RHEO-OPTICAL PROPERTIES OF POLYISOBUTYLENE

BY

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ABSTRACT

This study presents quantitative experimental data
on the various stress-optical characteristics of polymer
liquids, specifically, polyisobutylene. Through the use
of a concentric cylinder rheogoniometer and a rotational
viscometer, the temperature effects of a newtonian poly-
isobutylene liquid was studied and was found to have a
stress-optical coefficient independent of shear stress
and minor temperature changes. The experiments confirm
that the birefringence is a known function of the ex-
tinction angle and the shear stress. Various polyisobuty-
lene liquids were used in a simple flow device to ob-
serve the birefringence in the 1-3 plane and the 2-3
plane. The results indicate that the 1-3 birefringence
is proportional to the molecular weight of the material.
Contrary to theory, birefringence effects are observed
in the 2-3 plane. The study also included the transient
behavior of a highly non-newtonian polyisobutylene sol-
ution. The most notable aspect of this behavior was
that of an 'overshoot' effect, whose occurence and mag-
nitude is a function of the shear rate.

APPROVAL OF THESIS

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INTRODUCTION

The development of the field of rheo-optics has been quite different from that of other scientific fields. While many have remained an art rather than a science due to the lack of theories, the field of rheo-optics has suffered from the opposite effect, namely an over abundance of theories with little experimental data for support. The apparent scarcity of raw data is perhaps due to the high precision and expense of the instruments involved. It is the intention of this study to present pertinent data to help support or disprove the many mathematical theories that have been proposed throughout the years.

Although the field has been slow in developing, much interest has been generated in it in the recent years. This is due to its importance as a method for measuring stresses and flow without disturbing the medium. Often referred to as photoelasticity or in specific, birefringence, the field is of great importance to design work where it is necessary to know flow and stress profiles of the model. The birefringence effect is actually a measurement of the refractive index difference in the various planes of orientation in space. The refractive index, which is the ratio of the velocity of light in vacuum to its velocity in a transparent material, where it is always slower. One theory of the refractive index assumes that an electric field is generated

by the electrons in the atom which retards the movement of the light wave[1] A difference in the refractive index occurs when more electrons are aligned on one direction than in another. This occurs when a material is stressed by either mechanical means or subjected to flow when it is a liquid. Studies have shown that these pressures or stresses are proportional to the refractive index difference. These small differences are measured with the use of polarized light. When the light passes through the stressed material, it is divided into two component waves, each with its plane of polarization parallel to one of the principal planes[2]. Since one beam will be retarded a little more than the other, an interference pattern can be generated in the polariscope. These interference patterns appear as black bands where the two beams completely cancel one another. Fractions of a band can be measured with a compensator.

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[1] R.Feynman,R.Leighton and M.Sands, The Feynman Lectures on Physics,Vol.1 (Addison-Wesley Pub.Co., 1963)chap.31

[2] D.Post, "Photoelasticity",ed. Society of Experimental Stress Analysis

HISTORICAL DEVELOPMENT OF BIREFRINGENCE THEORIES

Although double refraction or birefringence of liquids is considered to be a very new field, its early beginnings date back over a century. Mach[3] was the first to observe double refraction in very viscous materials such as Canada balsam whan poured (transient birefringence), but failed to observe any for less viscous materials. Mach first published these findings in 1873.

In 1874 Clerk Maxwell described the transient results obtained from a concentric cylinder apparatus he built in 1866, where he subjected Canada balsam to shearing.[4] Similar results were obtained by Quincke in 1880 by immersing a heated wire in various liquids.

Kundt[5] improved on Maxwell's instrument by observing the movement of an interference band produced with a gypsum plate using a nitrocellulose solution; these were the first quantitative measurements to be done. Kundt then proposed that the incompressible liquid in the annular gap is subjected to compressive and tensile stresses perpendicular to

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[3] H.G.Jerrard,"Theories of Streaming Double Refraction" Chemical Reviews,59 (1959) p.345

[4] Wayland,"Streaming Birefringence as a Rheological Research Tool", Rheo-optics of Polymers,ed.R.Stein (New York: Interscience Pub.,1964)

[5] A.Kundt, Wied. Ann. 13 (1881) p.110

one another and oriented 45° to the direction of flow.These stresses were proportional to ηj, where η is the dynamic viscosity and j is the velocity gradient or shear rate. Kundt, using Maxwell's concepts expressed the decay birefringence as Δn = Ktj where t is the relaxation time.

In the 1890's DeMetz and Umlauf elaborated upon Kundt's experiments by using a Babinet compensator and varying the temperature, noting that the birefringence decreased with increasing temperature.[6] Schwedoff,[7]noting the departure of the extinction angle χ from 45° and using Maxwell's relaxation theory and Hooke's law, derived an equation for χ in terms of the finite recoverable shear of the liquid. In 1904 Natanson[8] derived the equation: cot $2\chi = \pm$ tj. Zakrewski confirmed this equation through his experiments.Presently, the recoverable shear is now defined as twice that of Natanson's

$$s = 2\cot 2\chi = tj$$

Zocher proposed an alternate theory in 1921 where the birefringence is a result of the orientation of asymmetrical molecules. Raman and Krishman likewise considered the birefringance to be an effect of asymmetric and optically anisotropic molecules which are orientated with their major axis

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[6] H.G.Jerrard, op.cit.,p.354

[7] T. Schwedoff, Journal of Physics (3)1,(1892)p.49

[8] M.L. Natanson,Bull. intern. acad. sci. Cracovie 1,(1904)

in the direction of principal tension. This orientation is opposed by thermal agitation, whereby the resulting orientation causes the double refraction. The theory leads to the following expression:[9]

$$\frac{\Delta n}{n \eta j} = \frac{(n^2-1)(n^2+2)(a_1-a_2)(\alpha_{11}-\alpha_{22})+(a_2-a_3)(\alpha_{22}-\alpha_{33})+(a_3-a_1)(\alpha_{33}-\alpha_{11})}{10n^2 \; N_0 \; k \; T \; (a_1+a_2+a_3)(\alpha_{11}+\alpha_{22}+\alpha_{33})}$$

where n=index of refraction, No=number of particles/cm^3, T= absolute temperature in $^\circ$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 $a_2=a_3$ and introducing the mean polarizability from the Lorenz-Lorentz equation, the quation simplifies to:

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

where f is a geometric form factor. Although the theory of Raman and Krishman predicted the dispersion of double refraction and the 45°extinction angle for pure liquids, this theory did not hold for colloids, where large values of birefringence and extinction angles less than $45^\circ$are observed, as found by Kundt.

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[9] W.Philippoff, "Determination of the Anisotropy of Bond Polarizability of Liquids Using Flow Birefringence Measurements", Journal of Applied Physics, Vol.31,No.11 (Nov.1960)pp.1899-1906

In 1932 Haller[10]published a paper dealing with the flow behavior of deformable particles and rigid anisodimensional particles. The latter were considered to be ellipsoids in revolution which exibit precessional motion in laminar flow. Although Haller's theory predicted why the extinction angle changed from 45° to 0° with increasing shear rate, many of his constants could not be evaluated nor did they have any physical meaning.

Boeder considered colloidal particles which were assumed to be large ellipsoids in revolution with a large axial ratio in a homogenous solution. The particles are orientated by flow and disoriented by Brownian motion, leading Boeder to an expression for the distribution function F of the major geometrical axes of the particles[11]Boeder then derived expressions for the effect of the interaction of the electric field of the incident light wave for a partially orientated system. Boeder assumed that the liquid was anisotropicdue to the anisotropic nature of the particles or to deformation from strain.

At this time W.Kuhn also presented his theory. Like Haller, Kuhn considered the particles to be isotropic and flexible or anisotropic and rigid. The rigid particles likewise, were assumed to be orientated during flow, however,

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[10]
    H.G.Jerrard, op.cit,,p.355

[11]
    H.G.Jerrard, op.cit.,p.358

Kuhn considered them to be a string of rigidly connected spheres, which executes an irregular rotational motion about its center of gravity in addition to translation.

Kuhn presents several models with various geometries. In each of these models the birefringence is presented as a function of the diffusion constant, however, Kuhn presents those equations applicable to limited conditions. While Kuhn's theory appears to be mathematically sound, it has been impossible to verify experimentally. One must also note that Kuhn's models were two dimensional in nature.

Later attempts were made by Peterlin and Stuart along with Snellman and Bjornstahl in 1939 to improve upon this theory by treating it as a three dimensional model and taking into account the effect of light absorption by the particles. Again, while these theories appear quite sound, the complexity of the equations and the many indeterminate constants make their theories all but useless to the practical researcher.

By 1943 the concept of the rigid particle was in question due to unexplained behavior in many liquids. Earlier attempts by Haller and Kuhn now led to the concept of a flexible chain molecule which, while normally in the coiled state, was subject to continuous change in shape due to thermal agitation. Haller's early theory of flexible particles,

like that of rigid particles, contended that it was an

ellipsoid, but birefringence was brought about by the de-

formation of the ellipsoids, rather than just by its orien-

tation. These ellipsoids were acted upon by external stres-

ses during flow, which in turn created internal stresses

within the particle, leading to an equilibrium orientation

which was not always 45° from the direction of flow. In

fact, with large gradients this angle would approach some

limiting angle larger than zero. The flexible particle

theory meant that there would be no saturation or maximum

birefringence due to total orientation of the particles.

W.Kuhn also concluded from the behavior of polysty-

rene and rubberlike materials that the birefringence was

due to the deformation of the particles as well as their

orientation. W.Kuhn then attempted a mathematical treat-

ment of a deformable sphere and an elongated particle.

Shortly after, W.Kuhn and H.Kuhn[12,13]proposed a "statis-

tical coil' model where the particle consisted of a num-

ber of 'statistical straight chain elements' which in turn

were composed of a number of monomers.[14,15]For solutions,

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[12] W.Kuhn and F.Grun, _Kolloid-Z._ 101 (1942)p.248

[13] W.Kuhn and H.Kuhn, _Helvetica Chimica Acta_, 26 (1943)
pp.1394

[14] W.Philippoff,"The Present Stand of Rheo-Optics of
Polymer Solutions", _Proceedings of the Fifth International
Congress on Rheology_, Vol.4 ed.Shigeharu Onogi(Tokyo:1970)

W.Kuhn and H.Kuhn[16] treated the molecule as a loose struc-
ture allowing free movement of the surrounding liquid, a
tightly structured one which prevented this flow, or more
likely, some intermediate structure which inhibited but
did not prevent this flow. The two limiting structures are
sometimes referred to as "free draining' and 'nondraining'
molecules. W.Kuhn and H.Kuhn, through probability and
entropy relationships have developed a two dimensional
equation for birefringence whereby each straight element
is assumed to be an ellipse in revolution:

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

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

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

in which D_t is the translatory diffusion constant perpen-
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, W.Kuhn and H.Kuhn have derived an equation

[15] H.G.Jerrard, op.cit.,pp.394-401

[16] W.Kuhn and F.Grun, Journal of Polymer Science,Vol.1
No.3 (1946) pp.183-199

for the extinction angle:

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

Shortly after, Hermans improved upon the theory by treating it as a three dimensional model. The results were similar for small gradients to that of the two dimensional model, necessitating only minor numerical factor changes. Similar theories were later put forth by Peterlin and Stuart, Kramers, Copic and Tsvetkov, Kirkwood, and Zimm. One of the latest attempts was that of Lodge in 1954.[17] Lodge treated dilute solutions of up to several per cent and considered only small gradients. Unlike the previous theory, Lodge proposed that the molecules were entangled with one another, forming a loose network throughout the solution.[18] Using a model similar to the statistical theory of rubberlike elasticity, Lodge assumes that the birefringence is caused by the orientation of the deforming network of optically anisotropic chain links. By evaluating some data on polystyrene solutions, Lodge was able to confirm that; the stress and the optic ellipsoids are coaxial, the orientation increases with shear rate, and the differences of the principle axes of the optic ellipsoids increase proportionately

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[17] A.S.Lodge, "Variation of Flow Birefringence with Stress", _Nature_, 176 (1955) p.838

[18] A.S.Lodge, "A Network Theory of Flow Birefringence and Stress in Concentrated Polymer Solutions", _Trans. Faraday Soc._ 52,(1956) p.120

to the differences of the corresponding principle axes of the stress ellipsoid. By applying some well known relationships, Lodge deduced the 'stress optical coefficient', similar to that of F. Muller and Kuhn;

$$\frac{\Delta n}{\Delta s} = \frac{\Delta p C}{\Delta s C}_0 = \frac{C_0}{kT} = \frac{2\pi\,\bar{n}}{5kT}\,\frac{n^2+2}{3\bar{n}}^2(\alpha_1-\alpha_2)$$

similarly from equation

$$\frac{\Delta n\,\sin 2\chi}{\bar{n}} = \frac{4\pi}{5}\left(\frac{n^2+2}{3\bar{n}}\right)^2\frac{(\alpha_1-\alpha_2)}{kT}\,(n-n_0)\,j$$

Lodge concluded that:

$$\frac{\Delta n}{\Delta p} = \frac{\Delta n\,\sin 2\chi}{2j\,(\eta-\eta_0)} = \frac{\Delta n\,\sin 2\chi}{2\,\tau}$$

which is very similar to that equation derived from Raman and Krishman.

While the equations have proved to be experimentally valid, some of Lodge's assumptions are questionable. Lodge assumed the coaxiality of the optical and the stress tensor without explaining why the axes differ from 45° in normal liquids. If the coaxiality of a third tensor for the recoverable deformation is assumed, its principal axis changes its angle toward the flow direction at 'finite shears'; explaining why all three tensors lead χ as a function of j. This assumption is supported by the relationship of the normal stresses, extinction angle χ, and the angle determined from the recoverable shear $s = 2\cot 2\chi$. Experimental

data obtained from various instruments appears to check, especially for low shear rates. This fact disagrees with Lodge's assumption that $s=(P_{11}-P_{22})/2\gamma$ is distinct from the equation for solids in finite shear: $s=(P_{11}-P_{22})/\gamma$. This factor of two has yet to be resolved theoretically.

DESCRIPTION OF THE APPARATUS

Optical Arrangement

All of the optical data was obtained through the use
of a polariscope designed by W.Philippoff and built in the
Franklin Institue of Philadelphia,Pennsylvania. The light
source is a 100 watt, high pressure, high intensity mer-
cury arc lamp, whose light passes through a compound pro-
jector lens (18 mm. focal length) and is then passed through
a green interference filter (5461 $\overset{o}{A}$) and limited by two sets
of variable Bjornstahl slits.

The Bjornstahl arrangement uses two sets of horizontal
slits whose images are focused on the entrance of the flow
chamber and the half wave plate. 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.

The light then becomes a parellel 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.

When using the half shadow technique (Senarmont-com-
pensator), half of the image passes through a quartz half
wave plate. The correct angle is found by matching the light
intensity of the two fields. For this to occur the image

MERCURY
LAMP

FILTER

POLARIZER

QUARTER
WAVE PLATE

ANALYZER

LENS

LENS

SAMPLE

HALF WAVE
PLATE

EYE PIECE

VARIABLE SLITS
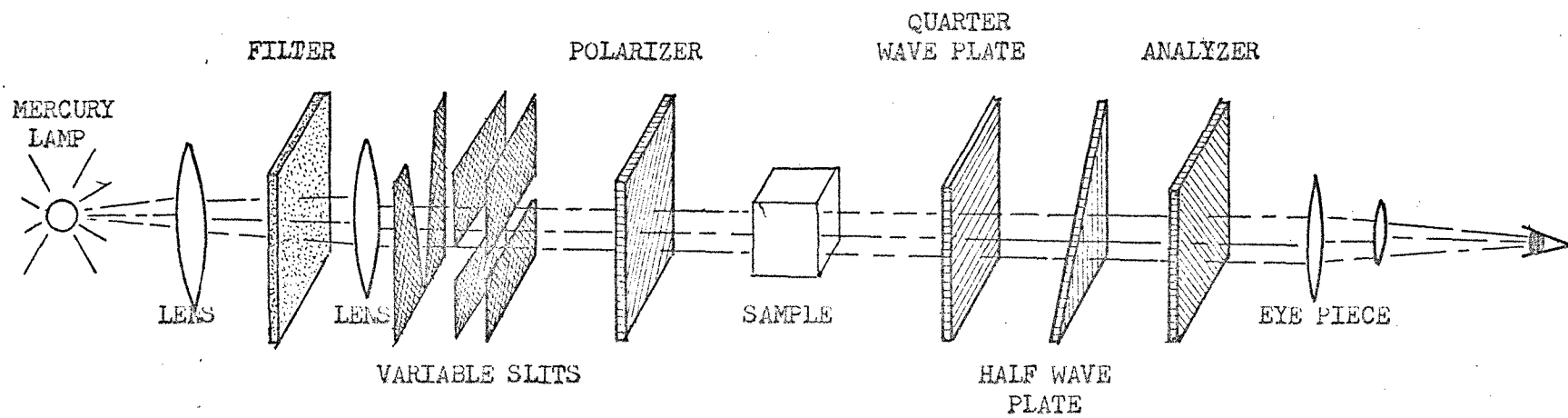
OPTICAL ARRANGEMENT OF THE POLARISCOPE

must be transmitted through the analyser and focused by the eye piece.

The polarizer and the analyser may be oriented independently, the polarizer is capable of a 180° rotation while the analyser-half wave plate combination is free to move a complete 360°. Each of their rotations is divided into fractions of a degree, which may be read to within a minute of an arc with the aid of a vernier scale. Further precision is unwarrented due to the limitations of the human eye. Electronic sensors have been attempted, however, inconsistant readings result from inhonogeneities in the sample liquid. When observing the 2-3 plane of flow, an additional lens is placed between the sample and the quarter wave plate to magnify the image.

Concantric Cylinder Apparatus

The primary device used in obtaining the double refraction data was a concentric cylinder arrangement. This device consists of the previously described optics and two concentric stainless steel cylinders, in which the outer one is stationary. The inner cylinder is rotated by a series of timing belts and gear boxes and are in turn driven by a synchronous constant speed motor.

Depending upon the cylinder used, the rate of shear range is from .000793 to 31450 sec.^{-1} For this study cylinder II was used, with a radius of 2.7535 cm. and a length
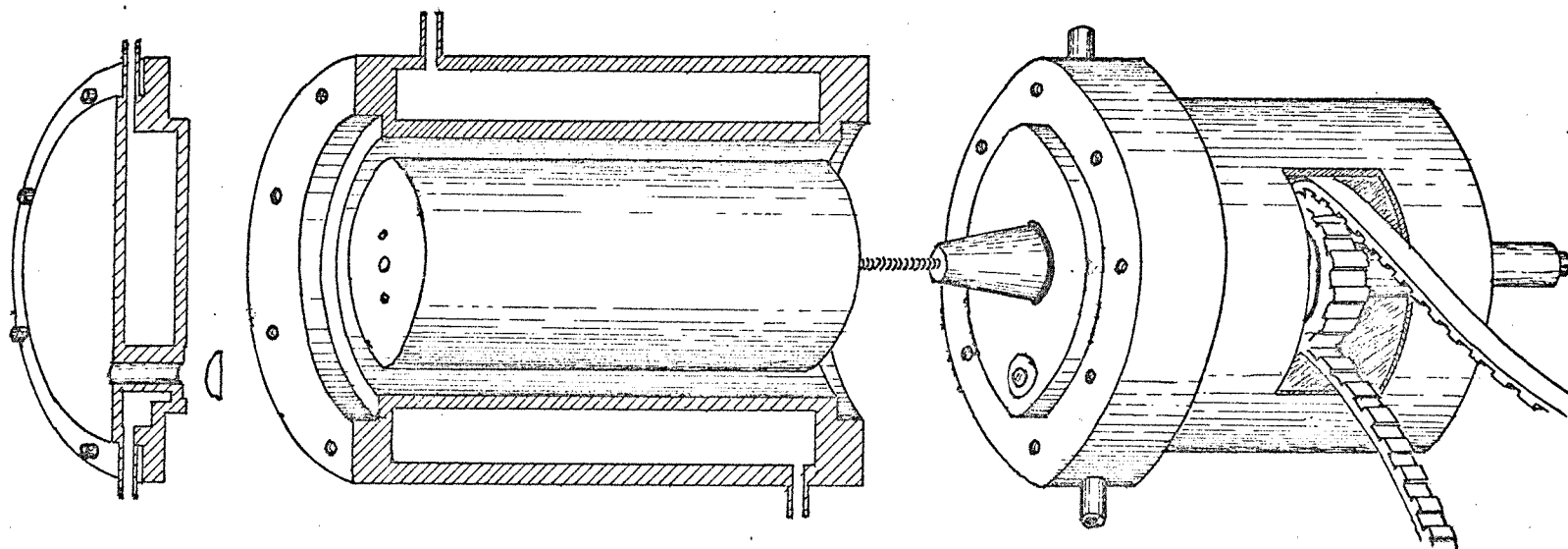
CONCENTRIC CYLINDER RHEOGONIOMETER

of 7.43 cm. The annular gap was 1.069 mm. On each end of
the stationary cylinder is mounted a small circular glass
window (12 mm. diameter by .15 mm.) through which the light
beam passes.

In order to conduct constant temperature measure-
ments, the outer cylinder contains a water jacket which is
divided into three sections. Before passing into the middle
jacket the water is circulated through an insulated jar
which contains a calibrated thermometer (accuracy of $\pm.02^{o}F$).
The entire cylinder, along with flexible tubing, is insulated
to minimize heat loses. A constant temperature bath, from
which the water originates, can be maintained to within $.01^{o}F$.

$n_{11}-n_{33}$ Apparatus

In measuring the refractive index difference $n_{11}-n_{33}$,
the fluid flows horizontaly in a plane perpendicular to the
light beam. The apparatus contains no moving parts, being
a simple slit arrangement. Constructed of stainless steel,
the apparatus employs two thin glass window similar to that
used in the concentric cylinder device. The slit is deter-
mined by steel and brass spacers of a known thickness
placed between a rigid stainless steel plate, which con-
tains one window, and the main body of the apparatus, which
contains the other window. Two different slits were employed;
the first measured 2.54 cm. innlength, 1.27 cm. in width
and .0635 cm. in thickness. The second one was 2.54 cm. long,

1.27 cm. in width and .127 cm in thickness.

For this apparatus and that of the n_{22}-n_{33} measurements, the liquid is supplied from a 400 cc stainless steel vessel which is pressurized with up to 250 psig of nitrogen gas.

n_{22}-n_{33} Apparatus

The device used in the refractive index difference n_{22}-n_{33} is also a simple slit arrangement. In this case the direction of flow coincides with the light beam. The apparatus consists of a 2.54 cm diameter stainless steel cylinder with a length of 4.36 cm. The slit measures 2.54 cm in length and .8 cm in width with a thickness of .0735 cm. On either end of the cylinder is a glass window (.37 cm thick) which is mounted within a brass holder and is in turn clamped to the cylinder. Due to the thickness of the windows, very high shear stresses are obtainable, the limitation being the pressure vessel.

Neither the n_{11}-n_{33} device nor the n_{22}-n_{33} device were originally designed with a water jacket to maintain a constant temperature. For the n_{22}-n_{33} device, however, a lucite container, which encloses the flow chamber as well as the pressure vessel, was constructed. To minimize extaneous birefringence, thin glass windows like those in the concentric cylinder device were used rather than the walls of the
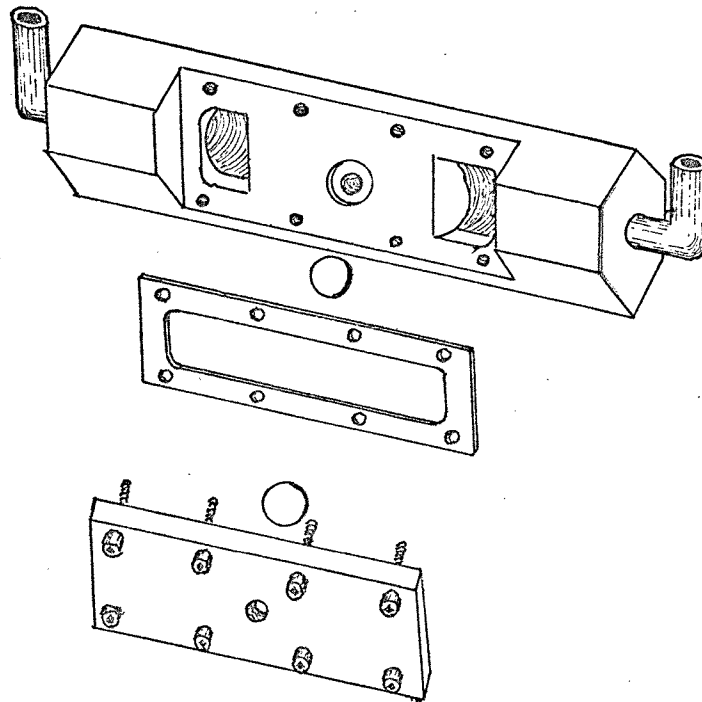
$n_{11}-n_{33}$ FLOW APPARATUS

$n_{22}-n_{33}$ BIREFRINGENCE DEVICE
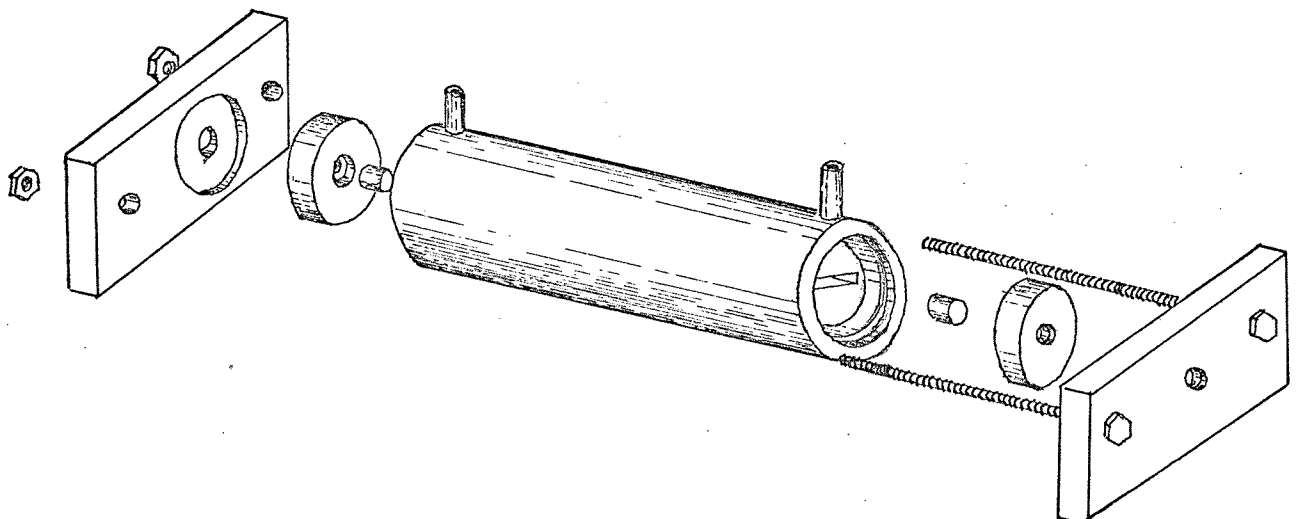
lucite container, which contains a large residual bire-
fringence. Provisions were made for a valve to start and
stop the flow of fluid. Water is circulated from a constant
temperature water bath into the bottom of the container.
It then exits from the top and is conducted to the insul-
ated jar, in which the thermometer resides, then back to
the water bath. For room temperature measurements the tem-
perature can be maintained to within $\pm.05^{\circ}$F. However, for
high temperatures (167°F) temperature loses of $.5^{\circ}$F occur.

Viscometer

A rotational viscometer was used to obtain the vis-
cosities. This apparatus was also designed by W.Philippoff
and built by Esso Research and Engineering Company. It con-
sists of two concentric cylinders with an annular gap of
2 mm. The inner cylinder is driven by a weight attached to
a string, which is wound around a drum that is connected
to the cylinder. The rate of shear is calculated from the
speed of angular rotation. This is obtained from a light
beam that is reflected off the mirrors mounted on the drum.
Two photocells, placed at a given distance, activate a re-
lay which controls a timer. By knowing the distances and
the time interval, it is quite easy to obtain the rotational
speed. The shear rate is given by: $j = .358 \, \phi/t$ where ϕ is
the angle of rotation in degrees and time t is in seconds.
The shear stress is simply a multiple of the weight on the

ROTATIONAL VISCOMETER

(4) CENTERING SCREW

(5) CARBALOY POINT

(13) YOKE

(12) AIR BEARING

(7) TOP FLANGE

MIRROR (15)

(10) DRUM

(11) COLUMN

(9) LOOSENING NUT

(8) VAPOR TRAP

(6) BOTTOM FLANGE

"O" RING (14)

(2) CUP

ROTOR (1)

(3) CARBALOY POINT
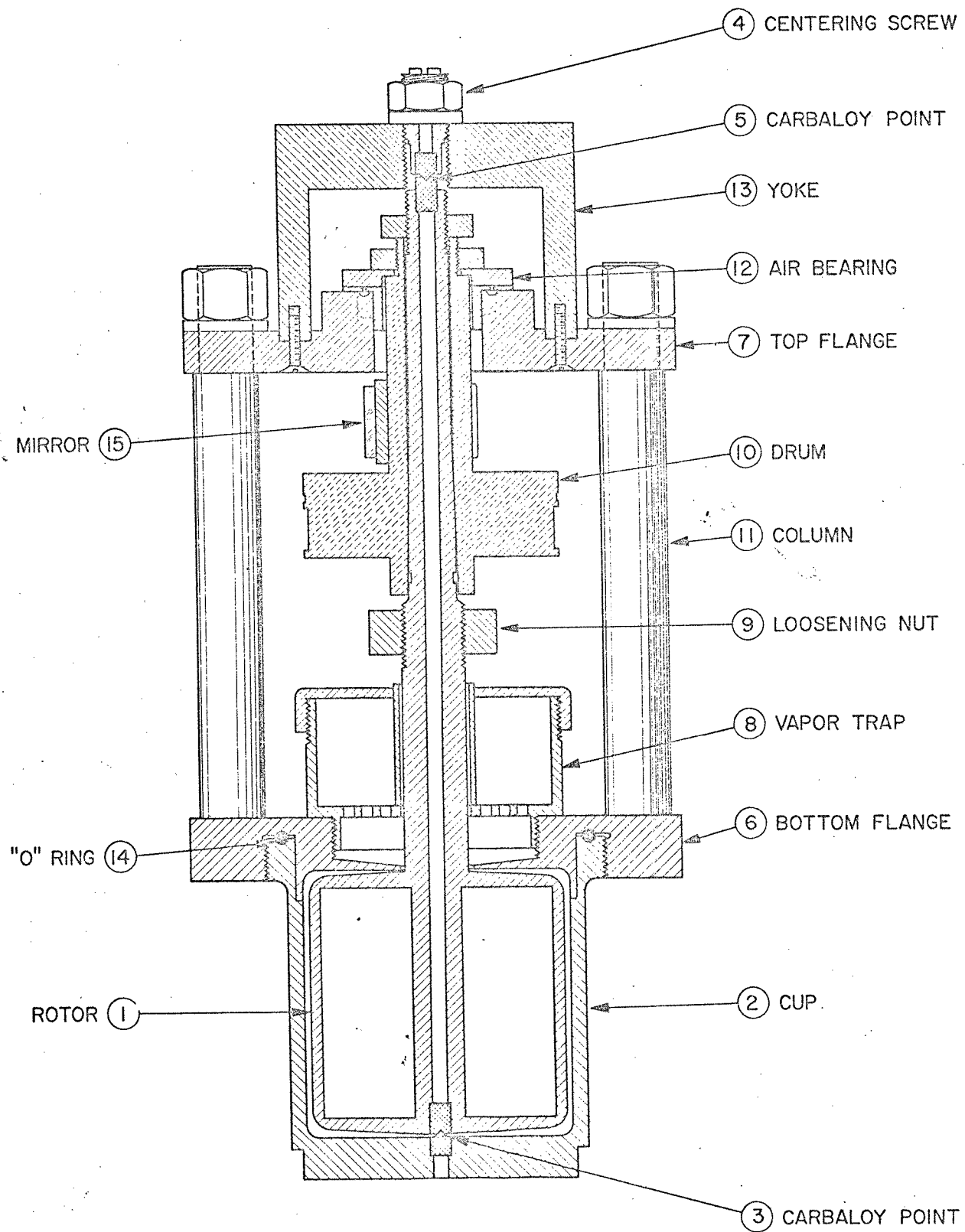
string, $\tau = 4$ W. For large shear rates the drum rotation is read directly.

The viscometer can be operated in two modes. For large weights the cylinder rides on a carbide point. For small weights, to minimize friction, an air bearing is employed. To obtain constant temperatures, the lower half of the viscometer is submerged in a constant temperature water bath which can be maintained within $.02^{\circ}$F. Depending upon the liquid and the care employed, accuracies of up to 1% can be achieved.

Materials

With the exception of the liquid used in the calibrations, all of the materials chosen for this study were polyisobutylene fluids. There were five nearly newtonian liquids of high purity and one non-newtonian polyisobutylene solution.

ORONITE N-16: This material has a relatively low viscosity $\eta = 23.6$ poise at 25°C. Its molecular weight is $M_n=550$. According to the manufacturer, California Chemical Co., it may be a mixture of polybutylene 'isomers', which may account for some optical discrepancies.

INDOPOL H-25: This material is a polyisobutylene liquid very

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E.A.Birkhimer,"Two New Viscometers for Measuring Viscosity at Recoverable Shear Over a Wide Range of Shear Rate",Esso Research and Engineering Co.;(Oct.1960) p.6

similar to ORONITE N-16. Produced by AMOCO, it has a molecular weight M_n between 593 and 670, depending upon the batch and the method used to measure it. It has a viscosity of 29.45 poise and a density of .8691 g/cc at 25°C.

ORONITE N-24: This material is a moderately viscous polyisobutylene, 209. poise at 25°C, produced by the California Chemical Company. Its molecular weight is around $M_n=900$.

INDOPOL H-1900: Produced by AMOCO, this material is a high viscosity, 5049. poise at 25°C, polyisobutylene exhibiting newtonian behavior at high shear stresses, over 200,000 dynes/cm^2. It is very temperature sensitive, varying by a factor of 100 for a $\Delta T = 65^{o}$C. It has a M_n between 1900 and 2560 and a density of .9224 g/cc at 25°C.

VISTANEX LM/MS: This is a very high viscosity (1.15×10^6 poise) polyisobutylene produced by Enjay. This material begins to exhibit non-newtonian characteristics for shear stresses above 10,000 dynes/cm^2. Its molecular weight M_n lies somewhere between 25,000 and 70,000; molecular weight determination becoming quite difficult at these ranges.

VISTANEX L-200 Solution: This is a polyisobutylene solution composed of 4.5 weight % 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 driven 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. VISTANEX L-200, originally produced by Enjay but discontinued now, has a molecular weight of about 5.5×10^6. (see Apendix for PRIMOL 355)

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

CALIBRATION OF THE CONCENTRIC CYLINDER INSTRUMENT

Procedure

To check the calibration of the concentric cylinder device, a polystyrene solution from the National Bureau of Standards was used. Shear rates from .0215 to 15.2 sec^{-1} were used in the birefringence measurements, which were all conducted at $25^{o}C$.

To obtain the birefringence value, the analyser is set to zero and the extinction angle χ is obtained by rotating the polarizer (45° for a newtonian liquid). In this position the polarizer and the analyser are locked at an angle of 89° to one another. The difference, which is already accounted for on the scale, is to allow for the balancing of the half wave plate field. This would be impossible at a 90° difference where total cancellation causes a zero light intensity. The polarizer is then set at an angle of $45-\chi^{o}$ and the compensator angle is read from the analyser, which when multiplied by a factor of 4.06×10^{-8} gives the birefringence. This factor is obtained from the relationship:

$$\Delta n = \frac{\theta \lambda (.01745 \frac{radians}{degree})}{\pi l}$$

where λ is the wave length of the light, l is the length of the cylinder and θ is the compensator angle in degrees.

Calibration Results

The birefringence agreed quite well with former measurements of the National Bureau of Standards liquid, with a reproducibility of about 1%. Both the birefringence and the viscosity measurements confirmed the fact that the liquid was non-newtonian. Extinction angles less than 45° occurred for shear stresses above 100 dynes/cm^2 decreasing to about 25° for a shear stress of 7000 dynes/cm^2. A 30% drop in the viscosity, from 681 to 460 poise, was also observed for this same range.

The stress-optical coefficient from the equation $C = \Delta n(\sin 2\chi)/2\tau$ was found to be negative, as to be expected with a polystyrene, and had a value of -4535 ± 114 Brewsters. The coefficient remained fairly constant for the shear stresses measured, despite the strong non-newtonian behavior, confirming the coefficient's independence of the shear rate.

There was a decrease, however, at the higher shear rates. This is caused by internal heating from excessive shearing. Since the heat is generated faster than the material can conduct it away, a rise in temperature is observed at the center of the gap. The refractive index also decreases, causing the light beam to refract outward. The image then rises out of the field of vision.

POLYSTYRENE   NBS 2-35967

Temperature= 77.0°F

SHEAR RATE j sec^{-1}	VISCOSITY η poise	SHEAR STRESS τ dynes/cm^2	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE Δn x 10^8	STRESS-OPTICAL COEFFICIENT C Brewsters
.0215	681	14.65	45°	20	1.35	4620
.0327	680	22.2	45°	29	1.96	4420
.0475	678	32.2	45°	41	2.77	4310
.0684	676	46.3	45°	66	4.46	4820
.0995	673	67.0	45°	90	6.10	4550
.152	669	101.8	45°	138	9.34	4590
.215	666	143.	44° 54'	188	12.72	4460
.327	661	216.	44° 50'	286	19.37	4510
.475	657	312.	44° 10'	418	28.3	4540
.684	654	448.	43° 26'	611	41.3	4620
.995	652	648.	42° 37'	871	59.0	4560
1.52	650	988.	41° 27'	1343	90.9	4550
2.15	648	1393.	40° 00'	1896	128.2	4530
3.27	640	2095.	37° 37'	2835	191.8	4430
4.75	625	2970.	35° 18'	4042	273.5	4350*
6.84	580	3970.	32° 08'	5708	386.	4400*
9.95	530	5270.	28° 57'	7981	540.	4340*
15.2	460	7000.	25° 17'	10634	720.	3980*

* heating

TEMPERATURE EFFECT ON THE STRESS-OPTICAL COEFFICIENT

Experimental Procedure

In the recent years there has been a serious debate as to whether the stress-optical coefficient C is affected by Brownian motion. Until recently it has been common practice to correct the coefficient with the equation;

$$C = C'T'/T$$

where C' is the stress-optical coefficient at some reference temperature T',usually $298^{\circ}K$. To test this equation, a highly birefringent and temperature sensitive material was used. A highly viscous polyisobutylene (Indopol H-1900) was chosen for these reasons and for its newtonian behavior.

Many of the pitfalls that plagued earlier investigators were eliminated, one being the mismatching of viscosity and birefringence data. By having available both devices, it is possible to obtain the data on the same batch of material. To eliminate any thermometer errors, the same thermometer was used for the viscosity and the birefringence measurements. The measurements were conducted in a temperature range of 25° to $90^{\circ}C$. For the viscosity studies normally shear stresses from 10 to 1000 dynes/cm^2 were employed, although shear stresses of up to 37,000 dynes/cm^2 were achieved.

In filling the concentric cylinder device, care must be taken in preventing any air bubbles to be introduced into the liquid. Should this occur, dispersion of the air due to shearing will cause the liquid to become opaque, and for large bubbles, inconsistant birefringence values will be obtained.

A period of 24 hours was allowed for thermal equilibrium to occur. A minimum of 10 minutes for each shear rate is allowed for steady state conditions to be achieved. To compensate for any optical misalignments, the material is sheared in a clockwise and then a counter clockwise direction and an average of the two values is used.

Results

The viscosity, obtained by N.Zwetkow, was observed to remain constant for the shear stress range employed including that of 37,000 dynes/cm^2, confirming the choice of a newtonian fluid. At 25°C the liquid had a viscosity of 5048.7 poise, which decreased by a factor of nearly one hundred to 52.6 poise at 90°C. The experimental error had a mean deviation of about 1.5%. Independent measurements conducted by the Esso Research Laboratories in an Ubbelohde viscometer were in reasonable agreement with these values. An empirical equation for the viscosity was derived, with about a 1% deviation from the experimental values, and had the form:

POLYISOBUTYLENE   INDOPOL H-1900

Temperature= $77.0^{\circ}F$

SHEAR RATE $j\ sec^{-1}$	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^{8}$	MAXWELL CONSTANT $M \times 10^{8}$
.00761	45°	15	1.05	138.0
.0111	45°	23	1.56	140.0
.0169	45°	33	2.23	132.0
.0215	45°	44	2.97	138.2
.0327	45°	67	4.53	138.5
.0475	45°	94	6.40	134.8
.0684	45°	135	9.14	133.7
.0995	45°	199	13.47	135.3
.152	45°	309	20.9	137.5
.215	45°	426	28.8	134.0
.327	45°	660	44.7	136.7
.475	45°	946	64.0	134.8
.684	45°	1371	92.8	135.7
.995	45°	1997	135.2	135.9
1.52	$44^{\circ}\ 52'$	3073	208.	136.8
2.15	$44^{\circ}\ 41'$	4291	290.	135.0
3.27	$44^{\circ}\ 38'$	6452	436.5	133.5
4.75	$44^{\circ}\ 31'$	9459	640.	134.8
6.84	$44^{\circ}\ 27'$	13521	915.	133.8
9.95	$44^{\circ}\ 05'$	20325	1375.	138.2
15.2	$43^{\circ}\ 44'$	29700	2019.	132.8
19.25	$43^{\circ}\ 27'$	37670	2550.	132.6
29.3	$42^{\circ}\ 24'$	57750	3910.	133.3
42.8	$41^{\circ}\ 24'$	83820	5680.	132.8

POLYISOBUTYLENE   INDOPOL H-1900

Temperature= 86.0°F

SHEAR RATE $j\ sec^{-1}$	EXTINCTION ANGLE χ		COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
.0215	45°		27	1.83	85.1
.0327	45°		42	2.84	86.9
.0475	45°		59	3.99	84.1
.0684	45°		86	5.82	85.1
.0995	45°		130	8.80	88.4
.152	45°		194	13.13	86.4
.215	45°		274	18.54	86.2
.327	45°		415	28.1	85.9
.475	45°		602	40.7	85.8
.684	45°		878	59.4	86.8
.995	45°		1257	85.1	85.5
1.52	45°		1933	130.8	86.1
2.15	44°	50'	2739	185.3	86.2
3.27	44°	42'	4156	281.	86.0
4.75	44°	27'	6010	407.	85.6
6.84	44°	35'	8580	581.	84.9
9.95	44°	20'	12453	843.	84.7
15.2	44°	03'	18960	1283.	84.4
19.25	43°	45'	24150	1632.	84.8
29.3	43°	15'	37020	2504.	85.6
42.8	42°	35'	51900	3513.	82.0

POLYISOBUTYLENE INDOPOL H-1900

Temperature= 100.0°F

SHEAR RATE $j \ sec^{-1}$	EXTINCTION ANGLE χ		COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
.0215	45°		14	.947	44.0
.0327	45°		21	1.421	43.5
.0475	45°		31	2.10	44.2
.0684	45°		45	3.04	44.5
.0995	45°		66	4.47	44.9
.152	45°		99	6.80	44.7
.215	45°		140	9.47	44.1
.327	45°		212	14.34	43.8
.475	45°		315	21.3	44.9
.684	45°		446	30.2	44.2
.995	45°		660	44.7	44.9
1.52	45°		990	68.0	44.7
2.15	45°		1392	94.2	43.8
3.27	45°		2099	142.0	43.4
4.75	45°		3067	207.	43.7
6.84	45°		4414	299.	43.7
9.95	44°	45'	6320	428.	43.0
15.20	44°	35'	9540	645.	42.4*
19.25	44°	23'	12000	812.	42.2*
29.3	44°	07'	18170	1230.	42.0*
42.8	43°	49'	25770	1745.	40.8*

* heating

POLYISOBUTYLENE INDOPOL H-1900

Temperature= 113.0°F

SHEAR RATE $j\ sec^{-1}$	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
.0327	45°	12	.812	25.2
.0475	45°	18	1.218	25.6
.0684	45°	25	1.691	24.7
.0995	45°	37	2.51	25.2
.152	45°	55	3.72	24.5
.215	45°	77	5.22	24.3
.327	45°	125	8.45	25.7
.475	45°	182	12.31	25.9
.684	45°	248	16.79	24.5
.995	45°	369	25.0	25.1
1.52	45°	554	37.5	24.7
2.15	45°	782	52.9	24.6
3.27	45°	1190	80.5	24.6
4.75	45°	1732	117.2	24.7
6.84	45°	2469	167.0	24.4
9.95	45°	3558	241.	24.3
15.2	44° 40'	5384	364.	24.0
19.25	44° 37'	6810	462.	24.0
29.3	44° 30'	10200	690.	23.6
42.8	44° 14'	15010	1016.	23.8

POLYISOBUTYLENE INDOPOL H-1900

Temperature= 130.0°F

SHEAR RATE $j \sec^{-1}$	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
.0995	45°	18	1.218	12.24
.152	45°	28	1.895	12.46
.215	45°	39	2.64	12.27
.327	45°	59	3.99	12.21
.475	45°	86	5.82	12.25
.684	45°	123	8.32	12.16
.995	45°	180	12.18	12.24
1.52	45°	273	18.47	12.15
2.15	45°	389	26.3	12.24
3.27	45°	591	40.0	12.23
4.75	45°	849	57.4	12.09
6.84	45°	1217	82.3	12.03
9.95	45°	1785	120.8	12.14
15.2	45°	2757	186.5	12.27
19.25	45°	3463	234.	12.14
29.3	45°	5296	358.	12.22
42.8	44° 39'	7470	506.	11.83
61.6	44° 25'	10620	719.	11.67*
89.7	44° 11'	15450	1045.	11.65*

* heating

POLYISOBUTYLENE INDOPOL H-1900

Temperature= 149.0°F

SHEAR RATE j sec^{-1}	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^{8}$	MAXWELL CONSTANT $M \times 10^{8}$
.215	45°	19	1.286	5.98
.327	45°	29	1.962	6.00
.475	45°	42	2.84	5.98
.684	45°	60	4.06	5.94
.995	45°	88	5.95	5.98
1.52	45°	133	9.00	5.92
2.15	45°	189	12.79	5.95
3.27	45°	288	19.49	5.96
4.75	45°	420	28.4	5.98
6.84	45°	600	40.6	5.94
9.95	45°	876	59.2	5.95
15.2	45°	1343	90.9	5.98
19.25	45°	1679	113.6	5.90
29.3	45°	2551	172.6	5.89
42.8	45°	3719	252.	5.89
61.6	44° 45'	5190	351.	5.70*
89.7	44° 35'	7380	500.	5.57*
137.0	44° 23'	11400	772.	5.63*

* heating

POLYISOBUTYLENE   INDOPOL H-1900

Temperature $= 167.0^{\circ}F$

SHEAR RATE $j\ sec^{-1}$	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^{8}$	MAXWELL CONSTANT $M \times 10^{8}$
.215	45°	10	.677	3.147
.327	45°	15	1.015	3.105
.475	45°	22	1.488	3.130
.684	45°	32	2.17	3.165
.995	45°	47	3.18	3.196
1.52	45°	71	4.80	3.161
2.15	45°	100	6.77	3.147
3.27	45°	155	10.49	3.207
4.75	45°	218	14.75	3.106
6.84	45°	313	21.2	3.096
9.95	45°	459	31.1	3.122
15.2	45°	696	47.1	3.098
19.25	45°	889	60.2	3.125
29.3	45°	1352	91.5	3.122
42.8	45°	1944	131.5	3.073
61.6	45°	2788	188.7	3.063
89.7	45°	4095	277.	3.089
137.0	45°	5961	403.	2.944 *

* heating

POLYISOBUTYLENE   INDOPOL H-1900

Temperature= 194.0°F

SHEAR RATE $j\ sec^{-1}$	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
.995	45°	19	1.285	1.292
1.52	45°	30	2.03	1.335
2.15	45°	42	2.84	1.322
3.27	45°	64	4.33	1.323
4.75	45°	94	6.36	1.339
6.84	45°	133	9.00	1.315
9.95	45°	195	13.20	1.327
15.2	45°	300	20.3	1.337
19.25	45°	371	25.1	1.305
29.3	45°	558	37.8	1.291
42.8	45°	816	55.3	1.291
61.6	45°	1187	80.3	1.303
89.7	45°	1743	118.0	1.315
137.0	45°	2651	179.4	1.309

POLYISOBUTYLENE

INDOPOL H-1900

Δn

TEMP. °F   77   86   100   113   130   149   167   194

RATE OF SHEAR j sec.⁻¹

POLYISOBUTYLENE
INDOPOL H-1900

TEMP. °F   77   86   100   113   130   149   167   194

SHEAR STRESS τ dynes/cm²
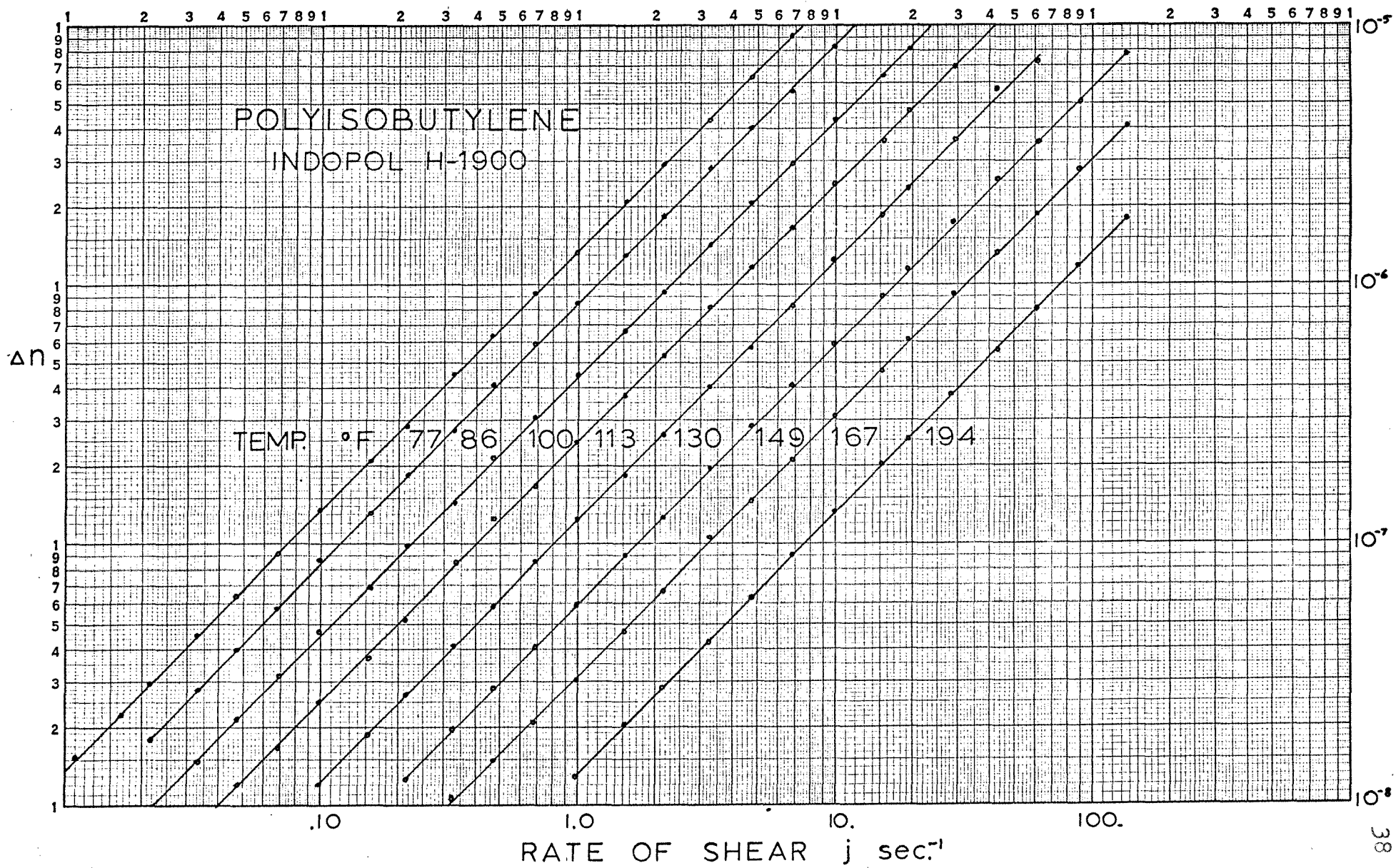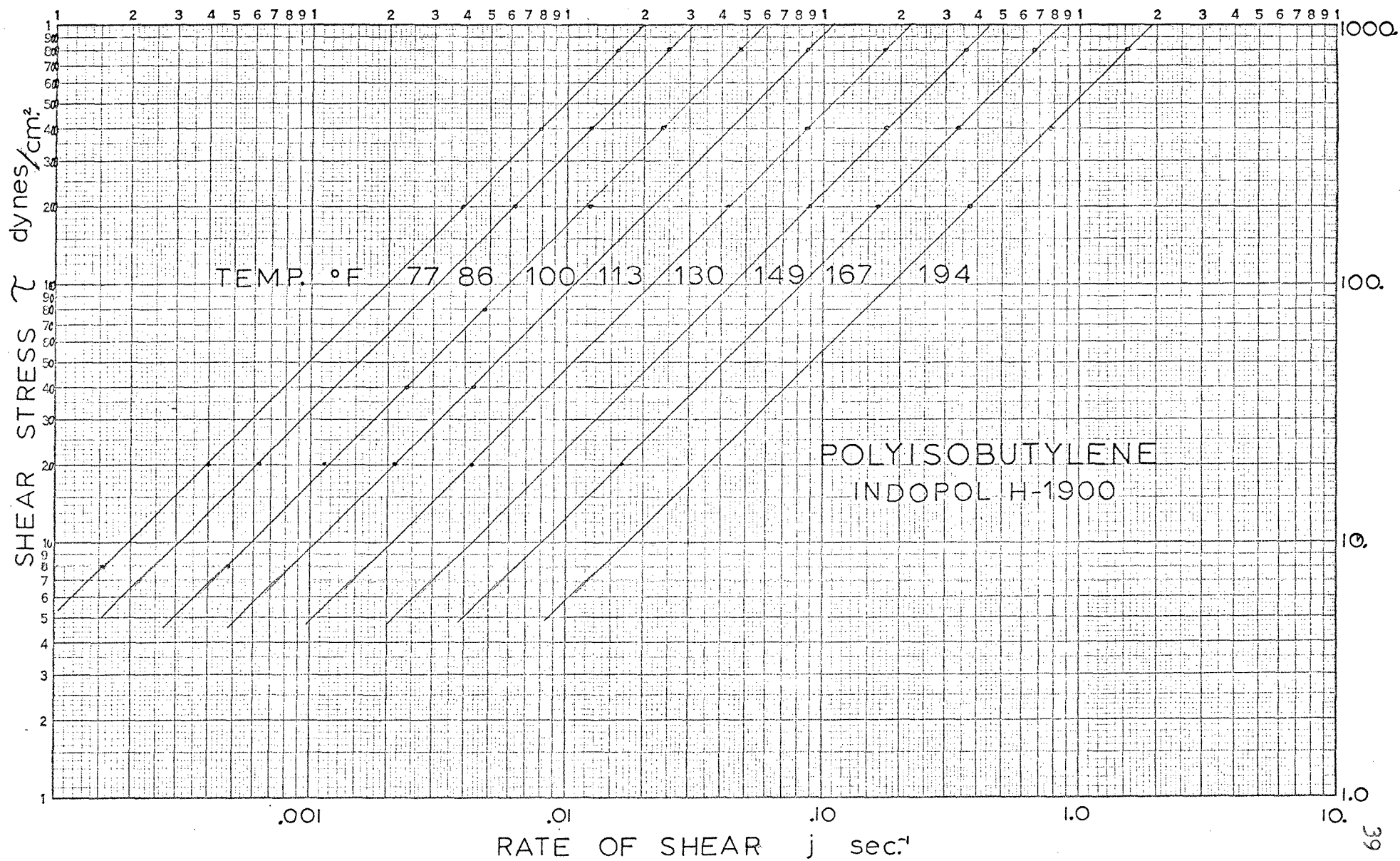
RATE OF SHEAR j sec.⁻¹

$$\log \eta = A (1/(B+T)-(1/(B+77)))+\log \eta_{77}$$

where T is in °F.

The birefringence Δn was also proportional to the rate of shear j and since $\eta = \tau/j$, proportional to the shear stress. A shear stress range from 38 to 216,000 dynes/cm^2 was obtained. At high shear rates heating occurred, necessitating shorter durations for steady state.

The extinction angle χ was observed to depart from 45° for shear stresses above 7000 dynes/cm^2. However, this departure was still small even at 216,000 dynes/cm^2. The Maxwell constant M = $\Delta n/j$ behaved very much like the viscosity, as would be expected. Experimental error was less than 1%. An empirical equation was also derived, with agreement to within .6% of the experimental data.

Being newtonian, the stress-optical coefficient was essentially equal to M/2η or $\Delta n/2\tau$. Despite the large effects of temperature, there was only a 6.7% decrease in the stress-optical coefficient, most of it occurring after 65°C. In the 25° to 65°C range, there was only a 1% variation, well within the experimental error of less than 2%. A stress-optical value of 1339 Brewsters was obtained at 25°C.

This temperature independence effect was first observed by Signer and Gross[20] in a polystyrene solution and later by

[20] R.Signer and H.Gross, _Journal of Physical Chemistry_, A165,(1933)p.161

POLYISOBUTYLENE INDOPOL H-1900

EMPIRICAL EQUATION FOR MAXWELL CONSTANT:

$$\log M = 3350 \left(1/(310+T) - 1/(310+77)\right) + \log M_{77}$$

TEMPERATURE °F	EXPERIMENTAL $M \times 10^8$	CALCULATED $M \times 10^8$	DEVIATION	% DEVIATION
77	135.2	135.2000	+.0000	+.0000
86	85.9	85.9492	-.0492	-.0572
100	44.2	44.1955	+.0045	+.0102
113	24.8	24.7895	+.0105	+.0857
130	12.17	12.2541	-.0841	-.6860
149	5.95	5.9309	+.0191	+.3220
167	3.125	3.1456	-.0206	-.6549
194	1.315	1.3227	-.0077	-.5821

EMPIRICAL EQUATION FOR VISCOSITY:

$$\log \eta = 2870 \left(1/(280+T) - 1/(280+77)\right) + \log \eta_{77}$$

TEMPERATURE °F	EXPERIMENTAL η poise	CALCULATED η poise	DEVIATION	% DEVIATION
77	5048.66	5048.66	+00.00	+.0000
86	3196.50	3202.51	- 6.01	-.1877
100	1663.00	1646.61	+16.39	+.9954
113	931.06	926.32	+ 4.74	+.5117
130	459.22	461.28	- 2.06	-.4466
149	225.06	225.91	- 0.85	-.3763
167	120.55	121.49	- 0.94	-.7737
194	52.63	52.34	+ 0.29	+.5656

VISCOSITY in poise // MAXWELL'S NUMBER × 10⁹

TEMPERATURE °C

MAXWELL CONSTANT

VISCOSITY

POLYISOBUTYLENE INDOPOL H-1900

42
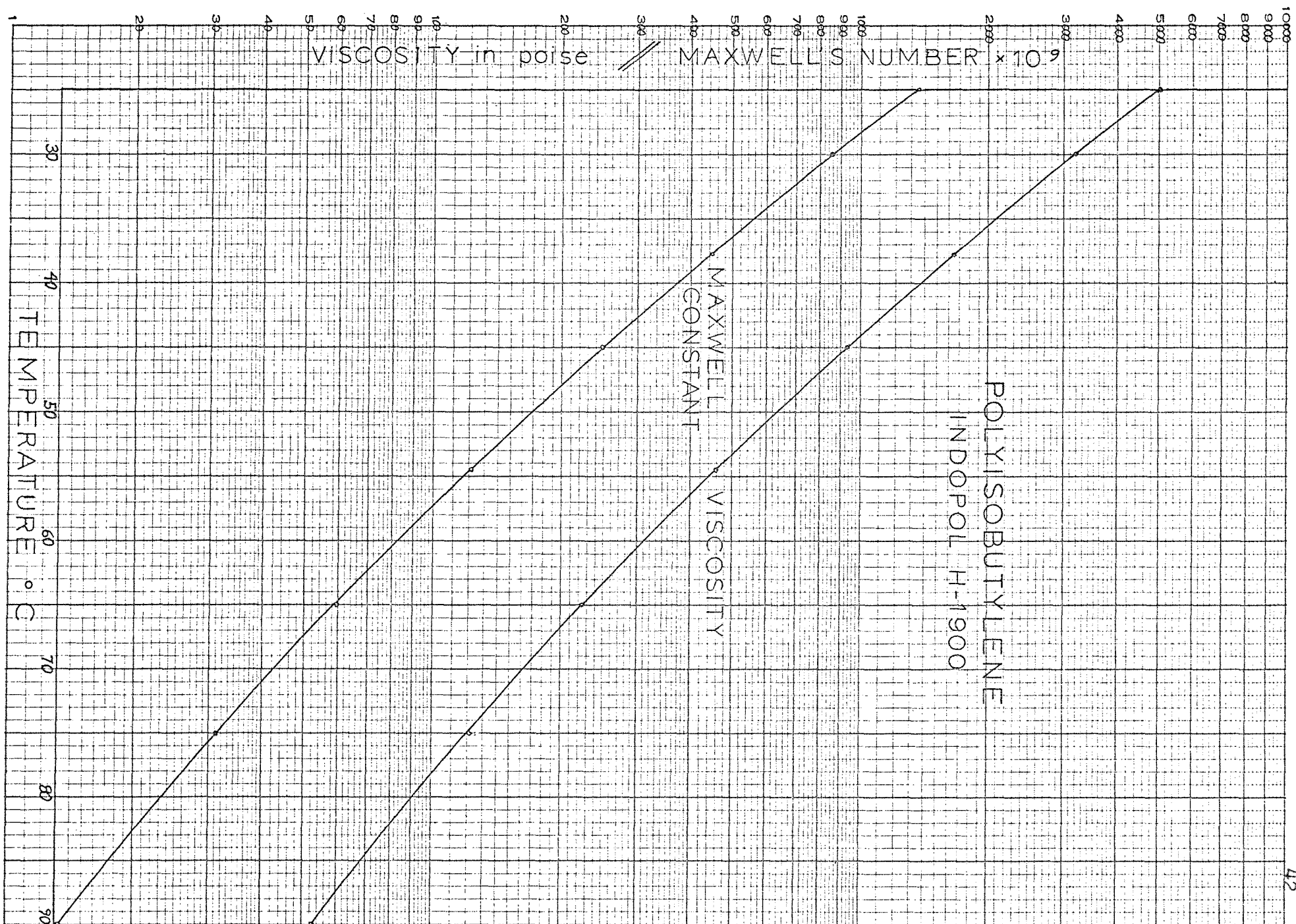
POLYISOBUTYLENE   INDOPOL H-1900

STRESS-OPTICAL COEFFICIENT

CALCULATED from combined empirical equations;

$$C = M/2\eta \times 10^{13} \text{ Brewsters}$$

THEORETICAL from temperature dependent equation;

$$C = C_{77} (460+77)/(460+T)$$

TEMPERATURE °F	EXPERIMENTAL C Brewsters	CALCULATED C Brewsters	% DEVIATION	THEORETICAL C Brewsters
77	1338.97	1338.97	+.0000	1338.97
86	1343.37	1341.90	+.1095	1316.89
100	1328.92	1342.01	-.9754	1283.95
113	1331.82	1338.06	-.4663	1254.80
130	1325.07	1328.27	-.2409	1218.63
149	1321.87	1312.67	+.7062	1180.59
167	1296.14	1294.59	+.1197	1146.68
194	1249.22	1256.53	-.5818	1099.32

ESSO RESEARCH DATA

TEMPERATURE °F	DENSITY ρ g/cc	KIN. VISCOSITY v cSt	VISCOSITY η poise
77	.9224	5601.59	5166.91
100	.9113	1767.26	1610.50
150	.8956	235.66	211.06
210	.8643	37.35	32.28

POLYISOBUTYLENE
INDOPOL H-1900

STRESS OPTICAL COEFFICIENT in brewsters

TEMPERATURE °C

experimental

theoretical

$C = C'T'/T$
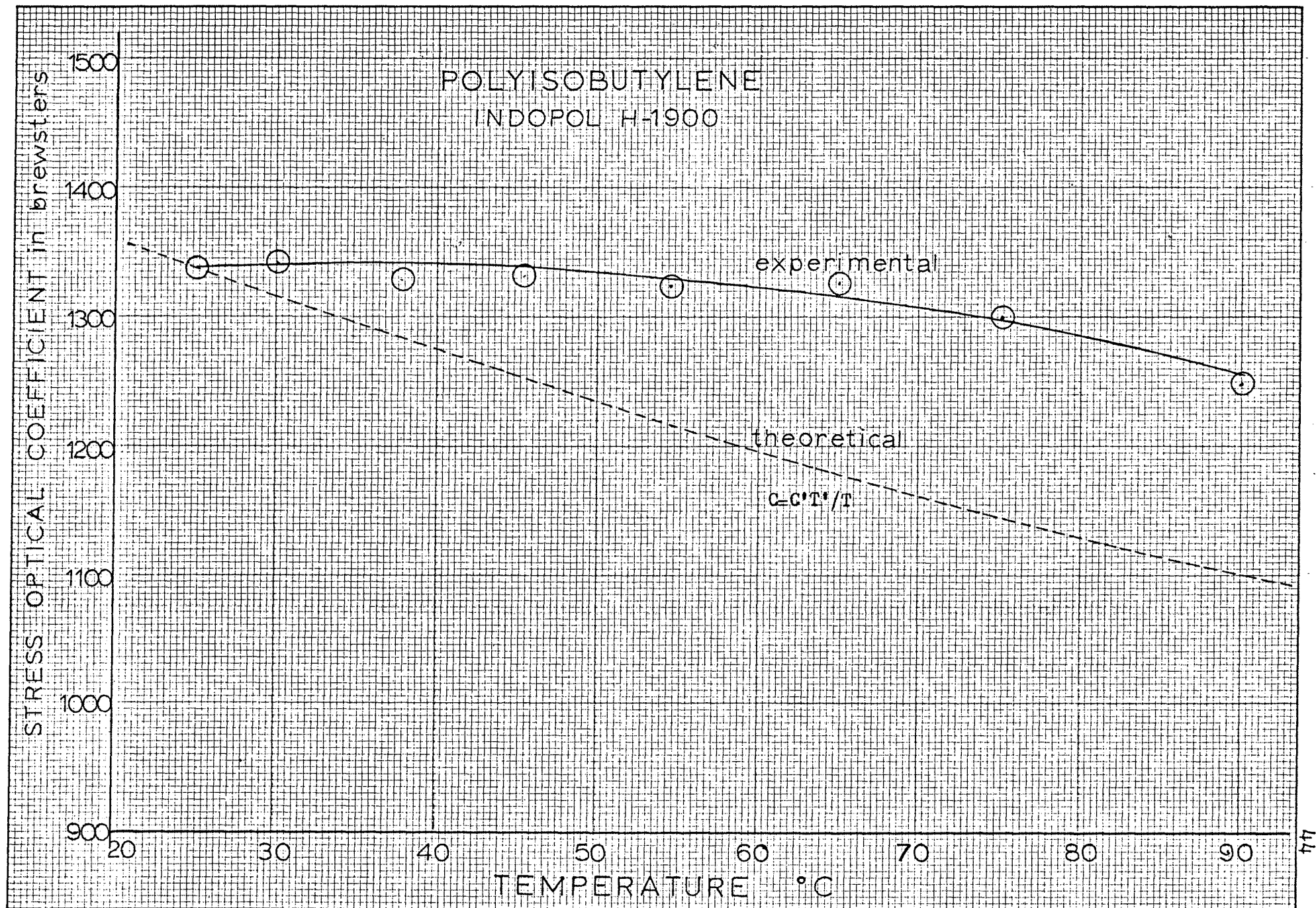
Philippoff[21] on a National Bureau of Standard polyisobutylene of about 200 poise viscosity. However, there was doubt about the effects due to the smaller temperature range and greater errors envolved. For practical purposes, the stress optical coefficient can be considered temperature independent in the vicinity of room temperature. The inverse temperature predicts a 17% decrease in the stress optical coefficient at 90°C, which is much greater than the observed decrease.

A series of straight lines were obtained at the various temperatures when the extinction angles between 45° and 40° were plotted against the shear rate. By correcting for the change in viscosity by plotting the angle versus shear stress, a single straight line was obtained. By applying the relationship;

$$s = 2 \cot 2\chi = \mathcal{T}/G$$

where s is the recoverable shear. By plotting the recoverable shear versus the shear stress, a straight line is obtained whose slope gives the shear modulus $G = 822,000$ dynes/cm^2.

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[21]
W.Philippoff,"The Temperature Dependence of Flow Birefringence Parameters",Transactions ofthe Society of Rheology III,(1959) pp.153-160

POLYISOBUTYLENE   INDOPOL H-1900

| | Temperature= 77.0°F | | | Temperature= 86.0°F | | |
| SHEAR RATE | SHEAR STRESS | EXTINCTION ANGLE | % RECOVERABLE SHEAR | SHEAR STRESS | EXTINCTION ANGLE | % RECOVERABLE SHEAR |
$j\ sec^{-1}$	$\tau\ dynes/cm^2$	χ		$\tau\ dynes/cm^2$	χ	
1.52	7674	44° 52'	.93			
2.15	10855	44° 41'	2.21	6872	44° 50'	1.16
3.27	16509	44° 38'	2.56	10453	44° 42'	2.09
4.75	23981	44° 31'	3.37	15183	44° 27'	3.84
6.84	34533	44° 27'	3.67	21864	44° 35'	2.91
9.95	50234	44° 05'	6.40	31805	44° 20'	4.66
15.20	76740	43° 44'	8.85	48587	44° 03'	6.63
19.25	97187	43° 27'	10.83	61533	43° 45'	8.73
29.3	147926	42° 24'	19.20	93657	43° 15'	12.23
42.8	216083	41° 24'	25.27	136810	42° 35'	16.91

	Temperature= 100.0°F			Temperature= 113.0°F		
9.95	16547	44° 45'	1.75			
15.20	25278	44° 35'	2.91	14152	44° 40'	2.33
19.25	32013	44° 23'	4.31	17923	44° 37'	2.67
29.3	48726	44° 07'	6.17	27280	44° 30'	3.49
42.8	71176	43° 49'	8.27	39849	44° 14'	5.35

POLYISOBUTYLENE   INDOPOL H-1900

Temperature= 130.0°F   Temperature= 149.0°F

SHEAR RATE j sec^{-1}	SHEAR STRESS τ dynes/cm^2	EXTINCTION ANGLE χ	% RECOVERABLE SHEAR	SHEAR STRESS τ dynes/cm^2	EXTINCTION ANGLE χ	% RECOVERABLE SHEAR
42.8	19655	44° 39'	2.44			
61.6	28288	44° 25'	4.13	13864	44° 45'	1.75
89.7	41192	44° 11'	5.70	20188	44° 35'	2.91
137.0				30833	44° 23'	4.31

TEMPERATURE

149 °F
130 °F
113 °F
100 °F
86 °F
77 °F

POLYISOBUTYLENE
INDOPOL H-1900

EXTINCTION ANGLE χ°

RATE OF SHEAR ⅃ sec⁻¹

POLYISOBUTYLENE

INDOPOL H-1900

TEMP.
- • 77 °F
- + 86 °F
- ○ 100 °F
- △ 113 °F
- ▫ 130 °F
- * 149 °F

EXTINCTION ANGLE χ °

SHEAR STRESS τ dynes/cm.²

POLYISOBUTYLENE
INDOPOL H-1900

$G = 822000 \frac{dynes}{cm^2}$

TEMP.

•	77° F
+	86° F
◦	100° F
△	113° F
▫	130° F
✳	149° F

PER CENT RECOVERABLE SHEAR

SHEAR STRESS τ dynes/cm²
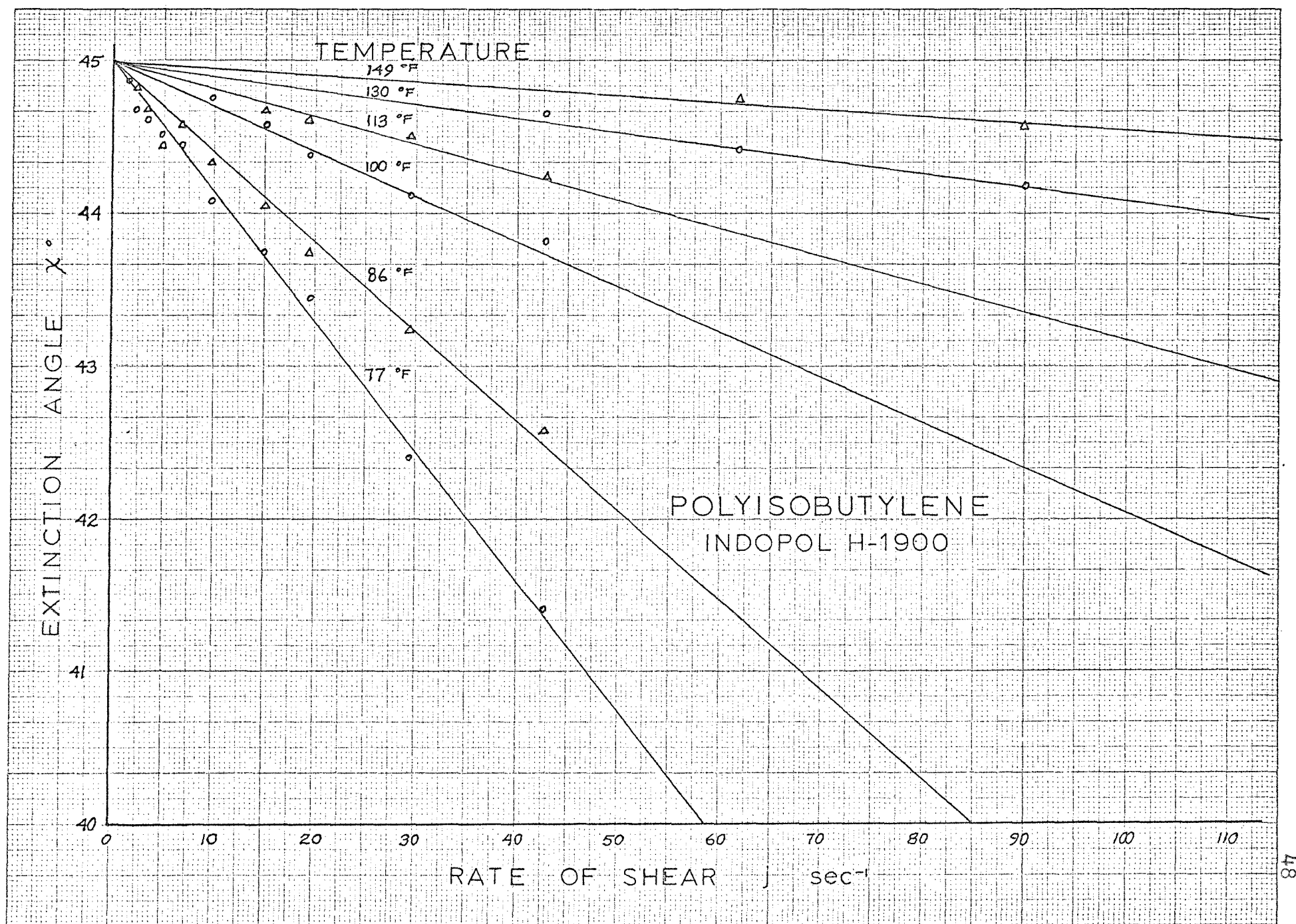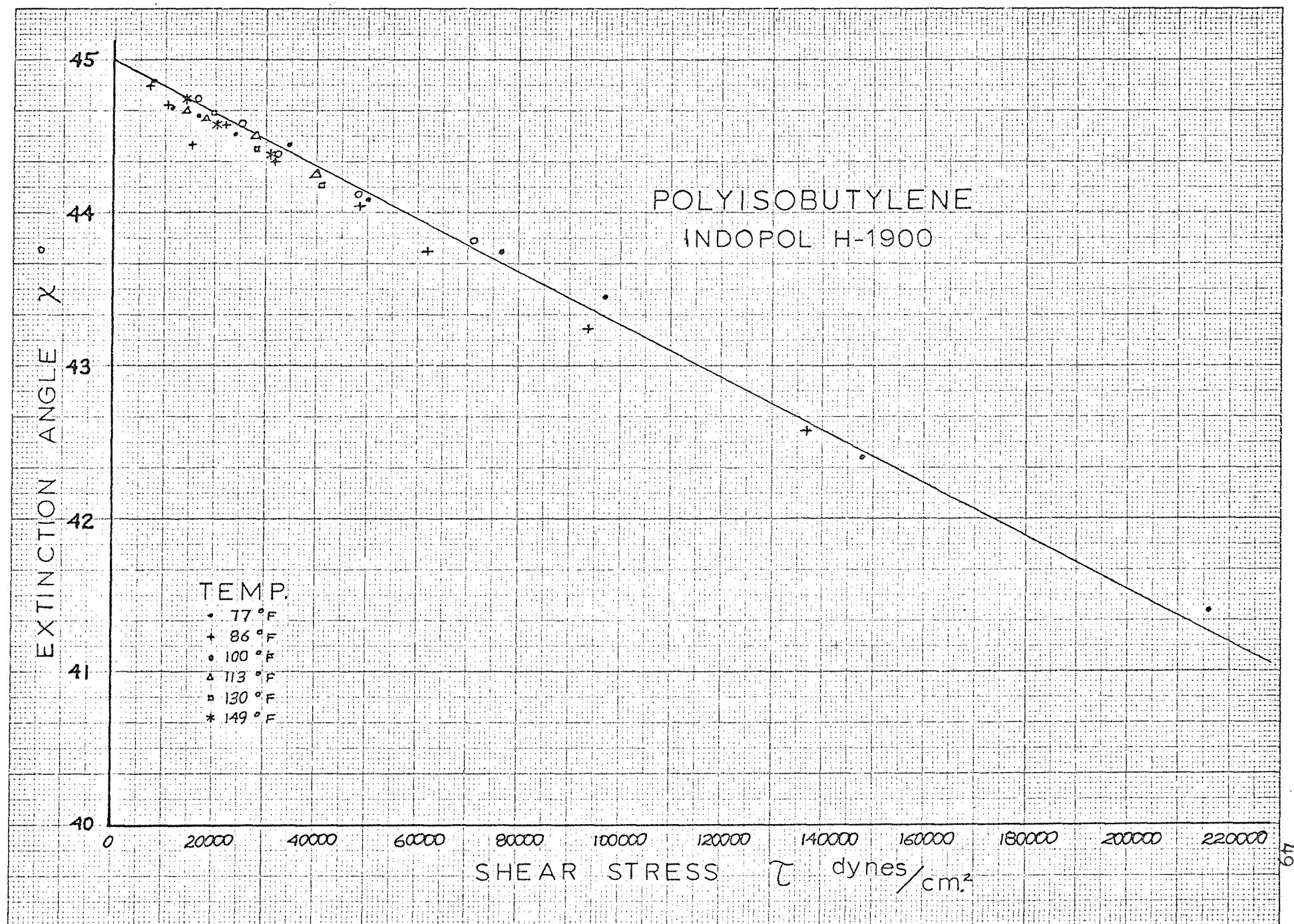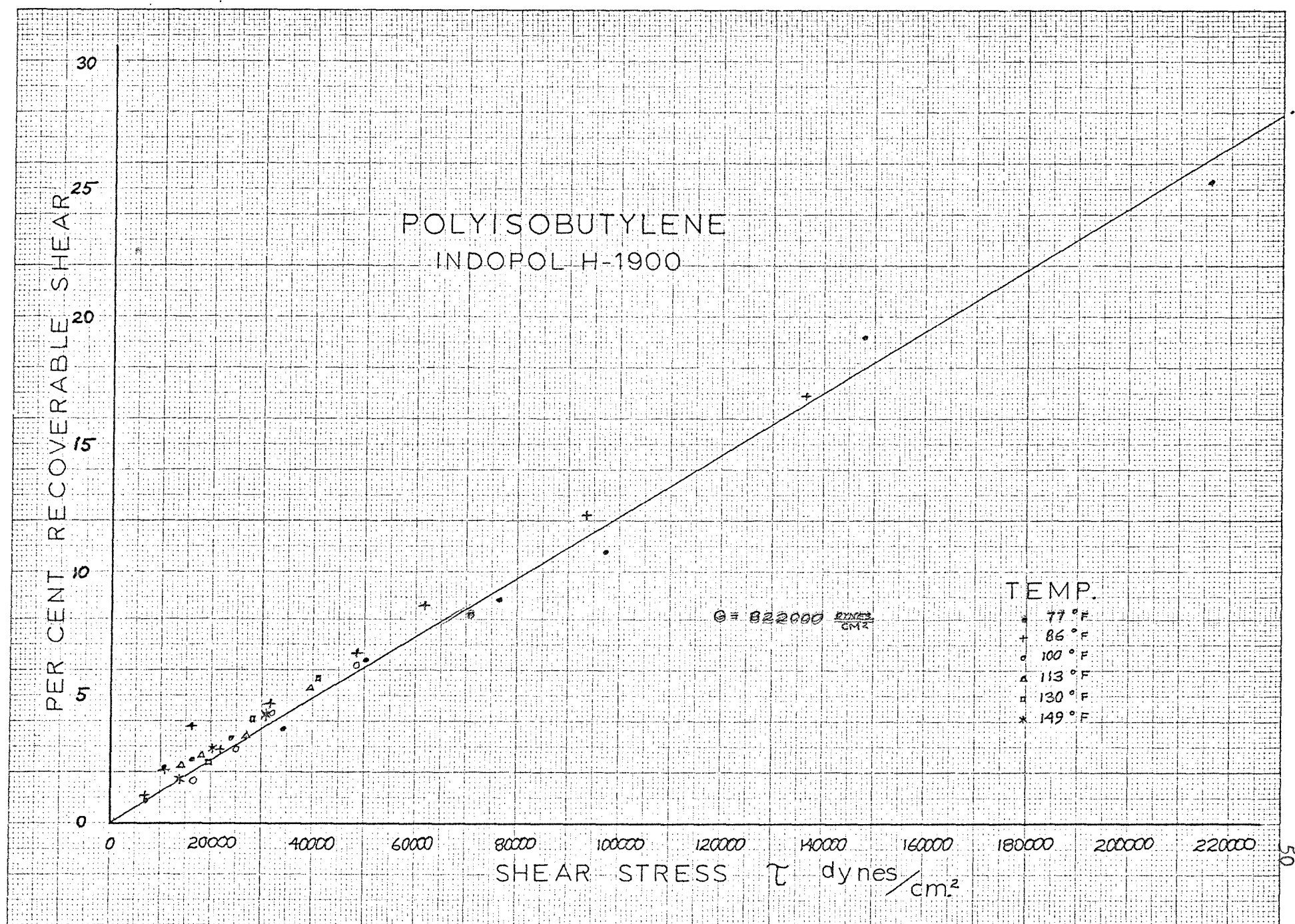
n_{11}-n_{33} REFRACTIVE INDEX DIFFERENCE
FOR VARIOUS POLYISOBUTYLENES

Procedure

For measuring the refractive index differences n_{11}-n_{33} five different polyisobutylene liquids were employed. Their number average molecular weight M_n ranged from 550 to about 27,000 and their respective viscosities at $25^{\circ}C$ varied from 23.65 poise to 1.15×10^6 poise. This large range permitted an evaluation of viscosity and molecular weight effect upon the n_{11}-n_{33} refractive index difference.

As previously described, the device had no provisions for constant temperature measurements and therefore had to be conducted at room temperature. The apparatus is a single pass system where the fluid is passed through the flow chamber once and then expelled. In this manner heating effects due to shearing can be neglected for these short dimensions. The liquid is contained in a 400cc vessel which is pressurized by nitrogen gas. The fluid flow is controlled by a quick close valve before the flow chamber.

To calibrate the device, Indopol H-1900 was used. Two burets fashioned into a manometer were connected to a 500cc receiving flask, which in turn was connected to the fluid exit line. By timing the flow and knowing its viscosity, it was possible to obtain the shear stress as a function of the

VARIOUS POLYISOBUTYLENES AT 25°C

| TYPE | MOLECULAR WEIGHT | | VISCOSITY | STRESS-OPTICAL COEFFICIENT |
	PUBLISHED M_n	EXPERIMENTAL M_n	η poise	C Brewsters
INDOPOL L-10			.408	590
INDOPOL L-50	460	400	1.95	915
INDOPOL L-100	520	435	4.45	985
ORONITE N-16	550	549	23.6	1120
INDOPOL H-25	670	593	29.45	976
INDOPOL H-35	730	594	41.3	1130
ORONITE N-18	625	661	53.8	984
INDOPOL H-50	770	665	86.8	980
ORONITE N-20	700	715	92.8	995
INDOPOL H-100a	830	782	154.	1115
OB-14			207.	1045
ORONITE N-24	900	882	209.	1150
ORONITE N-24a	900	911	212.5	1095
OB-20			223.7	1090
INDOPOL H-100	830	859	230.	1035
OPPANOL B5			500.	1300
ORONITE N-32	1190	1130	670.	1285
INDOPOL H-300	1100	1046	790.	1345
INDOPOL H-1900	1900	2560	5049.	1339
VISTANEX LM/MS	$(69000)_{visc.}$	$(30000)_{extrap.}$	1.15×10^6	1305

POLYISOBUTYLENES
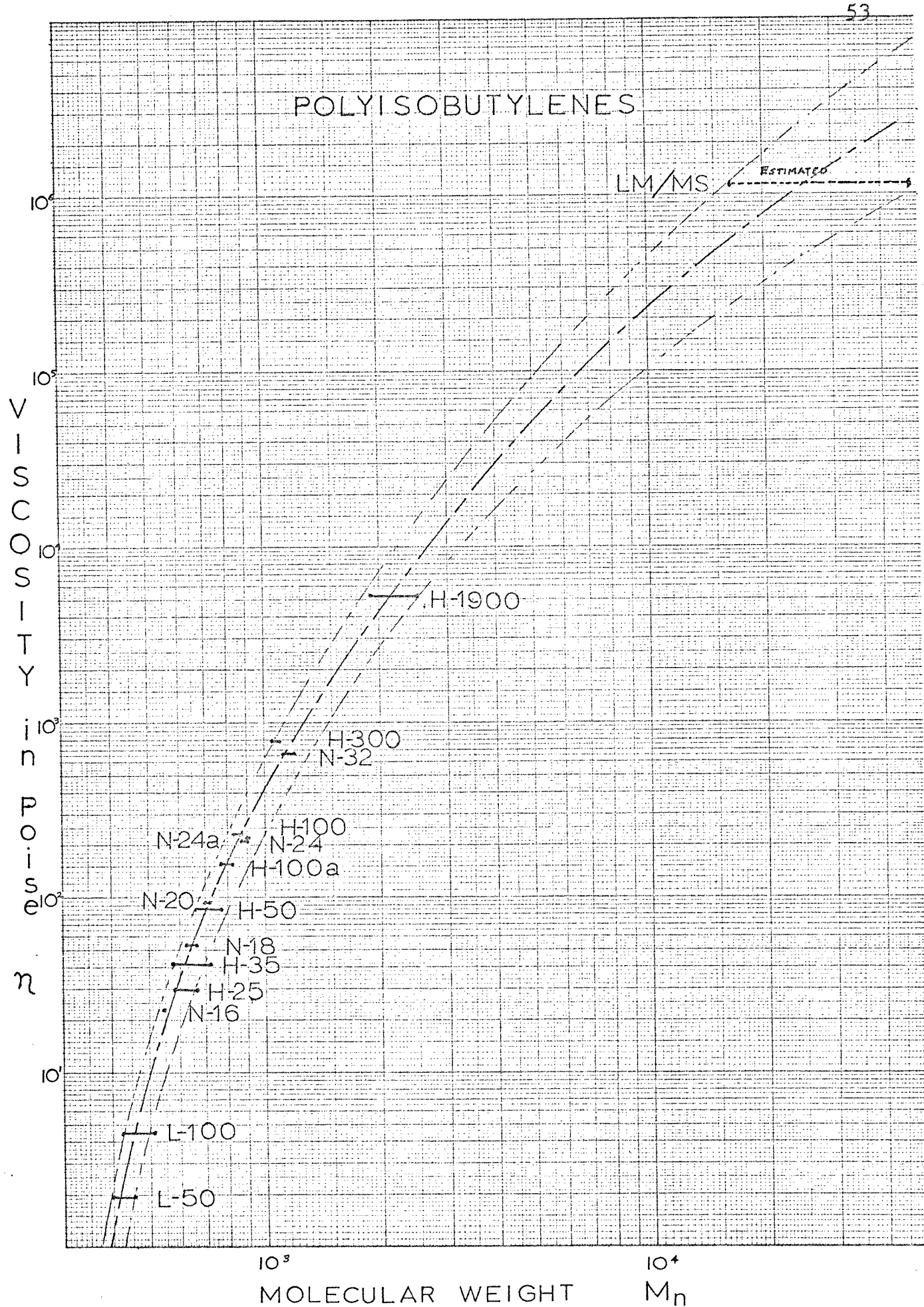
gauge pressure (see Appendix). Both the .025 in. and .050in. gaps were used with the Indopol H-1900 measurements. Since higher shear stresses were obtainable with the .050 in. gap, it was the only one used for the other liquids.

For the optical orientation, the flow chamber was positioned perpendicular to the light beam. The polarizer was set at a 90° angle (45° to the direction of flow) and the reading were obtained from the Senarmont compensator. Except for the Indopol H-1900, all viscosity and birefringence Δn data was obtained from Esso Research.

$n_{11}-n_{33}$ Results

Calibration of the flow apparatus yielded a shear stress range of 35,000 to 178,000 dynes/cm^2, the lower limit being the sensitivity of the Senarmont compensator and the upper limit due to the pressure vessel. In all cases the $n_{11}-n_{33}$ refractive index difference, which was found to have a positive value, was observed to follow the square of the shear stress. This tends to verify the relationship for newtonian liqiids that:

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

The values are calculated from the relationship

$$(n_{11}-n_{33})_w = 3\lambda S_n/(180\ d)$$

where λ = the wave length of the light (.546 x 10^{-4}cm), S_n

POLYISOBUTYLENE ORONITE N-16

Temperature= 70.0°F

Gap= .050 in

PRESSURE lbs/in^2	SHEAR STRESS γ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{11}-n_{33})$ x 10^6
100	71250	11	1.315
130	92630	19	2.270
160	114000	25	2.988
200	142500	34	4.063
250	178130	47	5.617

POLYISOBUTYLENE INDOPOL H-25

Temperature= 70.5°F

Gap= .050 in

PRESSURE lbs/in^2	SHEAR STRESS γ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{11}-n_{33})$ x 10^6
200	142500	6	.717
250	178130	10	1.195

POLYISOBUTYLENE ORONITE N-24

Temperature= 72.7°F

Gap= .050 in

PRESSURE lbs/in^2	SHEAR STRESS γ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{11}-n_{33})$ x 10^6
160	114000	7.5	.896
200	142500	12.5	1.494
250	178130	18.0	2.151

POLYISOBUTYLENE INDOPOL H-1900

Temperature= 73.4°F

Gap= .025in

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	$(n_{11}-n_{33})$calc. x 10^6	SENARMONT ANGLE θ min	$(n_{11}-n_{33})$ x 10^6
80	51400	.430		
100	64250	.673		
120	77100	.969	4	.957
150	96380	1.513	6	1.435
170	109230	1.945	8.2	1.958
200	128500	2.692	11	2.630

Gap= .050 in

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	$(n_{11}-n_{33})$calc. x 10^6	SENARMONT ANGLE θ min	$(n_{11}-n_{33})$ x 10^6
80	55580	.503	4	.478
100	69470	.786	6	.717
120	83360	1.130	10	1.195
150	104200	1.767	15	1.792
170	118100	2.268	18.7	2.235
200	138900	3.141	26.6	3.192

POLYISOBUTYLENE VISTANEX LM/MS

Temperature= 74.0°F

Gap= .050 in

PRESSURE	SHEAR STRESS		SENARMONT ANGLE	$(n_{11}-n_{33})$
	(Uncorrected)	(Corrected)		
lbs/in^2	τ dynes/cm^2	τ dynes/cm^2	θ min	x 10^6
50	35630	31920	27	3.227
80	57000	49080	56	6.692
100	71250	60330	81	9.680
130	92630	76150	119	14.22
160	114000	91000	148	17.69
180	128250	100350	174	20.79
200	142500	109600	199	23.78
220	156750	118280	230	27.49
250	178130	131500	276	32.98

POLYISOBUTYLENE

SHEAR STRESS 10^5 dynes/cm^2
TEMPERATURE $\sim 77°$F

$(n_{||} - n_{33})$

MOLECULAR WEIGHT M_n
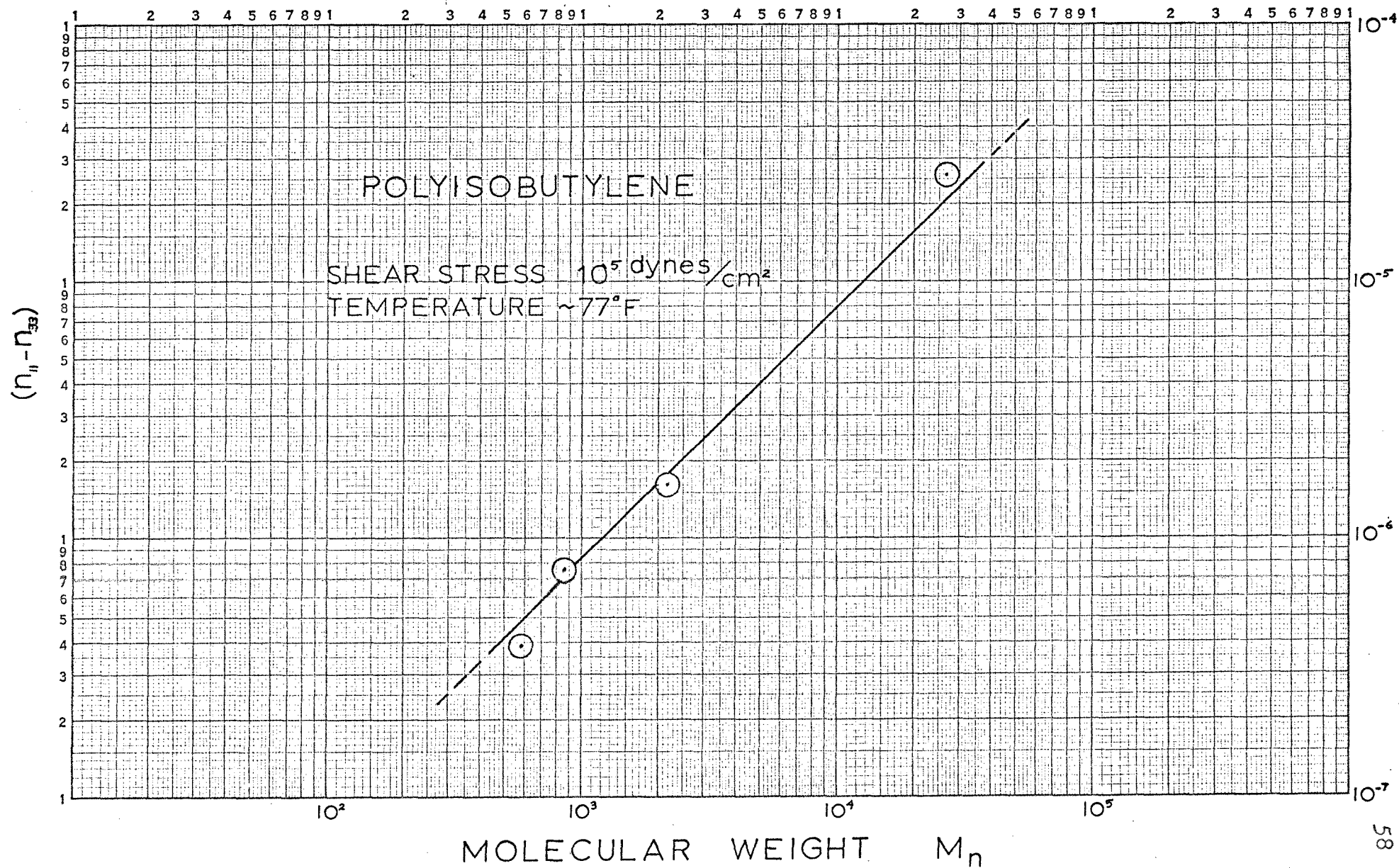
is the Senarmont angle in degrees, and d = the gap. This
equation can be reduced to the simple relationship:

$$n_{11}-n_{33} = K \, S_n'$$

where S_n' is the Senarmont angle in minutes and $K = 23.9$
x $10^{-8} min^{-1}$ for the small gap and 11.95 x $10^{-8} min^{-1}$ for
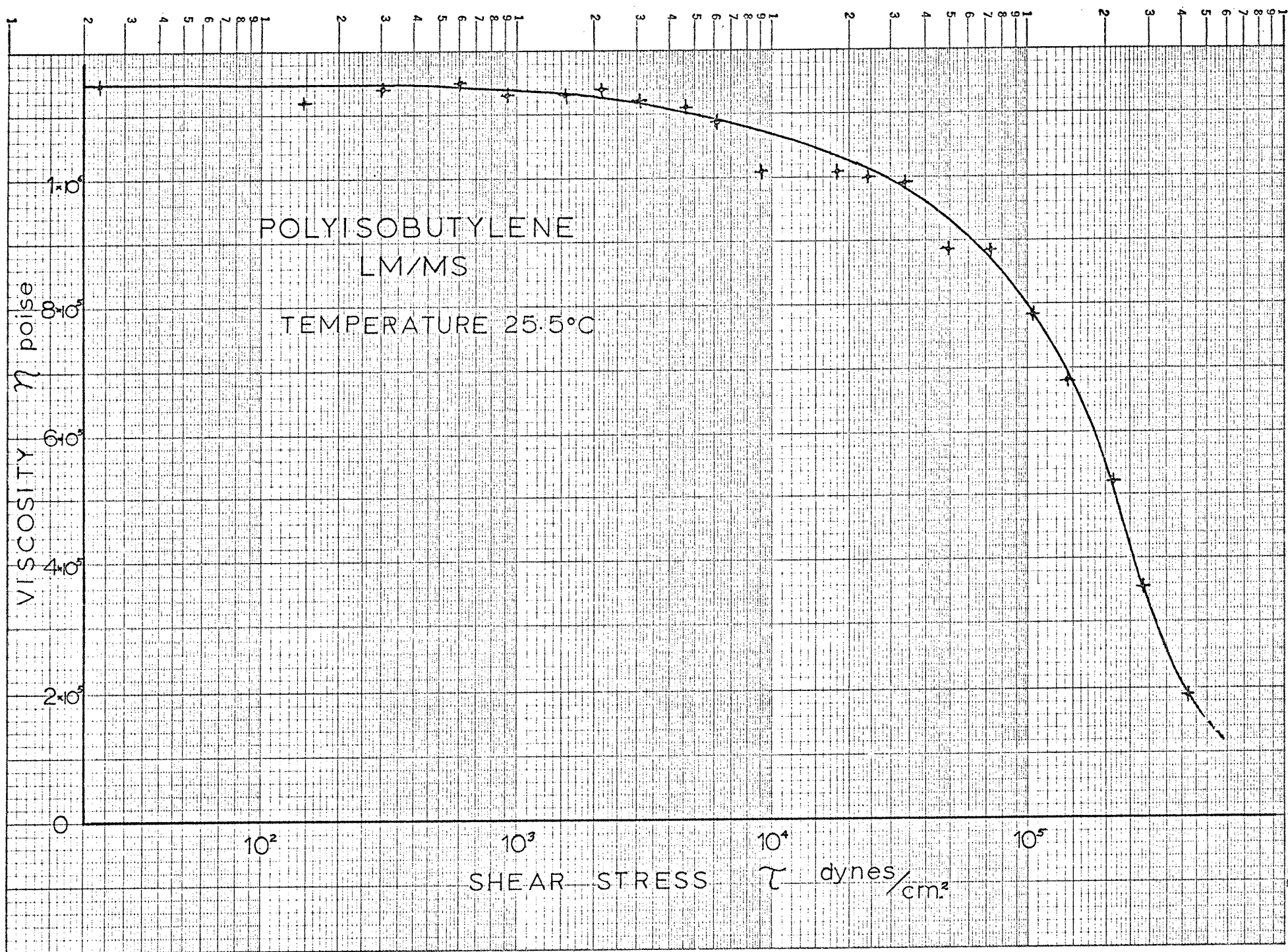the large gap.

The two equations were in close agreement with one
another for the Indopol H-1900 measurements. There was
some discrepancy for the LM/MS, which exhibited a non-new-
tonian behavior of its viscosity. With a shear modulus of
$G = 105,400$ dynes/cm^2 obtained from the extinction angle,
agreement was achieved with uncorrected shear stresses but
differed by a factor of two with the corrected values. This
error increases if one attempts to use the relationship
$G = \tau/s$, where s is the recoverable shear obtained from re-
coil measurements in a cone and plate viscometer. The shear
modulus could not be obtained for the lower molecular weight
polyisobutylenes.

For all of the polyisobutylenes except one (Oronite
N-16), a rise in the molecular weight was accompanied by an
increase in the $n_{11}-n_{33}$ values. With a closer inspection
the $n_{11}-n_{33}$ molecular weight relationship was observed to
be nearly linear. This fact agrees with the presence of the
molecular weight term in the equation:

POLYISOBUTYLENE VISTANEX LM/MS

Temperature= 25.5°C

SHEAR STRESS τ dynes/cm^2	SHEAR RATE j sec^{-1}	VISCOSITY η x10^{-6} poise	RECOVERABLE SHEAR S	SHEAR MODULUS G dynes/cm^2
23.1	.0000201	1.150		
146	.000131	1.145	.009	16000
300	.000263	1.141	.018	17000
608	.000529	1.150	.019	32000
916	.000807	1.135	.023	40000
1530	.00135	1.133	.026	59000
2150	.00188	1.143	.039	55000
3070	.00274	1.120	.054	57000
4610	.00415	1.111	.066	70000
6150	.00563	1.092	.066	93000
9230	.00910	1.014	.077	120000
18200	.0180	1.011	.143	127000
24300	.0243	1.000	.178	136500
33600	.0337	.997	.225	149000
49000	.0552	.888	.304	161000
72700	.0872	.834	.432	168000
104000	.133	.782	.590	176000
143000	.210	.681	.721	198000
213000	.409	.521	.983	216700
282000	.795	.355	1.31	215300
422000	2.20	.192		

POLYISOBUTYLENE
LM/MS

TEMPERATURE 25.5°C

VISCOSITY η poise

SHEAR STRESS τ dynes/cm²

$$G = c\rho RT/M_w$$

where c is the concentration, ρ= density, R is the gas constant, T = absolute temperature, and Mw is the weight average molecular weight. For a newtonian liquid this would lead to ;

$$(n_{11}-n_{33})_w = \frac{C\ M_W \tau_W^2}{c\rho\ R\ T}$$

Although this equation contains a weight average rather than a number average molecular weight, the two are nearly proportional.

The discrepancy of the Oronite N-16 is most likely due to the composition of the liquid. According to the manufacturer, some of the liquids are a mixture of polybutylene isomers. These other isomers do not necessarily exhibit the same optical properties as the 'iso' form.

TEMPERATURE AND MOLECULAR WEIGHT EFFECTS UPON $n_{22}-n_{33}$

Experimental Procedure

Unlike the refractive index difference $n_{11}-n_{33}$, very little is known about that of the $n_{22}-n_{33}$. In fact, conventional theory predicts that $n_{22}-n_{33}$ should be zero. Despite this, its effects have been noted by various investigators and an attempt to correlate the effect was made by Wales and Philippoff.[22] All that is known about it is that the effects are relatively small (5-10% of $n_{11}-n_{22}$) and that it occurs in nearly newtonian fluids more often than in non newtonian liquids.

The procedure for obtaining the flow rate calibrations and the pressure-shear stress relationship for the $n_{22}-n_{33}$ apparatus is identical tor that of the $n_{11}-n_{33}$ device. In this case;

$$n_{22}-n_{33} = \frac{3 \lambda S_n}{180} \frac{o}{1}$$

where 1 now equals the length of the slit (2.54 cm), reducing the final equation to $n_{22}-n_{33} = K \, Sm'$, where $K = 1.99 \times 10^{-8} min^{-1}$. The shear stress range in this case was from 29,000 to 146,500 dynes/cm^2. Similarly, Indopol H-1900 was used for these measurements. For this device however,

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22
    J.L.S.Wales and W.Philippoff,"The Anisotropy of Simple Shearing Flow",Rheological Acta 12 (1973)pp.25-34

a water jacket was constructed, enabling constant temperatures to be maintained. Various temperatures from 25° to 75°C were employed to study the effects of temperature.

An additional problem with this apparatus was the effect of internal strain on the windows. Since the windows are much thicker, these aberrations could not be ignored. However, it was possible to position the windows so that the effects would cancel one another out. To test the orientation, the chamber was pressurized without flow and the effects were noted. Any residual birefringence was subtracted from the measurements.

The same polyisobutylenes that were used in the previous apparatus were employed in this one. Only the Indopol H-1900 however, was subjected to temperature changes.

Results of the Temperature and Molecular Weight Study

For all of the polyisobutylenes studied, the $n_{22}-n_{33}$ refractive index difference was negative in sign. There was also a considerable temperature effect on the $n_{22}-n_{33}$ for the Indopol H-1900. By increasing the temperature from 25° to 75°C, the $n_{22}-n_{33}$ decreased by a factor of 30%. The introduction of the absolute temperature into the denominator would only account for a 14% decrease. This per cent appeared independent of shear stress, although the effect itself ($n_{22}-n_{33}$) was a direct function of the shear stress.

POLYISOBUTYLENE   INDOPOL H-1900

Temperature= $77.0\pm.04^\circ$F

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min	$(n_{33}-n_{22})$ x 10^6
50	29310	49	.0975
80	46890	105	.209
100	58610	198	.394
130	76190	317	.631
160	93780	476	.947
200	117220	585	1.164
250	146530	742	1.477

Temperature= $86.0\pm.08^\circ$F

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
50	29310	50	.0995
80	46890	96	.191
100	58610	154	.307
130	76190	320	.637
160	93780	478	.951
200	117220	621	1.236
250	146530	705	1.403

Temperature= $100.0\pm.15^{\circ}$F

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
50	29310	47	.0935
80	46890	115	.229
100	58610	188	.374
130	76190	309	.615
160	93780	418	.832
200	117220	555	1.105
250	146530	697	1.387

Temperature= $130.0\pm.25^{\circ}$F

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
80	46890	66	.131
100	58610	136	.271
130	76190	202	.402
160	93780	327	.651
200	117220	445	.886

Temperature= $167.0\pm.5^{\circ}$F

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
80	46890	72	.143
100	58610	123	.245
130	76190	200	.398
160	93780	325	.647
200	117220	403	.802

POLYISOBUTYLENE
INDOPOL H-1900

PRESS. (psig)

250

200

160

130

100

80

50

$-(n_{22}-n_{33}) \times 10^{7}$

TEMPERATURE °C
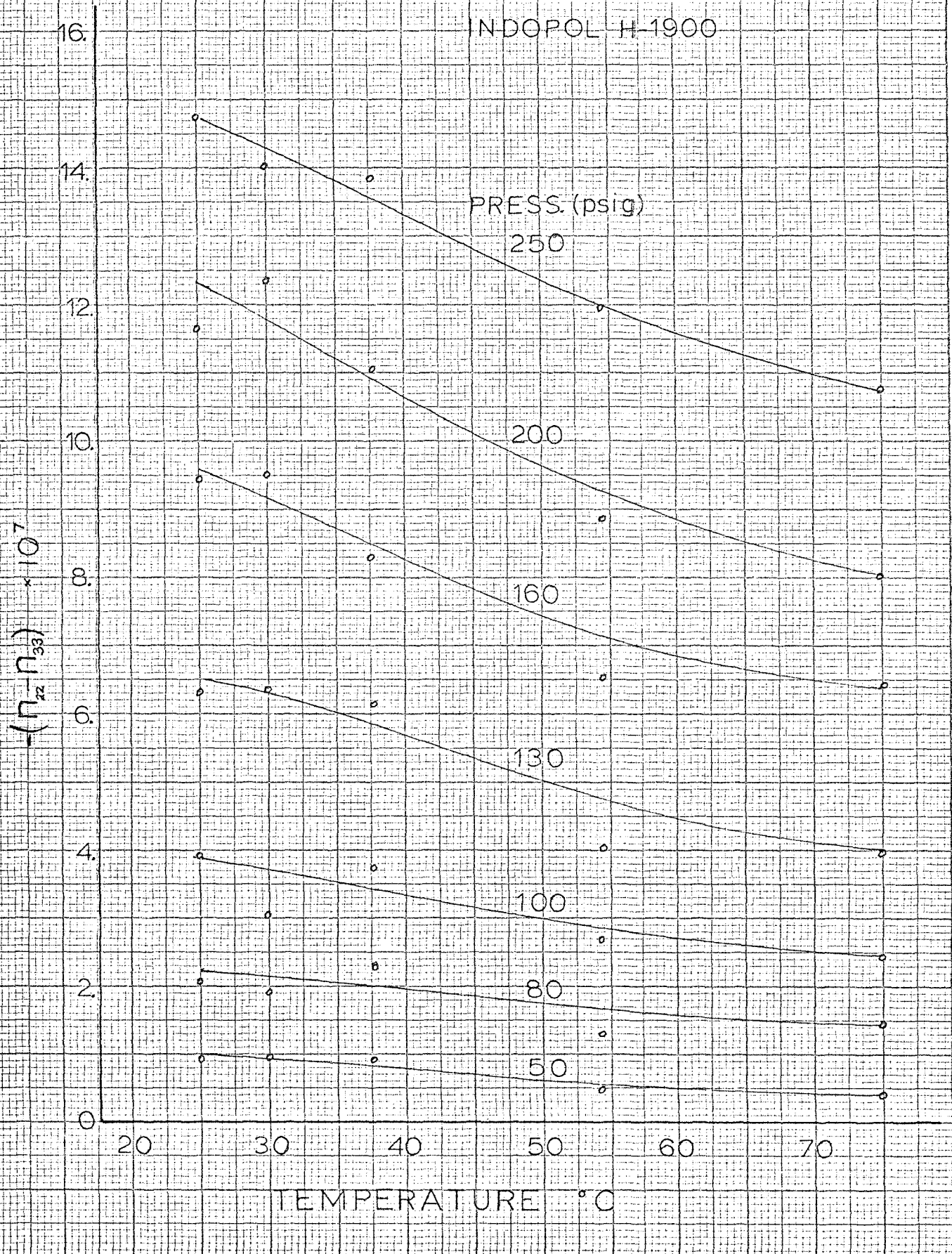
As in the case of the $n_{11}-n_{33}$ difference, the $n_{22}-n_{33}$ appeared to increase with the square of the shear stress, until around a shear stress of 80,000 dynes/cm^2. For higher shear stresses the rate of change decreases and becomes proportional to the shear stress. The effect is still relatively small, attaining a maximum of 4% of the birefringence Δn. This is quite similar to that observed by Wales and Philippoff on other materials such as silicone and styrene.

What is surprising is the fact that, except for the high viscosity LM/MS, the $n_{22}-n_{33}$ was nearly identical for the various polyisobutylenes despite the great variation in their molecular weight. The Vistanex LM/MS posed a special problem. Since the viscosity was very high, it was nearly impossible to eliminate, in a reasonable amount of time, any small bubbles that were introduced in filling the reservoir. Consequently, a narrow opaque dispersion band appeared at the center of the slit, necessitating observations above and below it. The measurements were repeated with a very similar material Vistanex LM/MH, with a zero shear viscosity of 1.19×10^6 poise. These measurements agreed quite well with the lower molecular weight polyisobutylenes.

This observation indicated that the $n_{22}-n_{33}$ effect was not uniform throughout the slit, having a maximum value

POLYISOBUTYLENE   ORONITE N-16

Temperature= 70.0°F

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
50	29310	53	.1055
80	46890	98	.1950
100	58610	161	.3204
130	76190	267	.5313
160	93780	389	.7741
200	117220	528	1.051
250	146530	624	1.242

POLYISOBUTYLENE   INDOPOL H-25

Temperature= 70.5°F

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
50	29310	65	.1294
80	46890	148	.2945
100	58610	194	.3861
130	76190	283	.5632
160	93780	362	.7204
200	117220	443	.8816

POLYISOBUTYLENE   ORONITE N-24

Temperature= $72.7^{\circ}F$

PRESSURE lbs/in^2	SHEAR STRESS τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
50	29310	43	.0846
80	46890	104	.2060
100	58610	156	.3104
130	76190	296	.589
160	93780	396	.788
200	117220	496	.987
250	146530	653	1.299

POLYISOBUTYLENE   VISTANEX LM/MS

Temperature= $74.0^{\circ}F$

PRESSURE lbs/in^2	SHEAR STRESS (Corrected) τ dynes/cm^2	SENARMONT ANGLE θ min.	$(n_{33}-n_{22})$ x 10^6
50	26530	145	.2886
80	41220	363	.7224
100	50580	575	1.144
130	64080	865	1.721
160	76900	1185	2.358
200	93070	1435	2.856
250	111950	1875	3.731

POLYISOBUTYLENE

$-(n_{22}-n_{33})$

SHEAR STRESS τ dynes/cm²

+ LM/MS
△ H-1900
○ N-24
□ H-25
* N-16
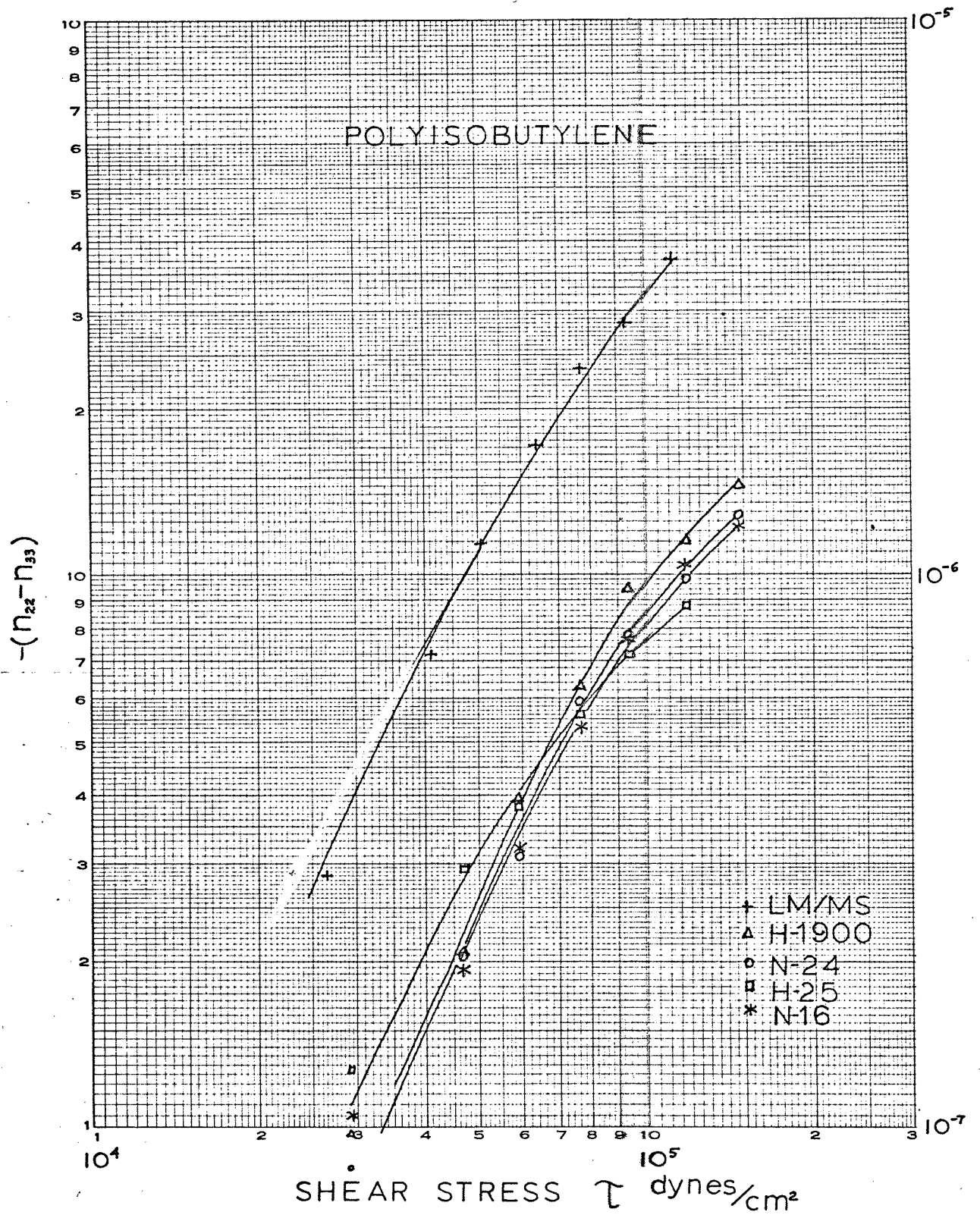
at the walls. Two possible expanations are that: it was caused by polarization of the light reflected of the walls; or that the effect was maximum at the walls and zero at the center of the slit.

The first possibility would account for the existance of the $n_{22}-n_{33}$ effect. As the shear stress increases, increasing internal heating would cause more of the light to be diffracted and reflected off of the walls, leading to a greater $n_{22}-n_{33}$ effect. However, a study of polarization due to reflection was performed by Harrick[23] The results of this study indicate that angles this large would be unlikely for a grazing light beam. When an air-silver interface was employed, which gave a high degree of polarization, an incident angle of 35° was necessary to achieve a polarized angle of 25°. A mercury-air interface required an incident angle of 45°.

The other explanation assumes a linear change in the effect, with a maximum at the wall. The observed reading is assumed to be a simple arithmetic average of the field. This alternate explanation would account for the change in the $n_{22}-n_{33}$ as a function of distance from the center of the slit, but not for the cause of the $n_{22}-n_{33}$ effect itself.

A preliminary attempt to verify this hypothesis was

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[23] N.J.Harrick,"Reflection of Infrared Radiation from a Germanium-Mercury Interface", Journal of the Optical Society of America 49,No.4 (1959)p.376

% of Max. vs Microns graph
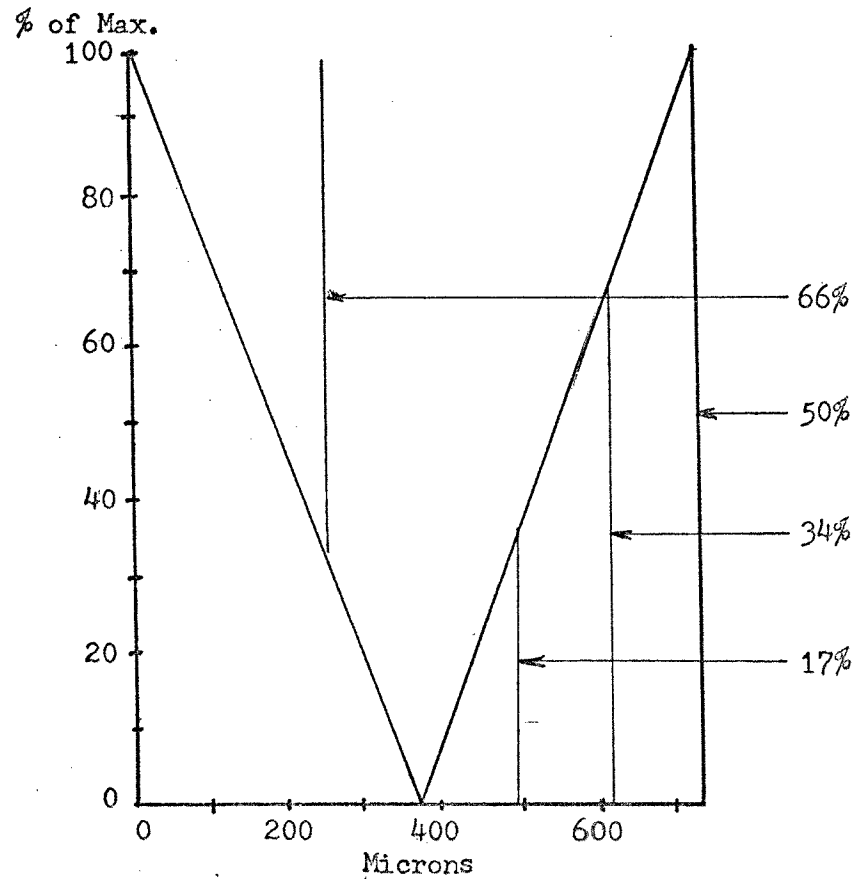
POLYISOBUTYLENE VISTANEX LM/MH

WIDE BEAM (735+)

$\frac{1}{2}$ (735/735) = .50

MEDIUM BEAM (500)

$\frac{1}{2}$ (500/735) = .34

NARROW BEAM (250)

$\frac{1}{2}$ (250/735) = .17

NARROW BEAM AT WALL

1-(250/735) = .66

Pressure= 160 psi   Temperature= 70.6°F

LIGHT BEAM μ microns	$(n_{33}-n_{22})x10^6$ Calculated	Experimental
250	.406	.428
500	.812	.955
735+	1.194	1.194
250 (at wall)	1.572	1.572
~0 (at wall)	2.388	

made with the Vistanex LM/MH using different width light beams at the center and at the walls of the slit. The results tended to agree with the predicted values; however, greater precision would be necessary to conclusively prove or disprove the theory. This can be accomplished by using a narrower beam of light and measuring its exact position within the slit. Further measurements with various temperatures would also be necessary to see if there really is a temperature effect or whether it was due to the positioning of the light beam within the slit.

It was also possible to obtain the n_{11}-n_{22} refractive index difference for Indopol H-1900 by using the following relationship:

$$n_{11}-n_{22} = \Delta n \cos 2\chi$$

With the three planes of observations it becomes quite obvious that there is a serious discrepancy in the stress optical relationship, where the sum of the refractive index differences is equal to zero:

$$(n_{11}-n_{22}) + (n_{22}-n_{33}) + (n_{33}-n_{11}) = 0$$

It seems apparent that the n_{22}-n_{33} effect is actually a combination of some other effects rather than the refractive index difference in the 2-3 plane, caused exclusively by the flow.

POLYISOBUTYLENE ORONITE N-16 ‡

Temperature= 77.0°F

SHEAR RATE j sec^{-1}	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
2.15	45°	18	1.22	.567
3.27	45°	25	1.69	.517
4.75	45°	37	2.50	.526
6.84	45°	54	3.65	.534
9.95	45°	78	5.27	.530
15.2	45°	118	8.00	.526
19.25	45°	150	10.15	.527
29.3	45°	230	15.6	.532
42.8	45°	333	22.5	.526
61.6	45°	480	32.5	.528
89.7	45°	706	47.8	.533
137.	45°	1066	72.1	.526
192.5	45°	1507	102.	.530
293.	45°	2276	154.	.526
428.	45°	3207	217.	.507*
616.	45°	4419	299.	.485*

* heating

‡ Philippoff 12/61

POLYISOBUTYLENE INDOPOL H-25 [‡]

Temperature= 77.0°F

SHEAR RATE $j\ \sec^{-1}$	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
2.15	45°	19	1.29	.600
3.27	45°	27	1.83	.560
4.75	45°	41	2.78	.585
6.84	45°	57	3.86	.564
9.95	45°	85	5.75	.578
15.2	45°	135	9.15	.602
19.25	45°	160	10.85	.564
29.3	45°	250	16.9	.577
42.8	45°	356	24.1	.563
61.6	45°	520	35.2	.571
89.7	45°	754	51.0	.569
137.	45°	1153	78.0	.569
192.5	45°	1626	110.	.571

[‡]Philippoff 11/61

POLYISOBUTYLENE ORONITE N-24 [‡]

Temperature = $77°F$

SHEAR RATE $j \; sec^{-1}$	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	MAXWELL CONSTANT $M \times 10^8$
.215	$45°$	16	1.08	5.02
.327	$45°$	23	1.56	4.77
.475	$45°$	34	2.30	4.84
.684	$45°$	47	3.18	4.65
.995	$45°$	70	4.74	4.76
1.52	$45°$	107	7.24	4.76
2.15	$45°$	150	10.15	4.72
3.27	$45°$	226	15.3	4.68
4.75	$45°$	346	23.4	4.93
6.84	$45°$	480	32.5	4.75
9.95	$45°$	720	48.7	4.89
15.2	$45°$	1098	74.3	4.89
19.25	$45°$	1345	91.0	4.73
29.3	$45°$	2106	142.5	4.87
42.8	$45°$	3074	208.	4.86
61.6	$45°$	4286	290.	4.71

[‡] Philippoff 12/61

POLYISOBUTYLENE VISTANEX LM/MS‡

Constant = 4.326×10^{-8} Temperature= $77.0°F$

SHEAR RATE j sec^{-1}	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	STRESS-OPTICAL COEFFICIENT C Brewsters
.000370	45°	129	9.30	1294
.000564	44° 05'	232	16.7	1288
.000793	44° 48'	336	24.2	1330
.00121	44° 45'	504	36.3	1306
.00177	44° 13'	749	54.0	1330
.00254	44° 20'	1004	72.4	1239
.00370	44° 14'	1470	101.5	1222
.00564	43° 38'	2440	176.	1354
.00714	43° 21'	3156	227.	1380
.0109	42° 31'	4851	349.	1385
.0159	41° 22'	6900	497.	1347
.0229	41° 16'	9300	670.	1261
.0333	40° 01'	13230	954.	1227

‡ Philippoff 8/56

POLYISOBUTYLENE

ORONITE N-16

$(n_{11} - n_{33})$

$-(n_{22} - n_{33})$

Δn

SHEAR STRESS τ dynes/cm²

POLYISOBUTYLENE
ORONITE N-24

Δn

$(n_{11}-n_{33})$

$-(n_{22}-n_{33})$

SHEAR STRESS $\quad \tau \quad$ dynes/cm²

POLYISOBUTYLENE
INDOPOL H-25

Δn

$(n_{11} - n_{33})$

$-(n_{22} - n_{33})$

SHEAR STRESS τ dynes/cm^2

POLYISOBUTYLENE

INDOPOL H-1900

Δn

$(n_{11} - n_{22})$

$(n_{11} - n_{33})$

$-(n_{22} - n_{33})$

SHEAR STRESS τ dynes/cm²

POLYISOBUTYLENE
LM/MS

Δn

$(n_{11}-n_{33})$
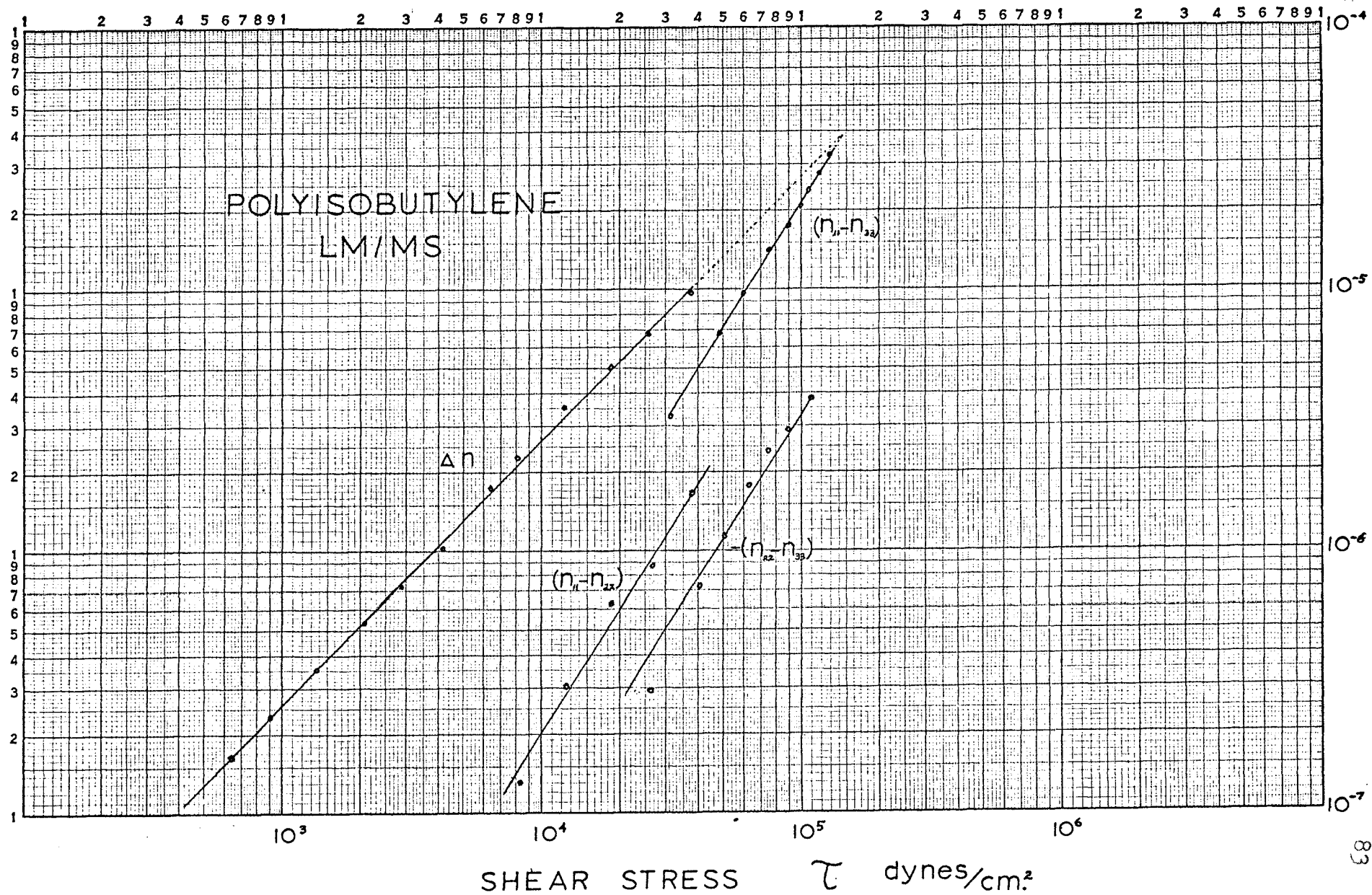
$(n_{11}-n_{22})$

$-(n_{22}-n_{33})$

SHEAR STRESS τ dynes/cm²
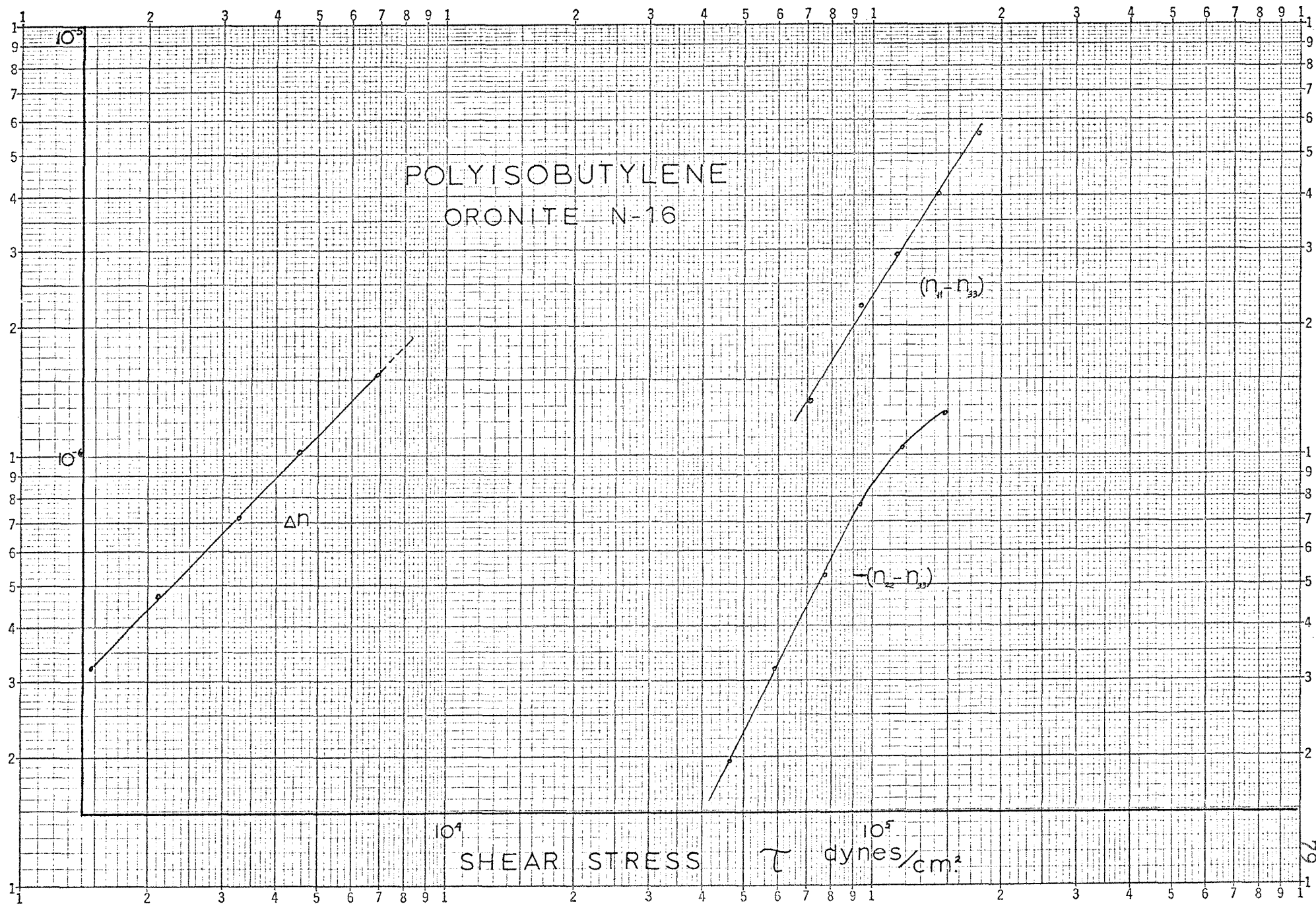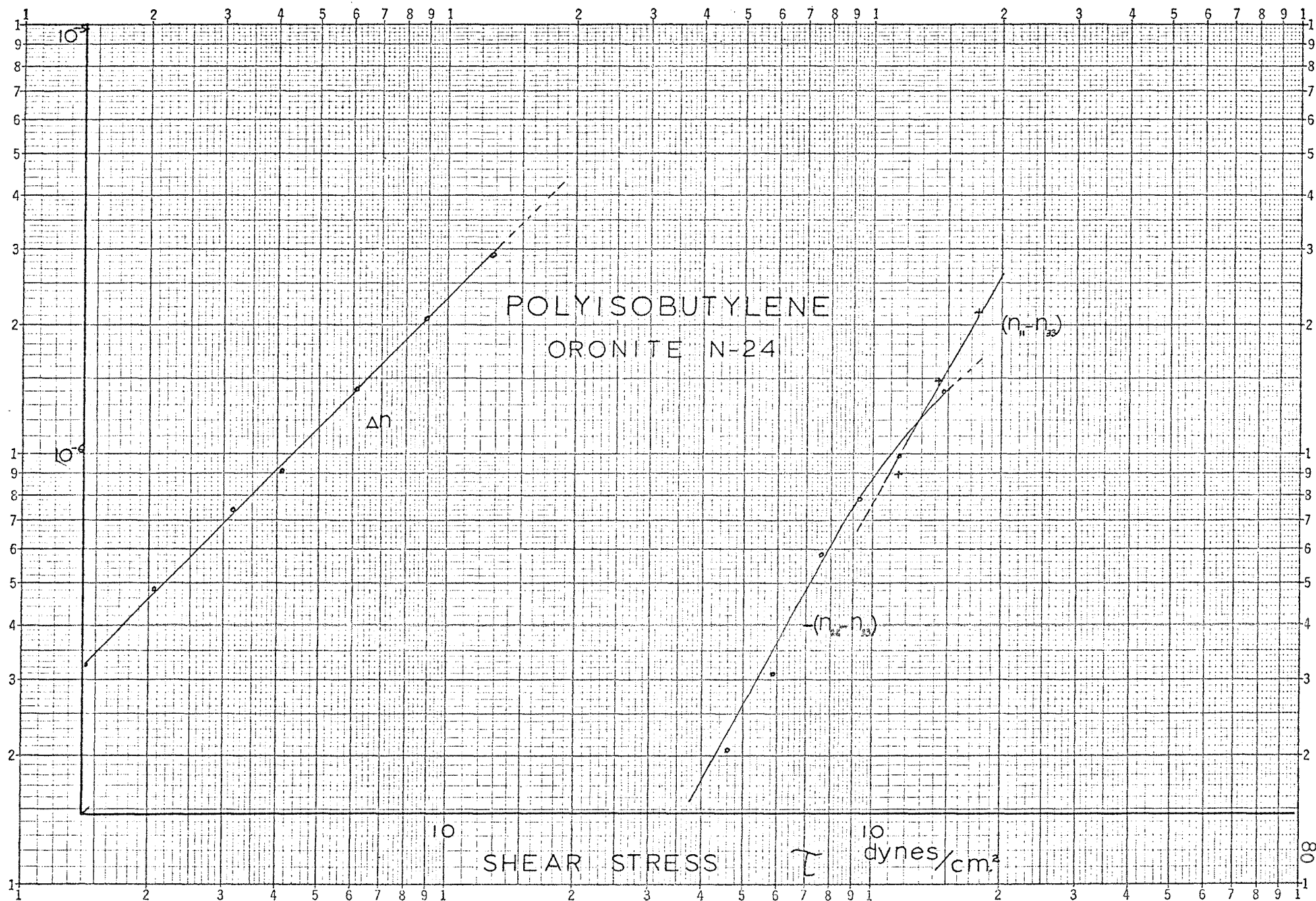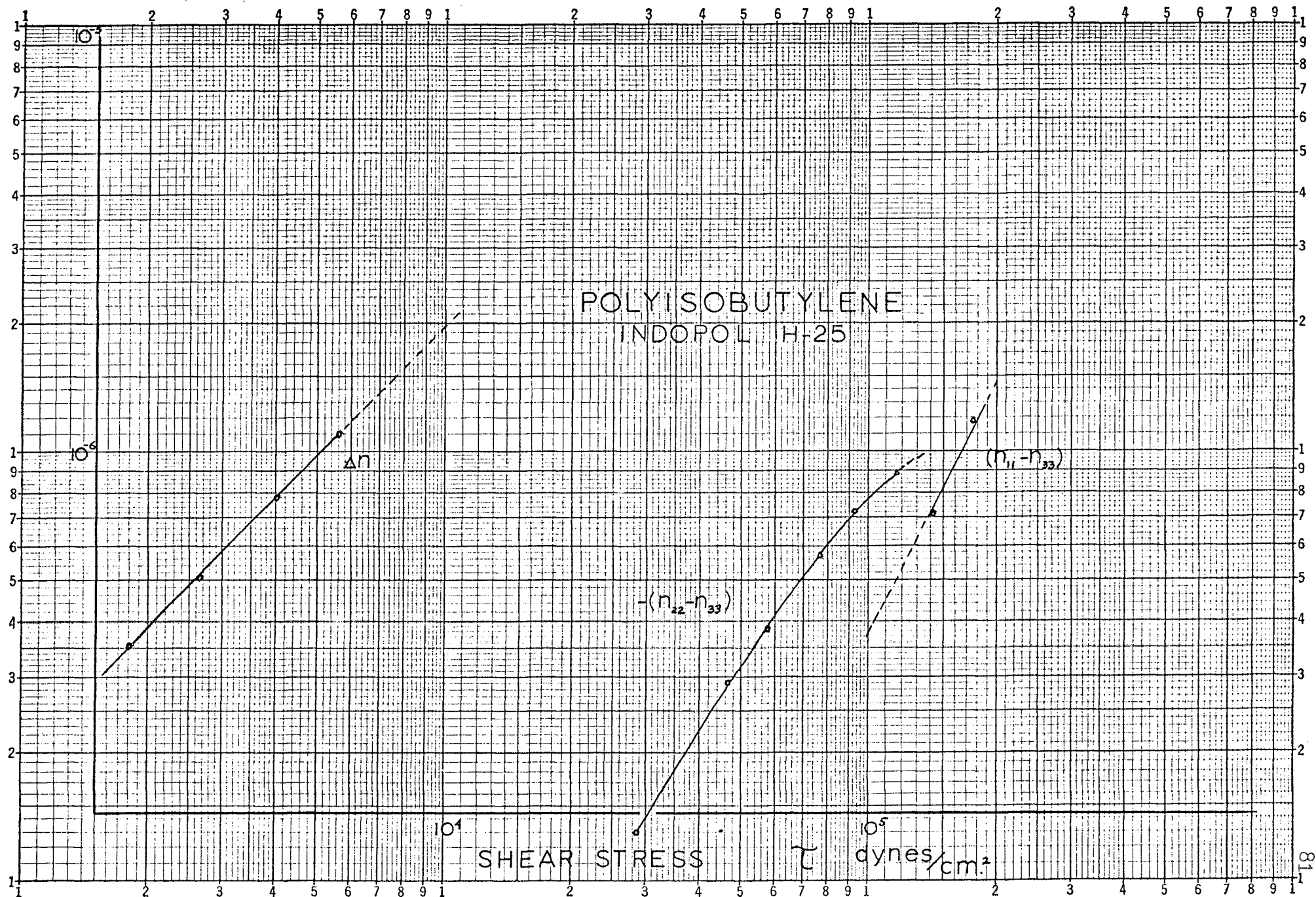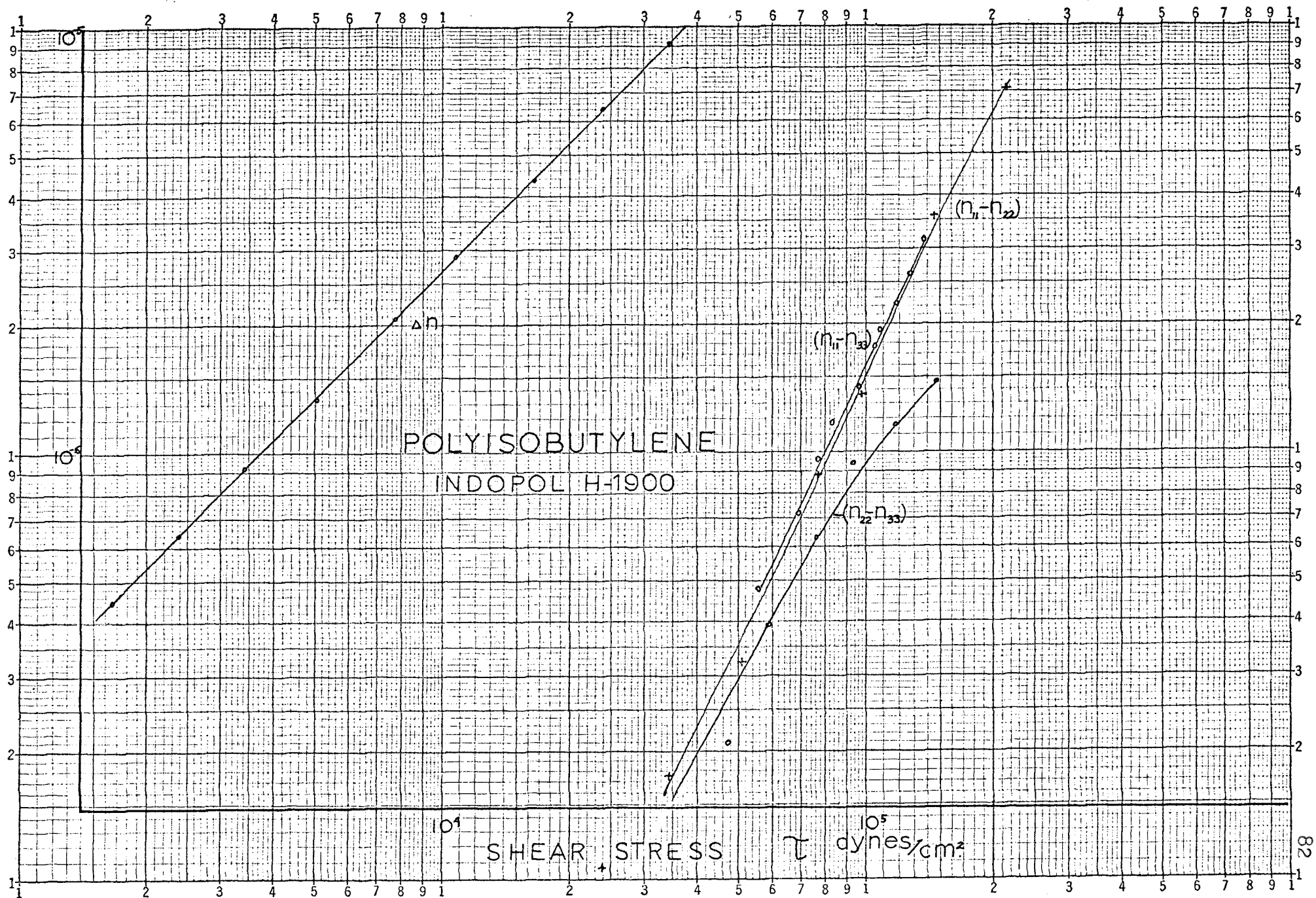
NON-NEWTONIAN BEHAVIOR OF POLYISOBUTYLENE

Experimental Method

For the following studies a polyisobutylene solution was used, which exhibited strong non-newtonian characteristics. The solution is a 4.5 wt % mixture of Vistanex L-200 (5.5×10^6 mol.wt.) in a white mineral oil, Primol 355. The solution is prepared by dissolving the Vistanex in hexane. The oil is then added to the mixture and the hexane is evaporated off under a vaccum with moderate heating to drive off any water vapor that may cloud the solution. The solution must also be thoroughly filtered to remove any particles that would hamper optical measurements.

The procedure was nearly identical as that for the newtonian polyisobutylenes. All the data was obtained at temperature of 25°C. The viscosity measurements were conducted in a shear stress range from 4 to 2924 dynes/cm^2. All of the optical data are an average of clockwise and counter-clockwise rotations to minimize any error arrising from optical misalignments. Due to the presence of the Primol oil, which has some optically active molecules, a fructose-water solution was inserted within the optical field. The compensating solution had an optical rotation of -4°. Because of the viscoelastic behavior of this solution, a longer period of time was necessary for steady state to be achieved. Shear rates of .00239 to 13.7 sec^{-1} were used

in the concentric cylinder device.

Results

The viscosity measurements by N.Zwetkow were in-
dicative of a highly non-newtonian liquid. For the shear
stress range investigated, the viscosity decreased from
40,282 poise to 221.5 poise. By extrapolation a zero shear
viscosity of about 80,000 poise was obtained.

Some difficulties were encountered in the optical
measurements. Initial measurements yielded birefringence
values nearly 10% greater than the latter runs, expecially
at the higher shear rates. This might have been due to in-
homogeneities in the solution incurred by a long shelf
life. High shear rates appeared to remove them, with latter
runs having reproducible values.

The non-newtonian behavior of the solution was appar-
ent throughout the entire observable shear rate range. The
largest extinction angle measured was 38°. At the higher
shear rates, χ decreased to less than 3°. After comparing
the various relationships of shear rate, shear stress, bi-
refringence and the extinction angle, the only combination
which leads to a linear relationship is: $\Delta n \sin 2\chi$ versus
the shear stress. This unique relationship tends to support
the supposition that the stress optical coefficient is equal
to: $n \sin 2\chi /2\tau = \Delta n/\Delta p$. The coefficient for this sol-

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Temperature= $77.0^{\circ}F$

WEIGHT W grams	SHEAR STRESS τ dynes/cm^2	SHEAR RATE j sec^{-1}	VISCOSITY η poise
1	4	.0000993	40282
2	8	.000217	36861
5	20	.000620	32263
10	40	.001455	27491
20	80	.003882	20608
50	200	.01792	11164
100	400	.07821	5114
200	800	.4261	1877
400	1600	2.690	594.8
531	2124	5.946	357.2
731	2924	13.198	221.5

POLYISOBUTYLENE (sol)
4.5% VISTANEX L-200 in PRIMOL 355

TEMP. 77°F

VISCOSITY η in kilopoise

RATE OF SHEAR j sec.$^{-1}$

ution was found to be 1754 ± 13 brewsters, nearly the same as other measurements of similar polyisobutylene solutions.

While much of the behavior of this non-newtonian liquid had been anticipated, some of its behavior has been unexplainable. The recoverable shear, which is calculated from the previous relationship: $s = 2\cot 2\chi$, was plotted against the shear stress to obtain the shear modulus $G = \tau/s$. The curve oscillated about a shear modulus of $G = 145$ dynes/cm^2. The points coincide to accurately to be explained by experimental scatter. This is cnnfirmed by the absence of this fluctuation in the normal shear stress difference calculated by:

$$p_{11}-p_{22} = \tau s = (\Delta n/C) \sin 2\chi$$

Recoverable shear values obtained by N.Zwetkow's recoil measurements on the rotational viscometer indicated a shear modulus of $G = 80$ dynes/cm^2 for shear stresses less than 20 dynes/cm^2, increasing to $G = 294$ dynes/cm^2 for a shear stress of 1000 dynes/cm^2. This increase is normally observed in most polymers.

As expected, the normal stress difference varies with the square of the shear stress for most of the range. However, for shear stresses greater than 10,000 dynes/cm^2, $p_{11}-p_{22}$ increases at a rate greater than τ^2, which is quite unusual. The more expected deviation would have been at a rate less

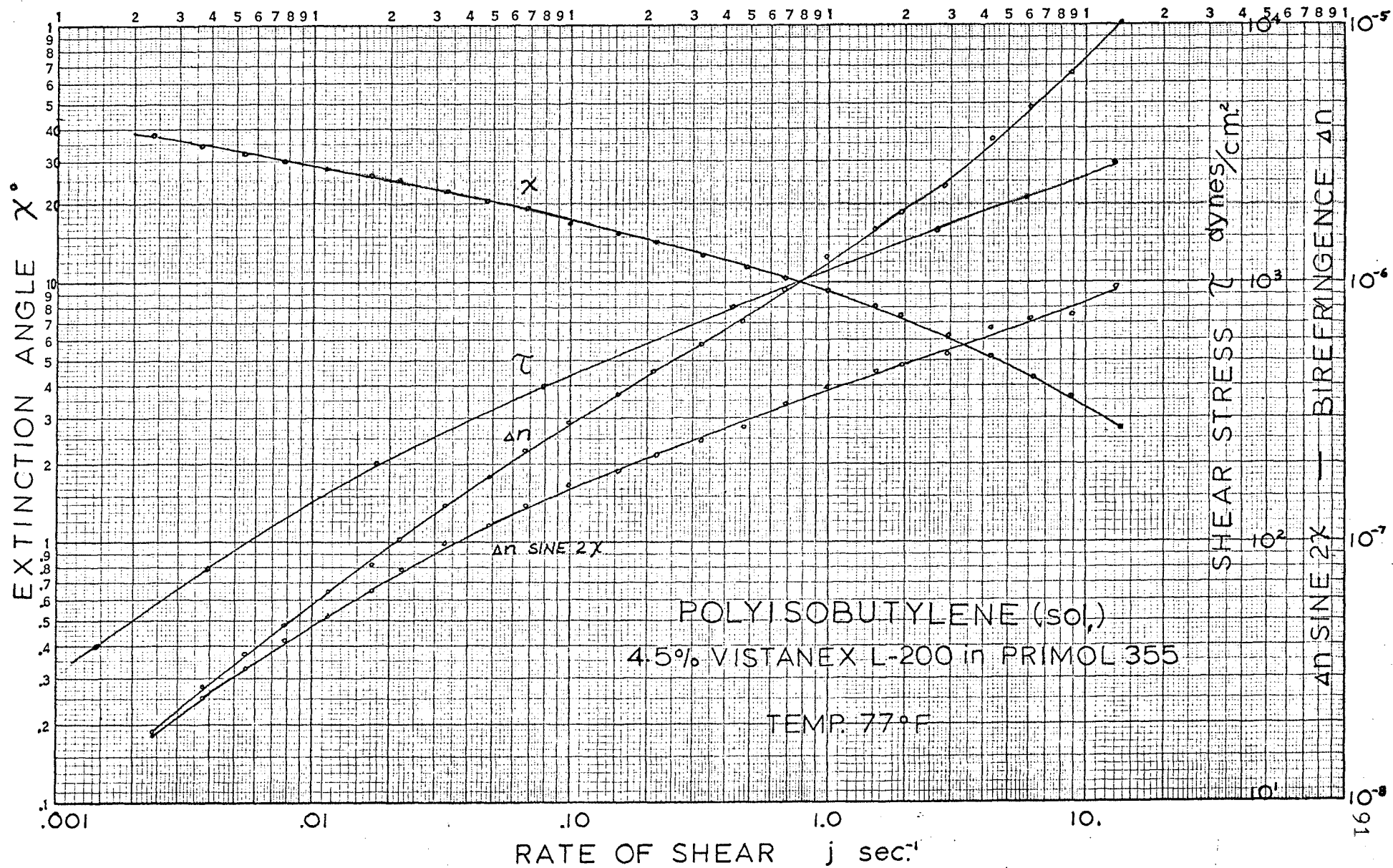POLYISOBUTYLENE
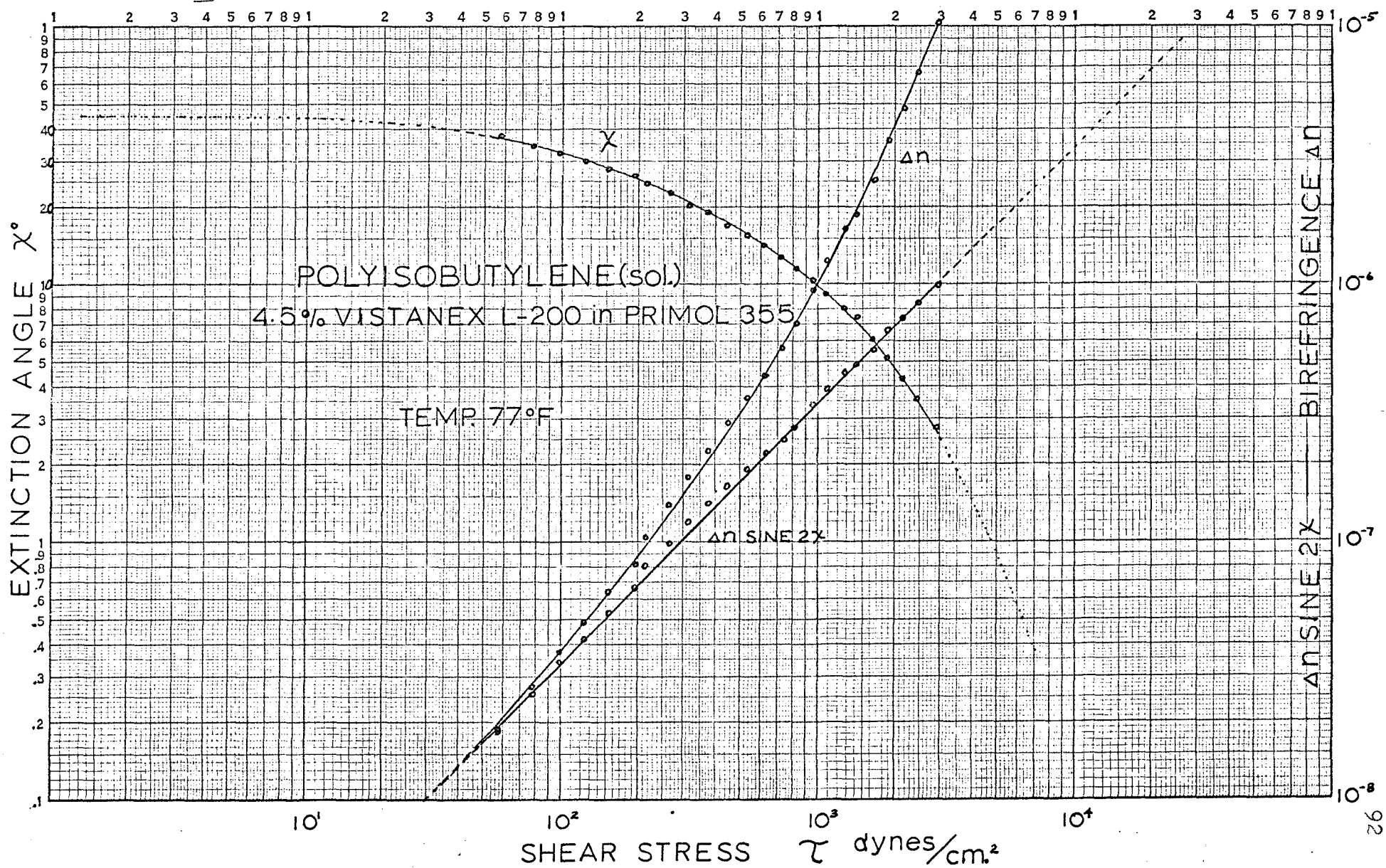4.5% VISTANEX L-200 in PRIMOL 355

Temperature= 77.0°F

SHEAR RATE j sec^{-1}	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^8$	Δn SINE 2χ $\times 10^8$
.00239	38.20°	28	1.895	1.842
.00364	34.70°	41	2.774	2.597
.00528	32.70°	55	3.722	3.384
.00761	30.30°	72	4.871	4.244
.0111	28.00°	95	6.428	5.329
.0169	26.65°	121	8.188	6.565
.0215	25.30°	153	10.35	8.000
.0327	22.75°	208	14.07	10.04
.0475	20.75°	265	17.93	11.88
.0684	19.25°	331	22.40	13.94
.0995	17.00°	431	29.16	16.31
.152	15.65°	540	36.54	18.98
.215	14.45°	670	45.34	21.91
.327	12.90°	845	57.18	24.88
.475	11.60°	1040	70.57	27.72
.684	10.45°	1411	95.48	34.06
.995	9.30°	1839	124.4	39.70
1.520	8.15°	2410	163.1	45.77
1.925	7.45°	2792	188.9	48.58
2.93	6.20°	3770	255.1	54.77
4.28	5.20°	5438	368.0	66.43
6.16	4.30°	7185	486.2	72.70
8.97	3.60°	9915	670.9	84.09
13.7	2.75°	15255	1032.3	98.94

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Temperature = $77.0^{\circ}F$

SHEAR RATE $j\ sec^{-1}$	SHEAR STRESS τ dynes/cm^2	RECOVERABLE SHEAR S	$(P_{11}-P_{22})$ $\tau \times S$	STRESS-OPTICAL COEFFICIENT C Brewsters
.00239	57.84	.4839	27.99	1592
.00364	76.80	.7518	57.74	1691
.00528	98.21	.9157	89.93	1723
.00761	122.5	1.127	138.1	1721
.0111	152.1	1.349	205.2	1752
.0169	194.4	1.491	289.8	1689
.0215	219.3	1.643	360.3	1824
.0327	268.1	1.965	526.9	1872
.0475	319.2	2.261	721.6	1861
.0684	375.5	2.574	944.1	1857
.0995	442.8	2.965	1313.	1842
.152	529.0	3.289	1740.	1794
.215	606.3	3.623	2197.	1807
.327	716.1	4.137	2963.	1737
.475	821.8	4.666	3835.	1687
.684	950.8	5.237	4979.	1791
.995	1086.	5.943	6454.	1830
1.520	1277.	6.839	8733.	1792
1.925	1403.	7.517	10546.	1731
2.93	1641.	9.097	14928.	1669
4.28	1883.	10.90	20519.	1764
6.16	2150.	13.22	28432.	1691
8.97	2485.	15.83	39343.	1692
13.7	2946.	20.77	61191.	1679

POLYISOBUTYLENE (sol.)
4.5% VISTANEX L-200 in PRIMOL 355

TEMP. 77°F

EXTINCTION ANGLE $\chi°$

RATE OF SHEAR j sec.$^{-1}$

SHEAR STRESS τ dynes/cm^2

BIREFRINGENCE Δn

Δn SINE 2χ

Δn SINE 2χ

χ

τ

Δn

POLYISOBUTYLENE (sol.)

4.5% VISTANEX L-200 in PRIMOL 355

TEMP. 77°F

EXTINCTION ANGLE $\chi°$

BIREFRINGENCE Δn

Δn SINE 2χ

SHEAR STRESS τ dynes/cm.²

χ

Δn

Δn SINE 2χ

92

POLYISOBUTYLENE (sol.)

45% VISTANEX L-200 in PRIMOL 355

TEMP. 77°F

VISCOMETER RECOIL

$G \approx 80 \ \frac{dynes}{cm^2}$

$G \approx 145 \ \frac{dynes}{cm^2}$

RECOVERABLE SHEAR S

SHEAR STRESS τ dynes/cm²

93

POLYISOBUTYLENE (sol.)
4.5% VISTANEX L-200 in PRIMOL 355

TEMP. 77°F

SHEAR STRESS τ dynes/cm².

$(P_{11} - P_{22})$ or $\tau \cdot S$

than the square, which could have been explained by internal heating. This heating, described earlier, leads to a smaller birefringence value, and so, to a smaller normal stress difference.

TRANSIENT BEHAVIOR OF NON-NEWTONIAN POLYISOBUTYLENE

Procedure

One of the most recent and perhaps the least understood field in polymer studies has been that of transient behavior. Most observations have been conducted on the steady state characteristics of fluids. This final chapter attempts to present some experimental data in the hope that suitable theories may be formulated to explain transient behavior.

The liquid used was the same one employed in the non newtonian studies, 4.5 wt% Vistanex L-200 in Primol 355. As in the previous measurements the temperature was held constant at 25°C. For the relaxation measurements it was necessary to run the instrument until steady state was achieved. A braking device was attached to the shaft of the motor. The compensator was positined on zero and the polarizer left free to rotate. To obtain the extinction angle, the power to the motor was shut off and the motion stopped in about .01 seconds. Simultaneously, a timer was started and the polarizer was moved to maintain balanced fields. The angles were recorded as a function of time. For the first ten seconds, the extinction angle was usually preset and the time of balance recorded. This required many runs to obtain a satisfactory curve. Once the extinction angle was known, it was possible to set the polarizer and repeat the procedure, this time recording the compensator angle for that time to which

the extinction angle corresponds.

The procedure was quite similar for obtaining the starting or delay transients. The only difference was that instead of stopping the motor, the measurements were taken from the time of its starting. Care was employed in taking up any slack in the drive belts before starting the motor. This entire procedure was repeated for various rates of shear. This method could be used because of the very large relaxation time of the solution, giving times in the tens of seconds for the effects.

Discussion of Results

The results of the transient experiments were quite informative. The shear rate range was between .0215 and 6.16 sec.$^{-1}$ The change in the angle was too small to observe for smaller shear rates,and for greater shear rates the change was too fast to be recorded with this procedure; the greatest change occuring within one second. Shorter times could be observed if a photoelectric cell were used to observe the change in the birefringence.

For the relaxation transients, the extinction angle decayed in the order of their magnitude; the lowest shear rate requiring the most time. The extinction angle was observed to decrease to zero, rather than return to a 45° orientation. Since the decay was asymptotic tozero, it was

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= .0215 sec^{-1} Temperature= 77.0°F

RELAXATION TIME t sec	EXTINCTION ANGLE χ	RELAXATION TIME t sec	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
0.0	21° 30'	0.0	3° 15'	13.20
6.5	20° 00'	3.8	2° 30'	10.15
31.0	17° 00'	10.5	2° 00'	8.12
64.0	13° 06'	23.0	1° 30'	6.09
93.0	12° 42'	60.0	1° 00'	4.06
100.0	13° 00'	120.0	0° 45'	3.05
125.0	12° 30'	200.0	0° 26'	1.75
170.0	9° 30'	300.0	0° 28'	1.91
189.0	11° 30'			
225.0	8° 12'			
450.0	1° 30'			

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= .0684 sec^{-1} Temperature= 77.0°F

RELAXATION TIME t sec.	EXTINCTION ANGLE χ	RELAXATION TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
6.1	13° 30'	2.5	5° 30'	22.33
13.8	12° 00'	5.7	5° 00'	20.30
22.0	10° 00'	11.5	4° 00'	16.24
100.0	5° 00'	22.0	3° 00'	12.18
170.0	3° 18'	50.0	2° 00'	8.12
230.0	1° 30'	115.0	1° 00'	4.06
300.0	0° 30'	160.0	0° 50'	3.37
		220.0	0° 35'	2.35
		300.0	0° 30'	2.03

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= .215 sec   Temperature= 77.0°F

RELAXATION TIME t sec	EXTINCTION ANGLE χ	RELAXATION TIME t sec	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
1.3	10° 00'	1.17	11° 00'	44.66
3.0	8° 00'	2.5	10° 00'	40.60
5.6	7° 00'	4.3	9° 00'	36.54
9.6	6° 00'	10.6	7° 00'	28.42
16.5	5° 00'	22.5	5° 00'	20.30
36.0	4° 00'	49.0	3° 00'	12.18
75.0	2° 24'	86.0	2° 00'	8.12
120.0	1° 30'	180.0	1° 00'	4.06
160.0	0° 48'	270.0	0° 41'	2.76
200.0	0° 12'			
240.0	0° 00'			

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= .684 sec^{-1} Temperature= 77.0°F

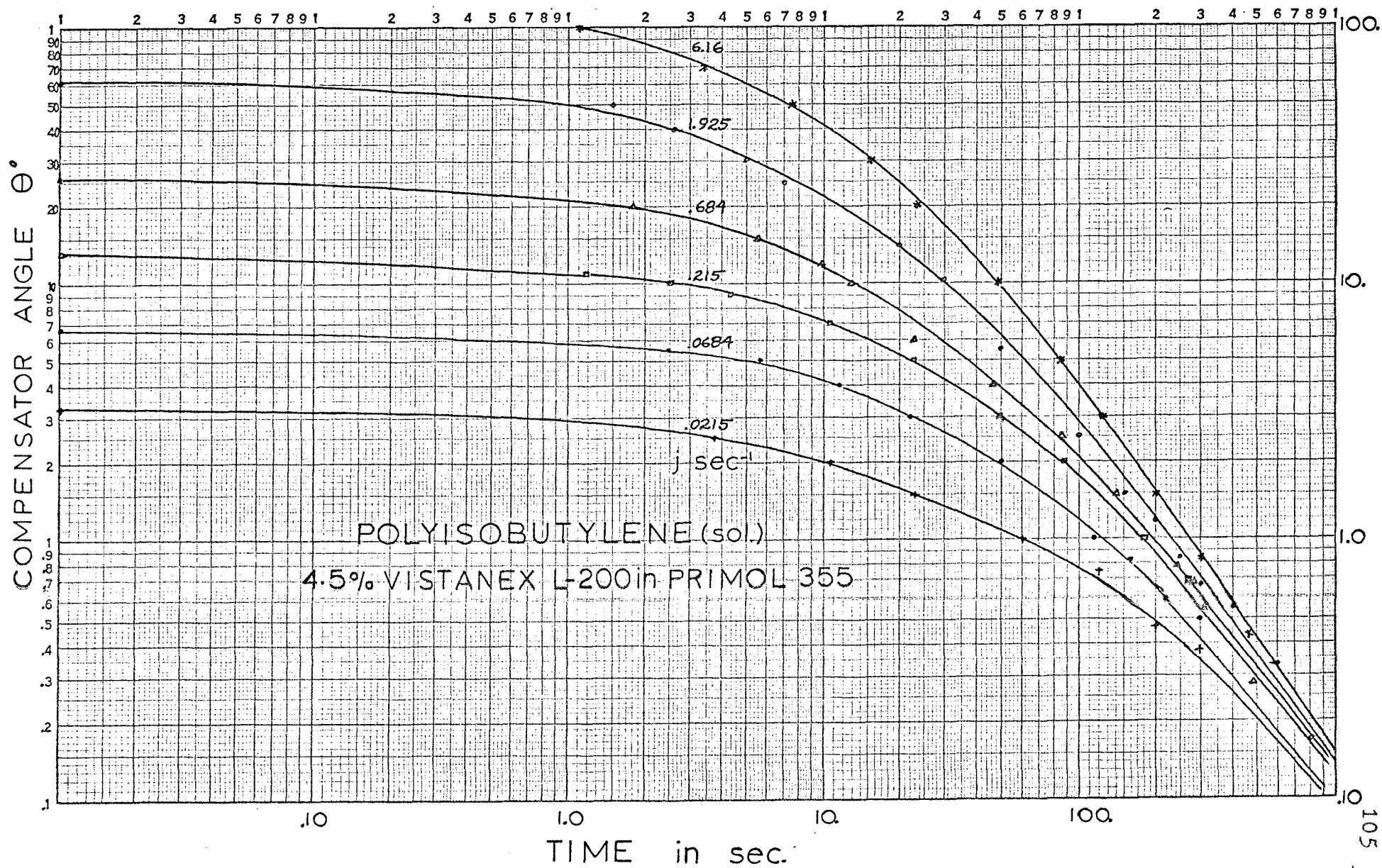| RELAXATION TIME t sec	EXTINCTION ANGLE χ	RELAXATION TIME t sec	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
0.0	9° 30'	1.8	20° 00'	81.20
0.8	8° 00'	5.5	15° 00'	60.90
1.3	6° 00'	9.6	12° 00'	48.72
5.2	4° 00'	12.8	10° 00'	40.60
17.0	3° 00'	22.7	7° 00'	28.42
35.0	2° 24'	46.0	4° 00'	16.24
80.0	1° 18'	85.0	2° 30'	10.15
150.0	0° 12'	140.0	1° 30'	6.09
		240.0	0° 47'	3.17
		280.0	0° 41'	2.76
		310.0	0° 33'	2.23
		475.0	0° 17'	1.14

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= 1.925 sec^{-1} Temperature= 77.0°F

RELAXATION TIME t sec.	EXTINCTION ANGLE χ	RELAXATION TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
0.0	6° 00'	0.0	64° 00'	259.8
1.0	3° 30'	1.5	50° 00'	203.0
1.9	3° 00'	2.6	40° 00'	162.4
4.0	2° 30'	5.0	30° 36'	124.2
10.0	2° 24'	7.0	24° 48'	100.7
10.1	2° 00'	20.0	14° 00'	56.84
20.0	1° 42'	30.0	10° 18'	41.82
30.0	1° 06'	50.0	5° 30'	22.33
40.0	1° 06'	100.0	2° 30'	10.15
60.0	0° 24'	150.0	1° 30'	6.09
80.0	0° 18'	200.0	1° 11'	4.83
100.0	0° 12'	250.0	0° 51'	3.45
150.0	0° 06'	300.0	0° 40'	2.72
		400.0	0° 33'	2.23
		600.0	0° 20'	1.35
		800.0	0° 10'	.69

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= 6.16 sec. Temperature= 77.0°F

RELAXATION TIME t sec.	EXTINCTION ANGLE χ	RELAXATION TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
0.0	3° 18'	1.1	100° 00'	406.0
1.0	1° 54'	3.4	70° 00'	284.2
1.3	1° 48'	7.5	50° 00'	203.0
2.0	1° 36'	15.1	30° 00'	121.8
5.3	1° 18'	23.5	20° 00'	81.20
8.0	1° 00'	48.5	10° 00'	40.60
12.0	0° 48'	84.5	5° 00'	20.30
40.0	0° 20'	125.0	3° 00'	12.18
		200.0	1° 30'	6.09
		300.0	0° 51'	3.45
		430.0	0° 26'	1.75

POLYISOBUTYLENE (sol.)
4.5% VISTANEX L-200 in PRIMOL 355

EXTINCTION ANGLE χ°

TIME in sec.

j, sec⁻¹

.0215
.0684
.215
.684
1.925
6.16

104

POLYISOBUTYLENE (sol.)
4.5% VISTANEX L-200 in PRIMOL 355
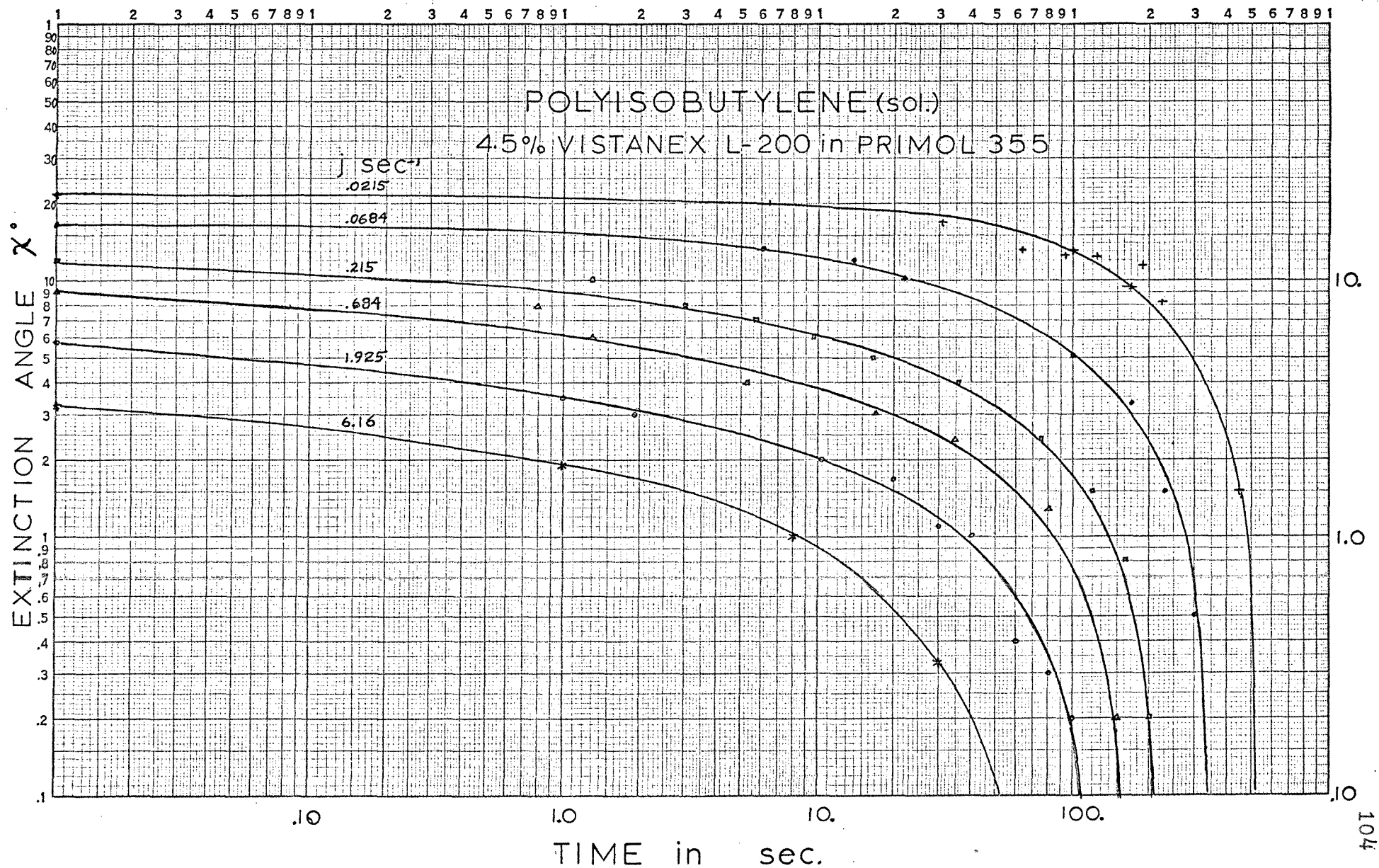
impossible to determine the exact time of total decay. However, for angles less than 6', relaxation times of 50 seconds were necessary for a shear rate of 6.16 sec^{-1} while 520 seconds were required for a shear rate of .0215 sec^{-1}.

The relaxation of the compensator angle was slightly different than that of the extinction angle. Instead of decaying as a function of the shear rate, the curves tended to merge into a common decay rate. Angles less than 6' were achieved at about 1000 seconds for each of the shear rates. As with the extinction angle, the curve was asymptotic to zero, making the exact time of total decay inpossible to determine. Any correlations would have to be made on a per cent basis.

The starting or delay transients exhibited a more un-usual behavior than that of the relaxation transients. The shear rates involved were the same as before. The extinction angle was observed to decrease from 45° to its steady state value. This rate of change increased with increasing shear rates. What is unusual is that the extinction angle undershoots its steady state value before coming to equi-librium. The degree of undershoot increased with increasing shear rates while the time of its occurance decreased. The compensator angle was found to have nearly the same behavior as that of the extinction angle. By plotting the effect as a function of the delay time and shear rate, it was possible

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= .0215 sec^{-1} Temperature= 77.0°F

DELAY TIME t sec.	EXTINCTION ANGLE χ	DELAY TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
10	43° 00'	10	0° 58'	3.92
20	41° 30'	20	1° 31'	6.16
30	38° 54'	40	2° 07'	8.59
40	37° 12'	60	2° 25'	9.81
50	35° 48'	80	2° 38'	10.01
60	34° 12'	120	2° 51'	11.57
70	32° 48'	140	3° 00'	12.18
80	31° 18'	180	3° 01'	12.25
90	29° 48'	200	3° 06'	12.59
120	27° 48'	250	3° 07'	12.65
140	26° 24'	300	3° 00'	12.18
160	25° 48'	350	2° 58'	12.04
180	24° 48'	400	2° 55'	11.84
200	23° 48'	500	2° 54'	11.77
250	23° 18'	1000	2° 52'	11.64
300	22° 06'			
400	22° 30'			
500	22° 30'			
1000	22° 30'			

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= .0684 sec^{-1} Temperature= 77.0°F

DELAY TIME t sec.	EXTINCTION ANGLE χ	DELAY TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
5	43° 06'	5	1° 45'	7.11
10	41° 18'	10	3° 30'	14.21
15	38° 36'	20	4° 18'	17.46
20	34° 48'	30	5° 00'	20.30
25	31° 42'	40	5° 37'	22.80
30	29° 18'	50	6° 00'	24.36
40	26° 36'	60	6° 10'	25.04
45	24° 18'	80	6° 38'	26.93
50	23° 30'	90	6° 33'	26.59
60	21° 30'	100	6° 22'	25.85
70	20° 30'	150	6° 30'	26.39
80	19° 48'	200	6° 20'	25.71
90	18° 54'	250	6° 00'	24.36
100	18° 24'	350	5° 56'	24.09
150	17° 48'	500	5° 55'	24.02
200	17° 30'			
250	17° 42'			
350	17° 30'			
500	17° 36'			

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= .215 sec^{-1} Temperature= 77.0°F

DELAY TIME t sec.	EXTINCTION ANGLE χ	DELAY TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
2	40° 30'	2	2° 28'	10.01
4	36° 30'	4	4° 30'	18.27
6	32° 12'	10	9° 20'	37.89
8	29° 12'	15	11° 00'	44.66
10	26° 36'	20	12° 10'	49.40
15	21° 00'	25	13° 07'	53.25
20	17° 48'	30	13° 20'	54.13
25	15° 24'	35	13° 30'	54.81
30	14° 12'	40	13° 48'	56.03
35	13° 36'	45	13° 09'	53.39
40	13° 18'	50	12° 56'	52.51
50	12° 48'	80	12° 50'	52.10
60	12° 36'	100	12° 19'	50.01
100	12° 48'	150	12° 02'	48.86
200	13° 00'	200	11° 59'	48.65
500	13° 30'	350	11° 39'	47.30
		500	11° 35'	47.03

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355
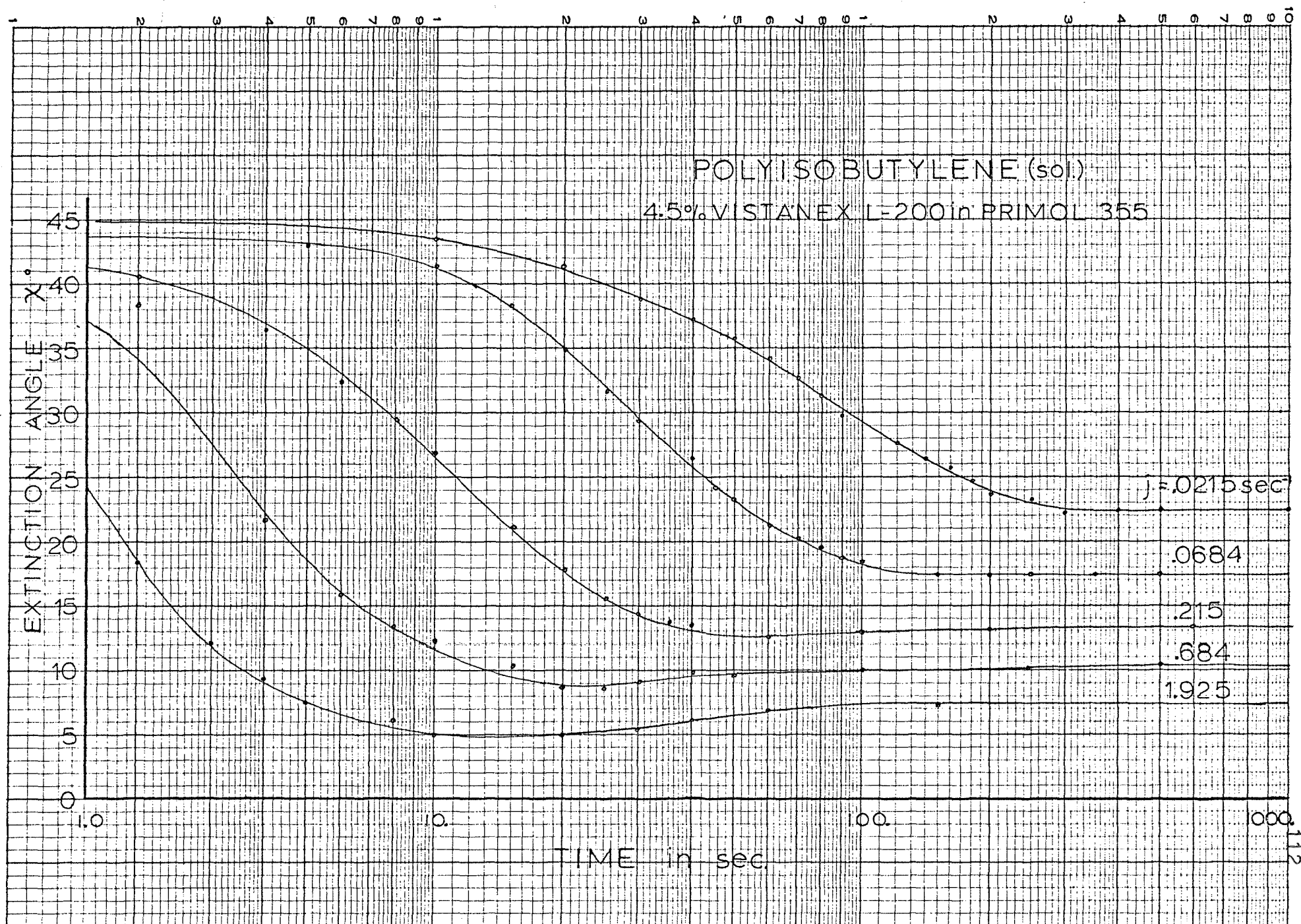
Shear rate= .684 sec^{-1} Temperature= 77.0°F

DELAY TIME t sec.	EXTINCTION ANGLE χ	DELAY TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
2	38° 30'	2	9° 30'	38.57
4	21° 48'	4	17° 05'	69.36
6	15° 48'	6	21° 53'	88.85
8	13° 30'	8	24° 32'	99.61
10	12° 06'	10	26° 48'	108.8
15	10° 06'	15	28° 40'	116.4
20	8° 36'	20	29° 10'	118.4
25	8° 42'	25	27° 40'	112.3
30	9° 00'	35	26° 53'	109.1
40	9° 48'	50	25° 13'	102.4
50	9° 24'	70	22° 43'	92.23
100	10° 00'	100	22° 38'	91.89
250	10° 06'	150	22° 28'	91.21
500	10° 30'	200	22° 45'	92.37
		250	22° 48'	92.57
		500	22° 45'	92.37

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Shear rate= 1.925 sec^{-1} Temperature= 77.0°F

DELAY TIME t sec.	EXTINCTION ANGLE χ	DELAY TIME t sec.	COMPENSATOR ANGLE θ	BIREFRINGENCE $\Delta n \times 10^8$
2	18° 24'	2	29° 00'	117.7
3	12° 06'	3	42° 30'	172.6
4	9° 24'	4	52° 40'	213.8
5	7° 42'	5	57° 10'	232.1
8	6° 06'	6	61° 30'	249.7
10	5° 00'	8	63° 07'	256.3
20	5° 00'	10	63° 07'	256.3
30	5° 24'	15	54° 10'	219.9
40	6° 06'	20	53° 30'	217.2
60	6° 54'	30	50° 05'	203.3
150	7° 12'	40	47° 30'	192.9
		60	46° 20'	188.1
		80	46° 22'	188.2
		100	46° 20'	188.1
		150	46° 23'	188.3

POLYISOBUTYLENE (sol)

4.5% VISTANEX L-200 in PRIMOL 355

$J = .0215 \text{ sec}^{-1}$

.0684

.215

.684

1.925

EXTINCTION ANGLE X°

TIME in sec

POLYISOBUTYLENE (sol)
4.5% VISTANEX L-200 in PRIMOL 355

$j = 1925 \, sec^{-1}$

.684

.215

.0684

.0215

COMPENSATOR ANGLE θ°

TIME in sec.
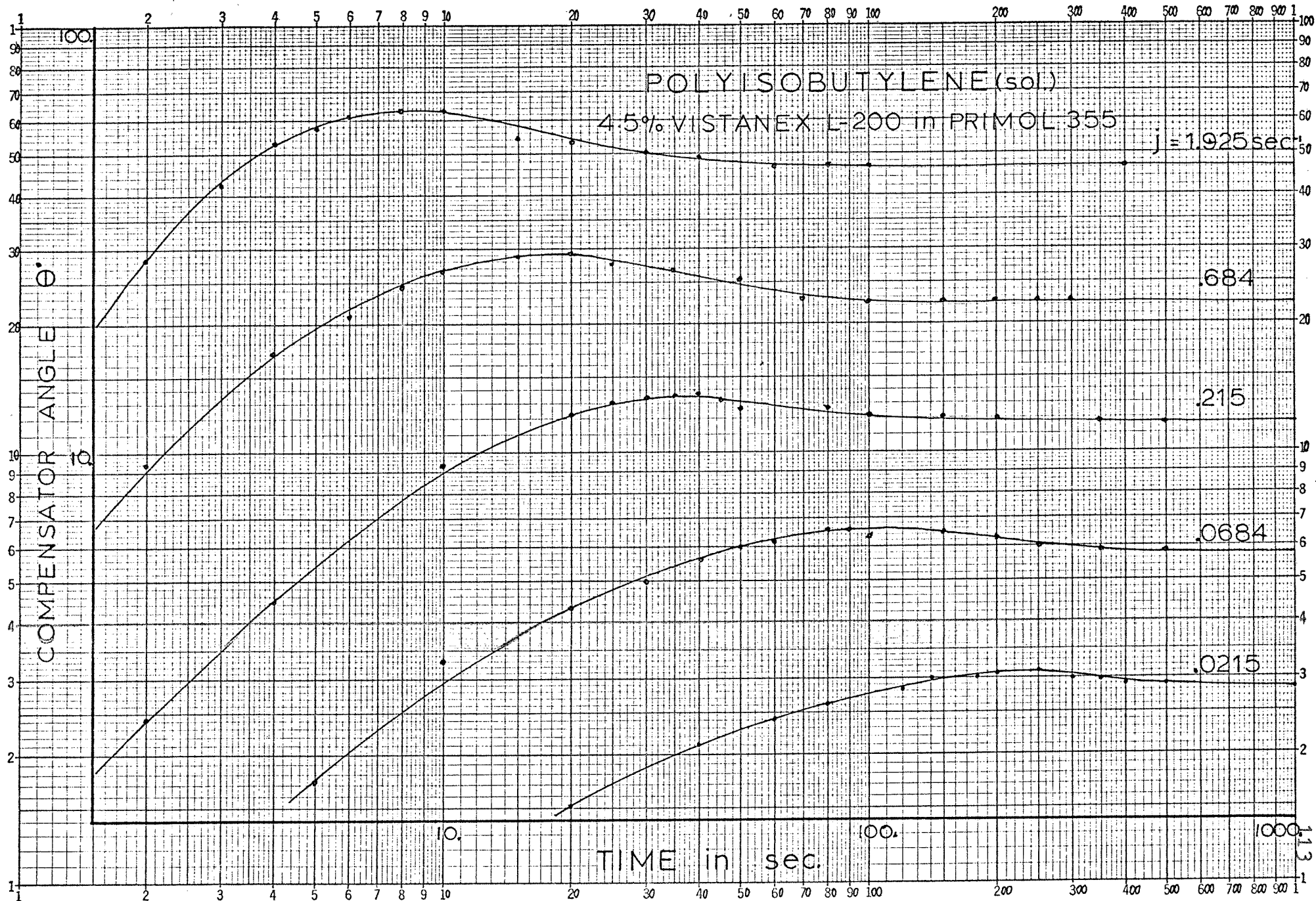
to derive an approximate empirical equation for the degree
of 'overshoot'(compensator angle) and its time:

$$\frac{\Delta n_{max} - \Delta n_{ss}}{\Delta n_{ss}} = .306 \; j^{.33} \; ; \quad t_{max} = 14.37 \; j^{-1/1.4}$$

where Δn_{ss} and Δn_{max} is the birefringence at steady state
and at maximum 'overshoot', respectively; t_{max} is the time
of maximum 'overshoot' and j is the shear rate. The moment
of 'overshoot' for the birefringence was nearly the same as
the 'undershoot' for the extinction angle.

A similar overshoot effect was observed by Den Otter[24]
when plotting the recoverable shear versus the preceding
total shear deformation for a polydimethyl silohexane. Short-
ly afterward, Zapas and Phillips[25] published similar findings
for a suddenly applied shear rate on a polyisobutylene sol-
ution. Experiments similar to Den Otter's are now being
conducted on this material (4.5% Vistanex). Although the
results have not been completely correlated, preliminary
indications are that the two effects occur within the same
instant of one another and to similar degrees.

As previously stated, it was impossible to obtain the

24
    H.Janeschitz-Kriegal,"Flow Birefringence of Elastico
Viscous Polymer Systems", Adv.Polymer Science,Vol.6 (1969) .
pp.170-318.

25
    L.J.Zapas and J.C.Phillips,"Simple Shearing Flows in
Polyisobutylene Solutions", Journal of Research of the National
Bureau of Standards,Vol.75A,No.1 (Jan-Feb 1971)

POLYISOBUTYLENE
4.5% VISTANEX L-200 in PRIMOL 355

Temperature= $77.0\,^{\circ}F$

EMPIRICAL EQUATIONS FOR THE OVERSHOOT PHENOMENON:

Time of maximum overshoot:

$$t_{max} = 14.37\ j^{-.732}$$

Per cent overshoot:

$$\%_{max} = 30.6\ j^{.33} = \frac{\theta_{max}-\theta_{eq}}{.01\ \theta_{eq}}$$

SHEAR RATE j sec^{-1}	TIME (experimental) t_{max} sec.	TIME (calculated) t_{max} sec.	% OVERSHOOT (experimental) $\%_{max}$	% OVERSHOOT (calculated) $\%_{max}$
.0215	240	238.8	8.7	8.6
.0684	105	102.38	12.1	12.6
.215	40	44.27	19.1	18.4
.684	19	18.98	28.2	27.0
1.925	8.8	8.90	36.5	38.0

exact time of equilibrium; therefore, the exact 'relaxation times' t are not known. However, it is quite apparent from the time of 'overshoot', which occurs before equilibrium, that the relaxation time calculated from Natanson's relationship will be much smaller than any observed one. While they differ greatly, the calculated t is nearly proportional to the 'overshoot' t_{max}. Assuming that the true relaxation time is nearly proportinnal to t_{max}, then Natanson's equation for the recoverable shear should be modified to read; $s = \pm ktj$, where k is some constant, t is the true relaxation time, and j is the shear rate.

CONCLUSIONS AND RECOMMENDATIONS

In summary the following can be said about the pre-vious experiments. All observations indicate that the equa-tion of the stress-optical coefficient is correct as:

$$C = \Delta n/\Delta p = (\Delta n \sin 2\chi)/2\tau$$

This coefficient applies both to newtonian and non-newtonian polymers as well as solids although the latter usually have a smaller stress-optical coefficient than a liquid. The co-efficient is a function of the shear stress and not of the shear rate. The coefficient can be considered independent of temperature for moderate temperature changes ($25-65^{\circ}C$). Further studies are needed on temperature effects on other materials to determine whether the small changes in the coef-ficient for extreme temperature variations is characteristic of the material or is due to experimental error. The former possibility is of particular interest since according to one molecular theory, polyisobutylene should not exhibit any bire-fringence. However, it is known to exhibit a very large effect. The polymer investigated should have a large stress-optical coefficient ($>|1000|$ Brewsters) and high viscosity (>1000 poise at $25^{\circ}C$).

Experimental evidence also confirms the dependence of the $n_{11}-n_{33}$ refractive index difference on the molecular weight as given by the relationship:

$$n_{11} - n_{33} = \frac{C \, M \, \tau^2}{c \rho \, R \, T}$$

Provisions for constant temperature measurements should be conducted to determine whether there is a temperature effect and if so, whether it agrees with that predicted by the previous relationship.

Investigations into the nature of the $n_{22} - n_{33}$ refractive index difference have so far been inconclusive. What is known is that the effect occurs only at high shear stresses and not necessarily at high $\triangle n$ values. Its existance is also contrary to all stress-optical laws. Greater precision will be needed to determine whether the effect is a function of the distance from the wall, polarization due to multiple reflections or to some other unexplained cause. Temperature measurements should be repeated to determine whether the decreasing effect was due to the temperature change and not from a variation in the light beam's position.

Finally, the experiments indicate that an overshoot phenomenon exists in the starting of delay transients. This overshoot appears to be a functin of the shear rate. Since this effect was first noticed nearly ten years ago, it has occurred in a variety of rheological devices. Furthrr studies are now being conducted with the hope of correlating the overshoot with the recoverable shear.

APPENDIX

ESSO RESEARCH AND ENGINEERING COMPANY

(FORMERLY STANDARD OIL DEVELOPMENT COMPANY)

P. O. BOX 51, LINDEN, N. J.

VISCOSITY-TEMPERATURE RELATION FOR
PRIMOL 355

Temp. °F.	Temp. °C.	Kim. Vis. ν cSt	Density ρ g/cc	Viscosity η cp
32	0	1256.6	(0.8954)	1125
59	15.00	340.46	0.8853	301.5
77	25.00	166.81	0.8788	146.6
100	37.78	77.49	0.8704	67.5
130	54.45	34.65	(0.8580)	29.75
210	98.89	8.202	(0.8275)	6.80

(Interpolated Values)

W. Philippoff/dm
1/29/62

PRIMOL 355   Batch #10608

Temperature= 77.0°F

SHEAR RATE j sec^{-1}	EXTINCTION ANGLE χ	COMPENSATOR ANGLE θ min.	BIREFRINGENCE $\Delta n \times 10^{8}$	MAXWELL CONSTANT $M \times 10^{8}$
19.25	45°	6	.406	.02109
29.3	45°	9	.609	.02079
42.8	45°	13	.880	.02055
61.6	45°	19	1.286	.02087
89.7	45°	30	2.030	.02263
137.0	45°	43	2.910	.02124
192.5	45°	59	3.992	.02074
293.	45°	89	6.022	.02055
428.	45°	130	8.797	.02055
616.	44° 59'	187	12.65	.02054
897.	44° 55'	272	18.41	.02052
1370.	44° 38'	413	27.95	.02040

$C = 678 \pm 6$ Brewsters

CALCULATIONS FOR FLOW RATE MEASUREMENTS

GAS LAW:

$$P_o V_o = (V_o - \Delta V + q\,\Delta P/2)(P_o + \Delta P)$$

$$P_o V_o = V_o P_o - \Delta V P_o + q P_o \Delta P/2 + V_o \Delta P + q\,\Delta P^2/2 - \Delta V \Delta P$$

$$\Delta V(P_o + \Delta P) = q\Delta P(P_o/2 + \Delta P) + V_o \Delta P$$

$$\Delta V = \frac{\Delta P}{(P_o + \Delta P)}(q P_o/2 + \Delta P q + V_o)$$

$$\Delta V = \frac{Pq/2}{1 + \Delta P/P_o}\left(1 + \frac{2(\Delta P q + V_o)}{q P_o}\right)$$

Since $\quad Pq/2 = $ displacement in cc. on one buret

Then:

$$\Delta V = \frac{cc.}{(1 + \Delta P/P_o)}\left(1 + 2\left(\frac{V_o}{P_o q} + \frac{\Delta P}{P_o}\right)\right)$$

Assuming $\quad \dfrac{\Delta P}{P_o} \ll 1$

Then $\quad \Delta V \approx cc.\left(1 + \dfrac{2V_o}{P_o q}\right)$

$$q = 1/1.54 = .64935 \ cm^2 = \text{Area of buret tube}$$

$$P_o = 764(13.534)/1.044 = 978 cm \ \text{butyl pthalate} = 1 \ \text{Atm.}$$

$$V_o = 530 \ cc. = \text{Flask volume (empty)}$$

$$\Delta V = cc. \ 2.67$$

CALCULATED PRESSURE CORRECTIONS

n_{11}-n_{33} DEVICE

.025 in. Gap:

Dimensions: a= .0635 cm. b= 1.27 cm. l= 2.54 cm.

Equivalent diameter:

$$D_e = (32\ a^3 b/3\pi)^{\frac{1}{4}} = 1.357\ a\ (b/a)^{\frac{1}{4}} = .182 cm$$

Small tube: D_1= .458 cm. L_1= 12.7 cm.

$$P_2/P_1 = (D_e/D_1)^4\ L_1/l = .125$$

Large tube: D_2= .774 cm. L_2= 10.2 cm.

$$P_2/P_1 = (D_e/D_2)^4\ L_2/l = .0124$$

Total pressure drop:

$$\Delta P = .125 + .0124 = .1374$$

$$P_{slit} = 1/1.1374 = .88\ (Psig)$$

.050 in. Gap:

Dimensions: a= .127 cm. b= 1.27 cm. l= 2.54 cm.

Equivalent diameter:

$$D_e = 1.357\ a\ (b/a)^{\frac{1}{4}} = .306\ cm.$$

Small tube: D_1= .458 cm. L_1= 12.7 cm.

$$P_2/P_1 = (D_e/D_1)^4\ L_1/l = 1.00$$

Large tube: D_2= .774 cm. L_2= 10.2 cm.

$$P_2/P_1 = (D_e/D_2)^4\ L_2/l = .0996$$

Total pressure drop:

$$\Delta P = 1.000 + .0996 = 1.0996$$

$$P_{slit} = 1/2.0996 = .477\ (Psig)$$

FLOW RATE CALIBRATIONS
Indopol H-1900

PRESSURE P psig	Temp.= 72.9°F .025 in Gap TIME/cc. sec.	Temp.=72.7°F .050 in Gap TIME/cc. sec.	Temp.= 72.9°F $n_{22}-n_{33}$ device TIME/cc. sec.
80	425.26	90.37	
100	337.04	70.00	
120	263.94	60.57	· 337.34
150	198.08	47.38	267.76
170	172.04		232.42
200			210.52
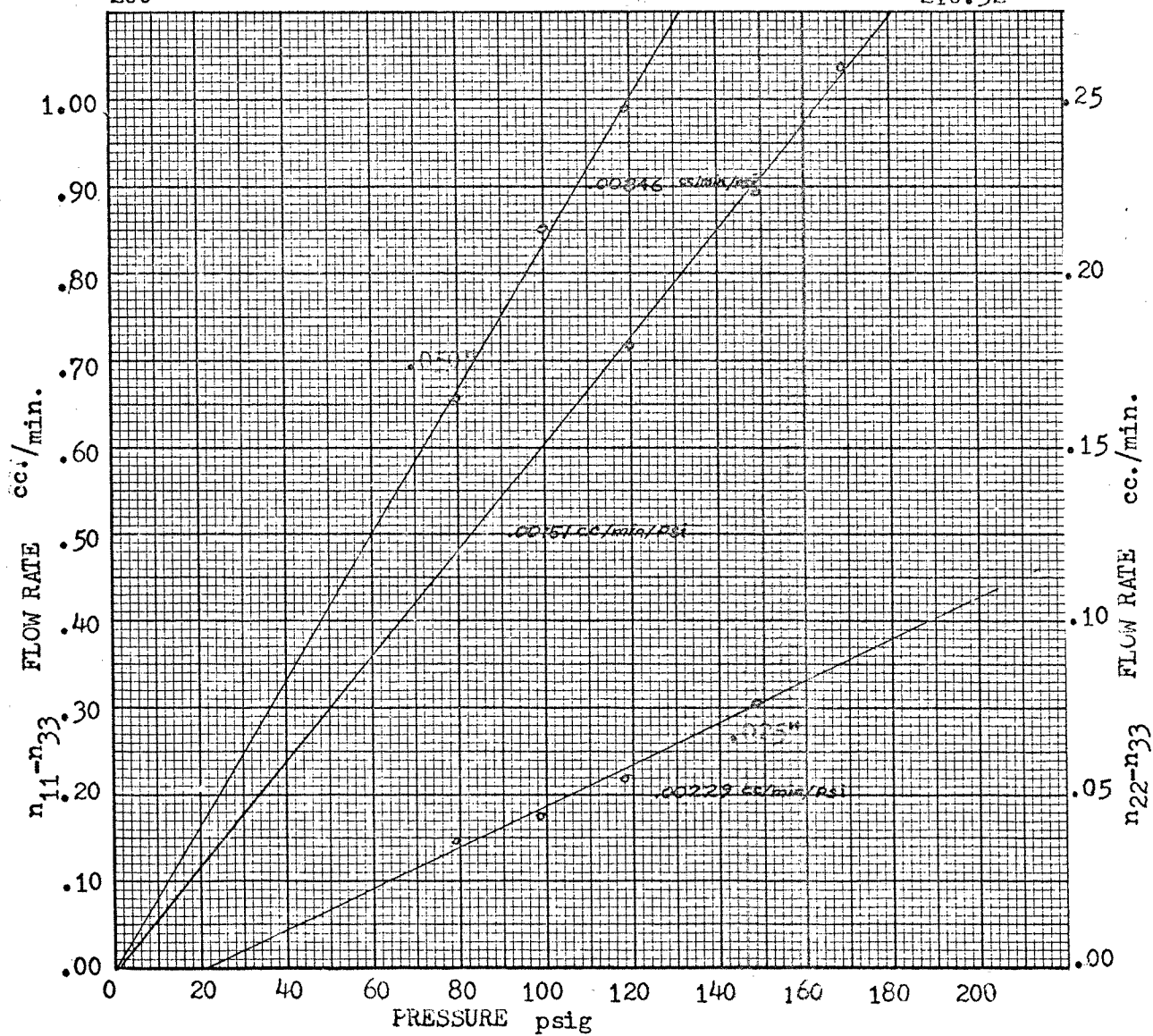
n_{11}-n_{33} DEVICE

.025 in. Gap:

$$j = \frac{6 \, Q}{a^2 \, b} = 1172 \, Q \quad sec^{-1} \qquad Q \text{ in cc/sec}$$

$$\tau = 68930 \, \frac{a(Psi)}{2 \, l} = 862 \, (P_{slit})$$

$$j_{exp} = 1172 \, (2.355).00229/60 = .1053 \, (Psi) \, sec^{-1}$$
$$V_0 = 430 \, cc$$

$$\eta = \frac{\tau}{j} = 8190 \text{ poise}$$

$$\eta_{exp} = 6264.7 \text{ poise}$$

Pressure correction = 6264.7/8190 = .765

$$\tau_{corr} = .765(862)(Psi) = 659(Psi) \, dynes/cm^2$$

.050 in. Gap:

$$j = \frac{6 \, Q}{a^2 \, b} = 293 \, Q \, sec^{-1}$$

$$\tau = 68930 \, \frac{a(Psi)}{2 \, l} = 1725(P_{slit})$$

$$j_{exp} = 293 \, (2.733).00846/60 = .1129 \, (Psi) \, sec^{-1}$$
old buret

$$\eta = \frac{\tau}{j} = 15330 \text{ poise}$$

$$\eta_{exp} = 6331.83 \text{ poise}$$

Pressure correction = 6331.8/15330 = .413

$$\tau_{corr} = .413(1725)(Psi) = 713(Psi) \, dynes/cm^2$$

n_{22}-n_{33} DEVICE

Dimensions: a= .0735 cm. b= .800 cm. c= 2.54 cm.

$$j = \frac{6 \ Q}{a^2 \ b} = 1388 \ Q \quad sec^{-1}$$

$$Q = 2.67 \ \Delta v/t = 2.67(.00151) = .00403 \ cc/min/psi$$

$$j_{exp} = 1388(.00403)/60 = .0933(Psi) \quad sec^{-1}$$

$$\eta_{exp} = 6264.7 \ poise$$

$$\tau = .0933(6264.7)Psi = 584.4(Psi) \quad dynes/cm^2$$

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