, P. and Schuff, W. (to Ruhrchmie Akt.), U.S. Patent 2, 106, 938 (1938).

10. Collins., Bares., and Billmeyer. Experiments in Polymer Science. Toronto, Canada: John Wiley and Sons, Inc., 1973, p. 505, 506.

11. Dyer, John R. Applications of Absorption Spectroscopy of Organic Compounds. New Jersey: Prinice-Hall Inc., 1965, p. 33, 34, 36, 37.

12. Ibid., p. 30, 31.

13. Hummel, Dieter O. Infrared Analysis of Polymers, Resins and Additives An Atlas. Sydney, Germany: Wiley-Interscience, A Division of John Wiley and Sons, Inc., 1969, Spectra Index. 1140.

14. Allinger., Cava., Dejongh., Johnson., Lebel., and Stevens. Organic Chemistry. New York: Worth Publisher, Inc., 1971, p. 367, 368.

15. Ibid., p. 169

16. Simons, W. W. and Zanger, M. The Sadtler Guide to The NMR Spectra of Polymer. Philadelphia: Sadtler Research Laboratories, Inc., 1973

17. Op. cit. Dyer, John R. p. 88.

18. NMR Standard Spectra. The Sadtler Spectra. Philadelphia: Sadtler Research Laboratories, Inc., 1967, Spectra Index. 191 M.

19. Op. cit. Simons, W. W. and Zanger, p. 150

20. Kirk, Raymond E. and Donald Othmer F. Encyclopedia of Chemical Technology "Aniline", Vol. I. New York: The Interscience Encyclopedia, Inc., 1947

21. Morrel, R. S. Synthetic Resins and Allied Plastics. London: Oxford University Press, 1943.

22. Bovey, Frank A. High Resolution NMR of Macromolecules. New York: Academic Press, 1972.

23. Peters, Dennis G., Hayes John M. and Hieftje Gary M. Chemical Separations and Measurements. Philadelphia: W. B. Saunders Co., 1969.

24. Masterlon, William L. and Slowinski Emil J. Chemical Principles, Second Edition. Philadelphia: W. B. Saunders Co., 1969.

25. Ham, George E. Copolymerization. New York: John Wiley and Sons, Inc., 1964.

26. Schmidt Alois X. and Marlies Charles A. Principle of High-Polymer Theory and Practice. New York: McGraw-Hill Co., Inc., 1948.