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The application of a non-Newtonian rheological equation to low-density polyethylene

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THE APPLICATION OF A

NON-NEWTONIAN RHEOLOGICAL EQUATION

TO LOW-DENSITY POLYETHYLENE

BY

JEFFREY N. GOLDSTEIN

A THESIS

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ABSTRACT

A generalized non-Newtonian equation describing the rheology of molten thermoplastics is verified for low-density polyethylenes. The equation is extended to account for both rheological temperature dependency and polyethylene molecular weight dependency. The prediction of the rheology of new polyethylenes without additional experimentation is thus possible.

APPROVAL OF THESIS

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TO LOW-DENSITY POLYETHYLENE

BY

JEFFREY N. GOLDSTEIN

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

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NOMENCLATURE

A	Constant = Equation VI (Huang)	lbm/second-inch
B	Constant = Equation VI (Huang)	lbm/second-inch
C	Constant = Equation VI (Huang)	seconds
E	Flow Activation Energy	
K	Constant = Equation XII (Arrhenius)	
Q	Volumetric Flow Rate	inch 3/second
R	Radius -Capillary	inch
	Gas Constant	$(lb_f/in.^2)(in.^3)/(lb\text{-}mole)(°R)$
T	Absolute Temperature	°R

C_3	Constant = Equation VI-A (Huang)	
dv/dr	Shear Rate-Cylindrical coordinates	$seconds^{-1}$
dv/dx	Shear Rate-Rectangular coordinates	$seconds^{-1}$
gc	Gravitational Constant	$inch/second^2$
k	Constant = Equation II (Power Law)	
n	Flow Behavior Index = Equation II (Power Law)	
p	Pressure	$lb_f/inch^2$
r	Radial Distance	inch
t_o	Constant = Equation VI-A (Huang)	

β^{ij}	Molecular Arrangement Parameter Tensor At Equilibrium Conditions	
$\dot{\gamma}$	Rate of Shear Tensor	
Δp	Pressure Drop - Across Capillary	$lb_f/inch^2$
μ	Viscosity	lbm/second-inch
τ	Shear Stress	$lb_f/inch^2$
τ_o	Yield Stress Constant = Equation VI (Huang)	$lb_f/inch^2$
τ^{ij}	Shear Stress Tensor	
∂	Constant = Equation VI-A (Huang)	

1. INTRODUCTION

A. Purpose

For the last several years the flow behavior of molten thermo-
plastics (rheology) has been the object of extensive research.   Consider-
able effort has been spent in developing means of predicting thermoplastic
rheological behavior.   Nevertheless, there still exists a need for a
simple and accurate defining equation describing the flow of molten
thermoplastics upon which reliable predictions may be based.   Such
an equation is presented and verified herein.   A summary of results
may be found in Table I, page 22.

In addition, a general procedure is demonstrated whereby empiri-
cally determined constants of the rheological equation can be found and
tabulated for thermoplastic materials.   Once such a computation is made
no further experimentation is necessary to determine rheological pro-
perties at new or extrapolated conditions, including different tempera-
tures.   These constants can be related to such fundamental thermoplastic
properties as molecular weight, thus allowing the prediction of the rheology
of new materials without additional experimentation once the molecular
weight is known.

The need to be able to accurately predict thermoplastic flow be-
havior is quite practical.   Thermoplastics are commonly utilized indus-
trially in the molten state.   High volumes of polyethylene, polypropylene,
polystyrene and other thermoplastics are fabricated into shapes and parts

by extrusion, injection molding and callendering. Metzger and Brodkey

state that "the high speed extrusion of film or wire jackets demands an

understanding of the flow behavior of the material". [1] All such processes

demand the accurate prediction of thermoplastic rheology if equipment

is to be designed and operated in an efficient and economical manner.

B.   Theoretical Background

If a sufficient driving force is applied to a confined fluid it will

flow.   However, the velocity of the flowing fluid will not be uniform

throughout.   The velocity will vary with distance perpendicular to the

point of application of the force; i. e., a velocity gradient will exist.

The molecular layer of fluid at the center of the applied force

will flow at some maximum velocity, greater than the layer adjacent

to it.   This is known as a shearing effect between the two layers.   Suc-

cessive layers of fluid will be sheared with resultant decreases in veloc-

ity until a wall of the fluid container is reached.   The velocity at this wall

will be zero.

The shearing force per unit cross-sectional area is termed shear

stress, γ.   The change in fluid velocity V with respect to perpendicular

or normal distance X is $\frac{dv}{dx}$, and is termed the shear rate.   In the cylin-

drical system normally encountered, e. g., an extruder tube or a

1.   A. P. Metzger and R. S. Brodkey, "Measurement of the Flow of
      Molten Polymers Through Short Capillaries," Journal of Applied
      Polymer Science, Vol. 7, (1963), p. 399

capillary, velocity changes with radius, $\frac{dv}{dr}$.

Many attempts have been made to develop a rheological equation that adequately describes molten polymer rheology. All such equations attempt to define the relationship between the shear stress and the shear rate of the fluid. The simplest of these equations is the Newtonian equation:

$$\text{I} \qquad \tau = -\mu \frac{dv}{dr}$$

This equation states that the shear stress τ is directly proportional to the shear rate, $\frac{dv}{dr}$. The constant of proportionality μ is the viscosity of the material.

A fluid that obeys equation I is termed a Newtonian fluid. Few materials and essentially no thermoplastics obey this equation; hence, molten thermoplastics are known as non-Newtonian fluids.

Newtonian and non-Newtonian behavior can be demonstrated graphically, as in Figure I. For a Newtonian fluid, a plot of shear stress against shear rate yields a straight line through the origin, with the slope of the curve equal to the viscosity.

Non-Newtonian behavior may follow any of the several types illustrated in Figure I. For a material exhibiting plastic behavior a minimum shear stress, called the yield stress, is required before flow will begin. For a Bingham plastic, once this yield stress is reached the

Figure 1

FLOW BEHAVIOR OF MOLTEN THERMOPLASTICS
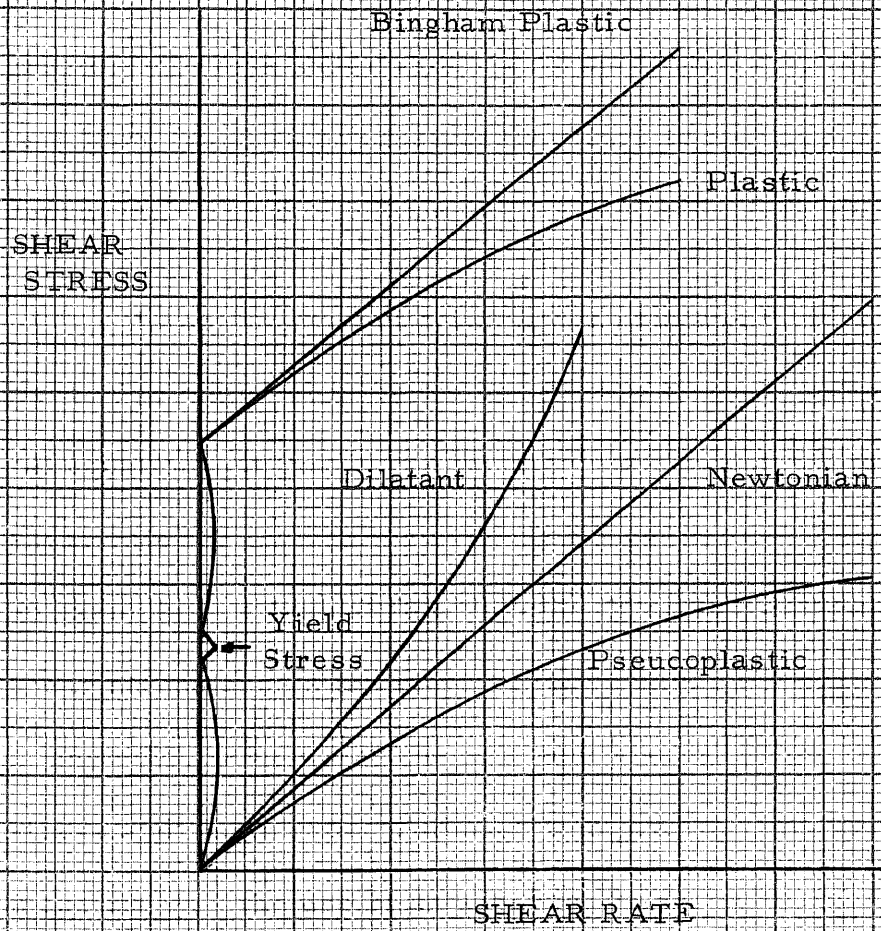
shear stress is directly proportional to the shear rate, as in Newtonian

flow. Pseudoplastic behavior is marked by a disproportionate gain in

shear rate for each increment of shear stress. This type of behavior

is common among thermoplastics. Plastic and pseudoplastic behavior

are equivalent, except that plastic behavior indicates a yield stress.

The opposite type of behavior, where shear stress increases at a

greater rate than shear rate, is termed dilatancy. Dilatant behavior

is seldom found among thermoplastics. In addition, flow may be time

dependent. For molten thermoplastics this effect may be ignored.

A common way of defining the complex flow behavior of a non-

Newtonian material is by the use of flow curves, rather than an analyti-

cal equation. A flow curve is an empirical plot of shear stress versus

shear rate for a given material at a given temperature. Figure II is

an example of a typical flow curve. At any given point on the curve,

shear stress equals the slope of curve times the shear rate. The slope

at any point is known as the apparent viscosity, valid only at that specific

stress and shear rate. Although this graphical method is somewhat useful

industrially, the use of an apparent viscosity may lead to serious errors.

An analytical expression is much more useful for extrapolating data and

relating the flow to inherent material properties.

The most commonly found mathematical equation describing

Figure II

TYPICAL THERMOPLASTIC FLOW CURVE
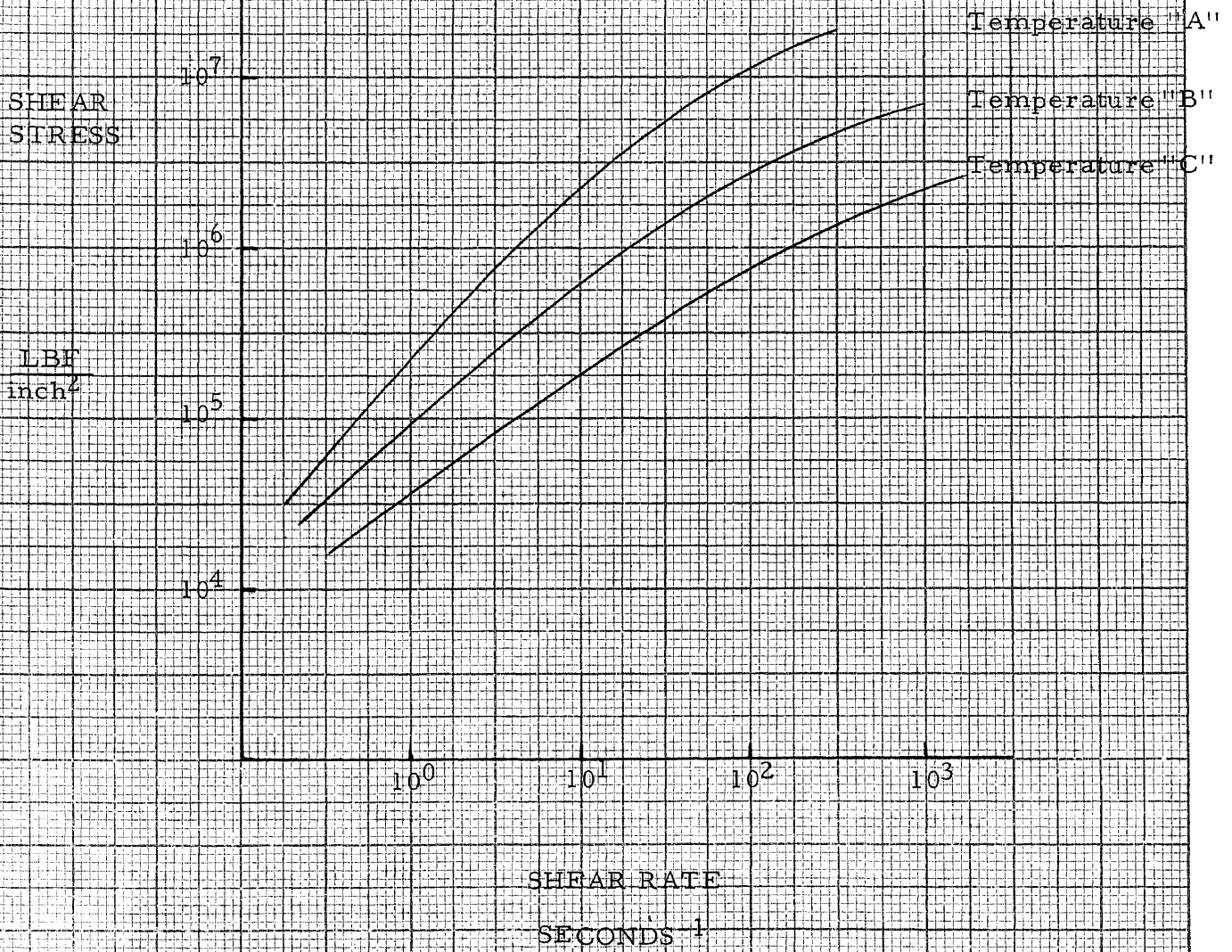
molten thermoplastic non-Newtonian behavior is the power law:

$$\text{II} \qquad T = K\left(\frac{dv}{dr}\right)^n$$

This is the simplest non-Newtonian expression, involving only two

constants. One of the constants, the exponent of the equation n is

known as the flow behavior index. For $n=1$, the equation reduces

to the Newtonian equation. Pseudoplastic behavior is indicated by

$n<1$, while $n>1$ indicates dilatancy.[2]

Although the power law is simple, it is not particularly accurate.

Both K and n are, by definition, constants determined for each ther-

moplastic material. However, K and n have been found to vary consid-

erably with shear rate for a given material at constant temperature. A

more reliable equation, therefore, is required.

Another non-Newtonian rheological equation found in the litera-

ture is the Eyring-Powell equation.[3]

$$\text{III} \qquad T = \mu \frac{dv}{dr} + \frac{1}{B}\sinh^{-1}\frac{\left(\frac{dv}{dr}\right)}{A_{EP}} \qquad A_{EP}, B, \mu = \text{constants}$$

Although more accurate than the power law, its considerable complexity

makes it impractical for use as a design equation for thermoplastic flow

behavior. Additionally, Metzner states "the theoretical concepts upon

which the equation is based have been pointed out to be unsound."[4]

2. Giovanni Pezzin, "Rheology of Molten Polymers", Materie
    Plastiche ed Elastomeri (1962) in Instron Application Series
    p-12, Instron Corp. (Canton, Ohio), p. 4.

3. A. B. Metzner, "Flow Behavior of Thermoplastics" in E. C.
    Bernhardt, ed., Processing of Thermoplastic Materials,
    (N. Y., N. Y., 1957) p. 28.

4. Ibid.

Other non-Newtonian defining equations found in the literature
are the Ellis equation:

$$\text{IV} \qquad \frac{dv}{dr} = \left(\frac{1}{\eta_0}\right) T + C T^A \qquad \eta_0, C, A = \text{constants}$$

and the Reiner-Philippoff model:[5]

$$\text{V} \qquad T = \left(\eta_\infty + \frac{\eta_0 - \eta_\infty}{1 - (T/D)^2}\right) \frac{d\left(\frac{dv}{dr}\right)}{dt}$$

Equations of even greater complexity have been presented.

5. M. H. Wohl, "Rheology of Non-Newtonian Materials", Chemical Engineering (February 12, 1968) pp. 131-132.

II. PRESENTATION OF THE EQUATION

As stated in the previous section, various types of flow behavior-
pseudoplastic, Bingham plastic, dilatent, etc. - have been described
for non-Newtonian fluids. It has been found that for any particular
material the type of rheological behavior applicable will, in general,
depend on the shear rate range being investigated. Thus a single material
may undergo several of the listed types of flow behavior in different shear
rate ranges (one result being the variation in the constants of the power
law).

Metzner and Reed state:[6]

> It is obvious...that some method must eventually be devel-
> oped which is universally applicable to all fluids - Newtonian
> and non-Newtonian alike.

A rheological equation for non-Newtonian thermoplastics has been
developed which satisfies the above criterion and is valid in all ranges of
shear rate. This equation, derived by Dr. C. R. Huang and subsequently
referred to as the Huang equation is:[7]

$$\text{VI} \quad T = T_0 + \left[A \left(-\frac{dv}{dr} \right) + B \left(\frac{dv}{dr} \right) e^{-C \left(-\frac{dv}{dr} \right)} \right] \left[\frac{1}{g_c} \right]$$

where T_0, A, B, C are temperature dependent constants empirically de-
termined for thermoplastic materials.

6. A. B. Metzner and J. C. Reed, "Flow of Non-Newtonian Fluids -
    Correlation of the Laminar, Transition, and Turbulent Flow Regions",
    A. I. Ch. E. Journal Vol. 1 (1955) p. 434.

7. Dr. C. R. Huang, private communication (1970).

The above equation is a simplified form of a more rigorous equation which accounts for time-dependent rheological behavior. This equation is thus applicable to both thixotropic and time-independent (e. g. polyethylene) materials. This more general equation, presented below, was developed by Dr. C. R. Huang from general principles of statistical mechanics and irreversible thermodynamics.

$$\text{VI-A} \quad T^{ij} - \frac{T_o}{\sqrt{\frac{1}{2}T^{ij}T_{ij}}} \; T^{ij} = \left(\mu - C_3 J \beta^{ij} e^{-C_3 |\dot{\gamma}^{ij}|} \ln q \; t_o \frac{|\dot{\gamma}^{ij}|}{\dot{\gamma}^{ij}} \right) \dot{\gamma}^{ij}$$

$$\mu, C_3, J, t_o = \text{constants}$$

The Huang equation, like the power law but unlike the Eyring-Powell and more complicated expressions, is simple, easy to apply, and explicit in shear stress. Unlike the power law, however, it is quite accurate over a large range of shear rate and shear stress.

It should be noted that with both T and $C = O$ equation VI reduces to the Newtonian equation I. Additionally A and B may be considered viscosity terms, and T_o is the yield stress.

The accuracy of the Huang equation has been verified by comparison of predicted and experimental data. The method of comparison and the results are presented herein. The method may be applied to any thermoplastic material to determine the four constants of the equation. Once this is done, the flow behavior at any shear stress or shear rate can be predicted.

III. EXPERIMENTATION

A. Experimental Background

Any instrument used for obtaining rheological data is called a rheometer. Two classes of rheometers are commonly employed for evaluation of polymer melts: the capillary rheometer and the rotational rheometer.

The principles of operation of both types of equipment are simple. In the capillary rheometer, the material under study is forced through a cylindrical heated capillary of precisely known length and diameter. The required driving force is obtained by the pressure of a dead weight or inert gas. Two parameters are measured. The pressure drop across the capillary is measured directly (and subsequently related to shear stress). Also, the amount of material forced through the capillary is determined as a function of time; i. e., the volumetric flow rate is found (and related to shear rate). This measurement is accomplished by weighing the amount of material collected. Operating temperature and pressure are controlled and measured carefully.

In one type of rotational rheometer the molten polymer is placed in an annular space between two concentric cylinders. One of the cylinders is rotated, shearing the polymer. The rate of rotation (shear rate) is measured, as well as the torque (shear stress) required for the rotation.

A second type of rotational rheometer is the cone and plate type. Here the molten material is placed in the gap between a flat plate and a cone immediately above the plate. The cone is rotated, shearing the fluid. Torque and angular velocity are again the measured parameters. An advantage of this type of instrument is that for small cone-plate angles the shear rate and shear stress are uniform throughout the material, so that no subsequent corrections are required for non-Newtonian fluids.

Extrusion, the forcing of a material through a cylindrical die, is analogous to the capillary rheometer operation described above. Industrially, polyethylene and other thermoplastics are commonly processed by extrusion. Therefore, it is desirable to obtain rheological data in the high shear rate range normally encountered in extrusion. At these high shear rates a molten thermoplastic will tend to climb out of the gap inherent in a rotational rheometer. No such problem exists with capillary rheometers.

Additionally, the heat generated by the continuous shearing of the thermoplastic also limits the ability of rotational rheometers to operate at high shear rates. Best and Rosen state that extensive modifications to commercial rotational rheometers are required for the attainment of accurate measurements.[8]

8. D. M. Best and S. L. Rosen "A Simple Versitile and Inexpensive Rheometer For Polymer Melts", Polymer Engineering and Science Vol. 8, (1968)

For these reasons data based on capillary rheometer experiments, are
to be preferred. Data derived from capillary rheometry experiments,
therefore, are used in the verification of the Huang equation.

B. Experimental Data (Literature)

The data required for the experimental verification of the
Huang equation (equation VI) were obtained from experimentally
determined flow curves presented in the literature relating $\frac{\Delta p \beta}{2L}$
to $\frac{4Q}{\pi R^3}$. The data are part of a collection of flow curves compiled
by Westover in Bernhardt's PROCESSING OF THERMOPLASTIC MATERI-
ALS. [9] Severs has called this collection of flow curves the greatest ever
compiled. [10] All data were obtained in capillary rheometers by the manu-
facturer of the thermoplastics.

Low density polyethylene is the thermoplastic chosen for experi-
mental verification of the Huang equation. This material is extruded in
large volumes, and the knowledge of its rheological properties is of more
than theoretical interest.

Specifically, data on Tenite Polyethylene 856, manufactured by
Eastman Chemical Products Company, and Alathon 3, Alathon 10, and
Alathon 17, all manufactured by E. I. DuPont de Nemours and Co. are

9. R. F. Westover, "Processing Properties" in E. C. Bernhardt,
   Processing of Thermoplastic Materials (N. Y., N. Y., 1957) pp. 547-627.

10. E. T. Severs, Rheology of Polymers (N. Y., N. Y., 1962) p. 26.

the thermoplastics used to verify the Huang equation. Tenite 856 is

evaluated at three temperatures: 334, 374, and 446°F, while the

Alathon series is evaluated only at 374°F. The original flow curves

are presented in Figures XVIII - XXIII, Appendix A. A sample cal-

culation shown in Appendix B demonstrating the means of verifying

and obtaining the constants of the equation utilizes Tenite 856 at 374°F.

C. Correction of Experimental Data

It may be assumed that the flow of a molten thermoplastic

through a capillary is laminar and isothermal. Non-laminar flow is

easily observed. The onset of turbulence can be noted visually by

examination of the product. Turbulence will result in melt fracture;

a smooth uncracked product will no longer exist.

Once laminar, isothermal flow is assumed, the well known

Hagen-Poiseuille equation for Newtonian flow through a capillary is

given as:[11]

$$\text{VII} \qquad Q = \left(\frac{\pi R^4}{8\mu}\right)\left(\frac{dP}{dL}\right)$$

where R equals capillary radius and L equals capillary length. Re-

arranging and, in the limit, letting $dP = \Delta P$ and $dL = L$, we obtain

$$\text{VIII} \qquad \frac{\Delta P R}{2L} = \mu\left(\frac{4Q}{\pi R^3}\right)$$

ΔP equals the pressure drop across the capillary.

11. I. J. Duvdenani and I. Klein, "Analysis of Polymer Melt flow in Capillaries Including Pressure Effects", SPE Journal Vol. 23 (December 1967) p. 42.

The specific parameters measured by the manufacturers of Tenite Polyethylene 856 were the pressure drop, ΔP , across a capillary of 0.019 inches diameter and the volumetric flow rate, Q , where Q is defined as the amount of material collected per unit time. All parameters of equation VIII except μ , therefore, are experimentally determined.

It can be readily seen that equation I, the Newtonian equation, and equation VIII, the Hagen-Poiseuille equation, take the same form. It is common practice (although incorrect) to report τ as $\frac{\Delta P R}{2L}$ and $\frac{dV}{dr}$ as $\frac{4Q}{\pi R^3}$ and plot $\frac{\Delta P R}{2L}$ against $\frac{4Q}{\pi R^3}$ on a flow curve. Obviously, such a procedure equates equations I and VIII and is valid only for Newtonian fluids. The polyethylene rheological data obtained at Eastman on Tenite 856, and in fact the great majority of all thermoplastic rheological data, is presented in the form of such an erroneous flow curve.

There are serious errors in both the shear stress and shear rate terms described by the Hagen-Poiseuille equation when applied to non-Newtonian molten thermoplastics. Defining shear stress equal to $\frac{\Delta P R}{2L}$ does not account for entrance effects (sometimes referred to as end effects). Entrance effects are due to the resistances resulting from the velocity gradients encountered by the molten fluid as the

cross-sectional area is reduced at the entrance to the capillary.[12]

The error involved in not correcting shear stress for this entrance

effect is small in comparison with the error in shear rate, and will

be ignored.

Considerable error is encountered if the shear rate, $\frac{dv}{dr}$,

is evaluated as $\frac{4Q}{\pi R^3}$. It is necessary to apply the Rabinowitsch cor-

rection to obtain the true shear rate. Pearson has shown the Rabinowitsch

equation to reduce to:[13]

$$\text{IX} \qquad \frac{\tau_R^3}{\pi R^3} = -\int_0^{\tau_R} \tau^2 \left(\frac{dv}{dr}\right) d\tau$$

where τ_R is the maximum shear stress, evaluated at the wall of the

capillary. If equation IX is differentiated we find:

$$\text{X} \qquad \frac{1}{\pi R^3} \left(\frac{d(\tau_R^3 Q)}{d\tau_R}\right) = -\tau_R^2 \frac{dv}{dr}$$

Rearranging,

$$\text{XI} \qquad -\frac{dv}{dr} = \left(\frac{1}{\pi R^3 \tau_R}\right) \left(\frac{d(\tau_R^3 Q)}{d\tau_R}\right)$$

Equation XI is the Rabinowitsch equation for defining the actual shear

rate of a non-Newtonian, laminar, isothermal fluid. It is important

to note that the Rabinowitsch correction is rarely applied to literature

data, and not at all to the flow curves compiled by Westover.

12. E. B. Bagley, "End Corrections in the Capillary Flow of Polyethylene",
    Journal of Applied Physics, Vol. 28 (1957) p. 624.

13. J. R. A. Pearson, Mechanical Principles of Polymer Malt Processing,
    (Oxford, England, 1966) p. 34

IV. RESULTS AND DISCUSSION OF RESULTS

A. Verification of the Equation

As stated, the main objective of this thesis is to verify equation VI, the Huang equation. The procedure used, in essence, was to find the correct values of shear stress as a function of shear rate for a thermoplastic (polyethylene) from experimentally determined data. If the experimentally determined and corrected shear stress-shear rate relationship can be generated by the Huang equation over the entire range of shear rates, and at various temperatures, the Huang equation will have to be assumed valid. A sample calculation, on Tenite Polyethylene 856 at 374°F extrusion temperature, may elucidate the procedure. This sample calculation may be found in Appendix B.

Reiterating, the Huang equation is valid if plots of the corrected original experimental data and data generated directly from the Huang equation coincide. Figures III, IV, and V demonstrate that this is indeed the case for Tenite Polyethylene 856 at 334°F, 374°F and 446°F respectively. Differences between the calculated and experimental values certainly fall within the error limit of the experimental data. The Huang equation, therefore, is valid over the range of temperatures and shear rates investigated.

B. Constants of the Equation

Values of the constants of the Huang equation are obtained for

Figure III

PREDICTION OF EXPERIMENTAL DATA BY HUANG EQUATION
334°F EXTRUSION TEMPERATURE

SHEAR
STRESS

$\frac{LBF}{inch^2}$

———— Experimental Data
Material = Tenite Polyethylene 856
Source = Bernhardt: Processing of
Thermoplastic Materials

— — — Calculated data

$$\tau = \tau_o + \frac{1}{\zeta_c}\left[A(-\frac{dv}{dr}) + B(-\frac{dv}{dr})e^{-C(-\frac{dv}{dr})}\right]$$

Rabinowitsch Correction Applied

SHEAR RATE
SECONDS⁻¹

Figure IV

PREDICTION OF EXPERIMENTAL DATA BY HUANG EQUATION
374°F EXTRUSION TEMPERATURE - SAMPLE CALCULATION

SHEAR STRESS

$\dfrac{LB_F}{inch^2}$

Experimental Data
Material: Tenite Polyethylene 856
Source: Bernhardt Processing of
Thermoplastic Materials

Calculated Data

$\tau = \tau_o + \frac{1}{3c}\left[A\left(\frac{4Q}{\pi r^3}\right) + B\left(\frac{4Q}{\pi r^3}\right)e^{-c\left(\frac{4Q}{\pi r^3}\right)}\right]$

Rabinowitsch Correction Applied

SHEAR RATE
SECONDS⁻¹
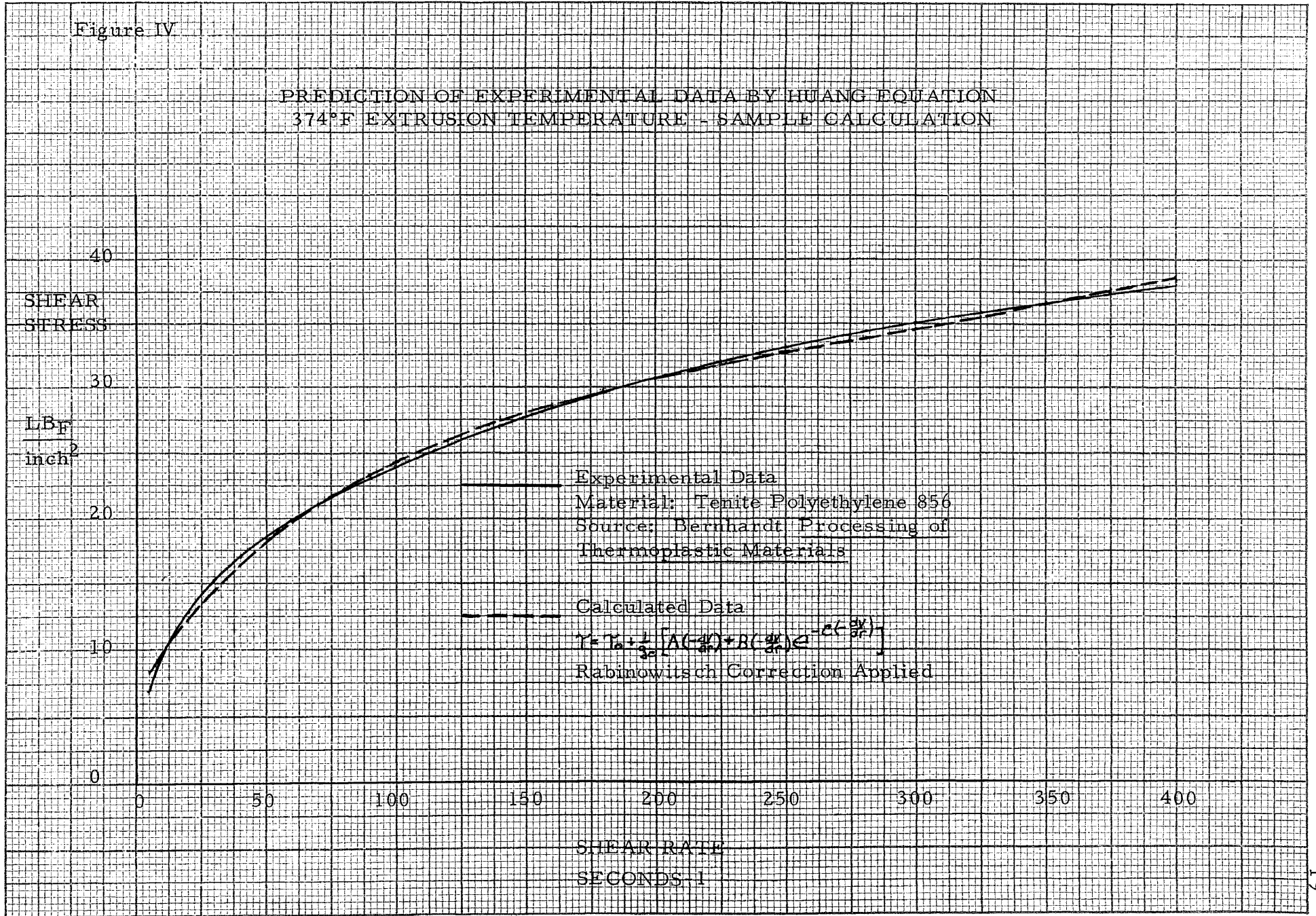
Figure V

PREDICTION OF EXPERIMENTAL DATA BY HUANG EQUATION
446°F EXTRUSION TEMPERATURE
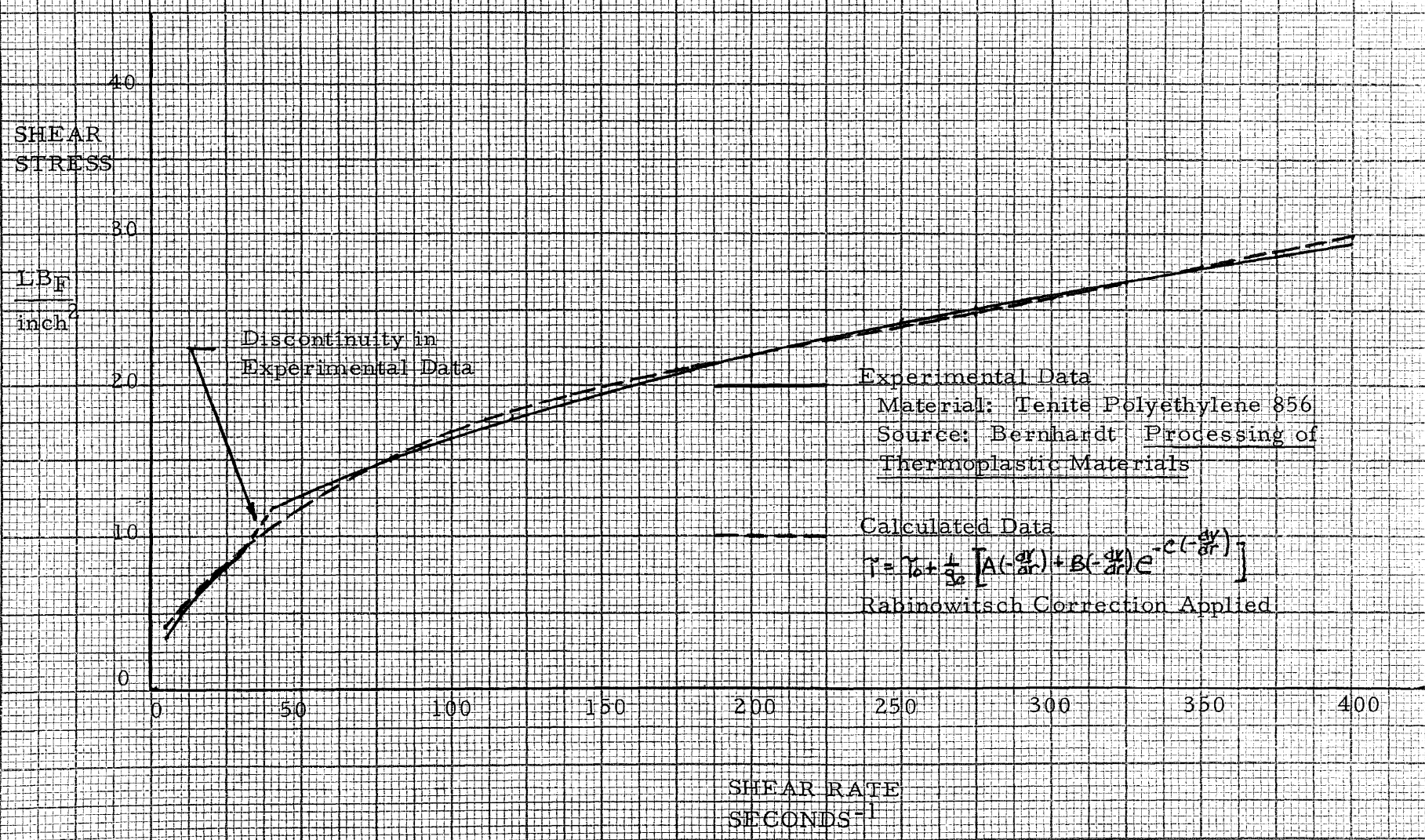
SHEAR
STRESS

$\frac{LBF}{inch^2}$

Discontinuity in
Experimental Data

Experimental Data
  Material: Tenite Polyethylene 856
  Source: Bernhardt Processing of
  Thermoplastic Materials

Calculated Data

$$\tau = \tau_b + \frac{1}{g_c}\left[A\left(-\frac{dv}{dr}\right) + B\left(-\frac{dv}{dr}\right)e^{-c\left(-\frac{dv}{dr}\right)}\right]$$

Rabinowitsch Correction Applied

SHEAR RATE
SECONDS^{-1}

Tenite Polyethylene 856 at 334°F, 374°F and 446°F. Results are

presented in Table I. The method of obtaining the constants is out-

lined in the sample calculation, Appendix B.

Constants of the Huang equation were also obtained for the

Alathon series of polyethylenes previously described (Alathon 3, 10

and 17, E. I. DuPont de Nemours and Co.). The results are given

in Table II.

Extrapolation of the data is valid using the Huang equation;

however, caution must be exercised. If the shear rate is increased

to a point such that turbulence and melt facture occur, the Huang equa-

tion, and indeed no equation yet developed, will hold.

C. Temperature Dependence

It is possible to extend the generality of the Huang equation

(equation VI) by defining the temperature dependence of the constants

of the equation. The temperature dependence of the constants is shown

graphically in Figures VI, VII, VIII, and IX, for Tenite Polyethylene 856.

It is possible, therefore, to predict the flow behavior of Tenite

Polyethylene 856 at temperatures other than those for which data have

been given. One merely finds the appropriate values of the constants A,

B, C, and T_0 from Figures VI - IX and evaluates the Huang equation with

Table I

CONSTANTS OF THE EQUATION
FOR TENITE POLYETHYLENE 856

$$\text{Equation} = T_R = T_o + \frac{1}{g_c}\left[A\left(-\frac{dv}{dr}\right) + B\left(-\frac{dv}{dr}\right)e^{-C\left(-\frac{dv}{dr}\right)}\right]$$

$$T_R = \text{lbf/inch}^2$$
$$-\frac{dv}{dr} = \text{seconds}$$
$$g_c = 386.09 \text{ inch/second}^2$$

Uncorrected Computer Output

| | Extrusion Temperature - °F | | |
	334	374	446
A	0.07613	0.06861	0.06072
B	0.2363	0.2248	0.1756
C	0.007683	0.007532	0.008284
T_o	9.697	6.992	3.091

Corrected Values

| | Extrusion Temperature - °F | | |
	334	374	446
A = $\frac{\text{lbm}}{\text{second-inch}}$	29.39	26.49	23.44
B = $\frac{\text{lbm}}{\text{second-inch}}$	91.22	86.79	67.78
C = seconds	0.007683	0.007532	0.008284
$T_o = \frac{\text{lbf}}{\text{inch}^2}$	9.697	6.992	3.091

Table II

CONSTANTS OF THE EQUATION
FOR ALATHON 3, ALATHON 10, ALATHON 17
AT 374° F EXTRUSION TEMPERATURE

Equation:
$$T_R = T_0 + \frac{1}{g_c}\left[A\left(-\frac{dv}{dr}\right) + B\left(-\frac{dv}{dr}\right)e^{-C\left(-\frac{dv}{dr}\right)}\right]$$

T_R = lbf/inch^2
$-dv/dr$ = seconds^{-1}
g_c = 386.09 inch/second^2

Material	Weight Average Molecular Weight	A $\frac{lbm}{second\text{-}inch}$	B $\frac{lbm}{second\text{-}inch}$	C seconds	$\frac{lbf}{inch^2}$
Alathon 3	525,000	3.009	18.41	0.0002849	26.34
Alathon 10	300,000	2.206	12.16	0.0002600	10.61
Alathon 17	225,000	2.035	6.15	0.0002500	1.91

Figure VI

TEMPERATURE DEPENDENCE OF THE CONSTANT "A"
FOR TENITE POLYETHYLENE 856
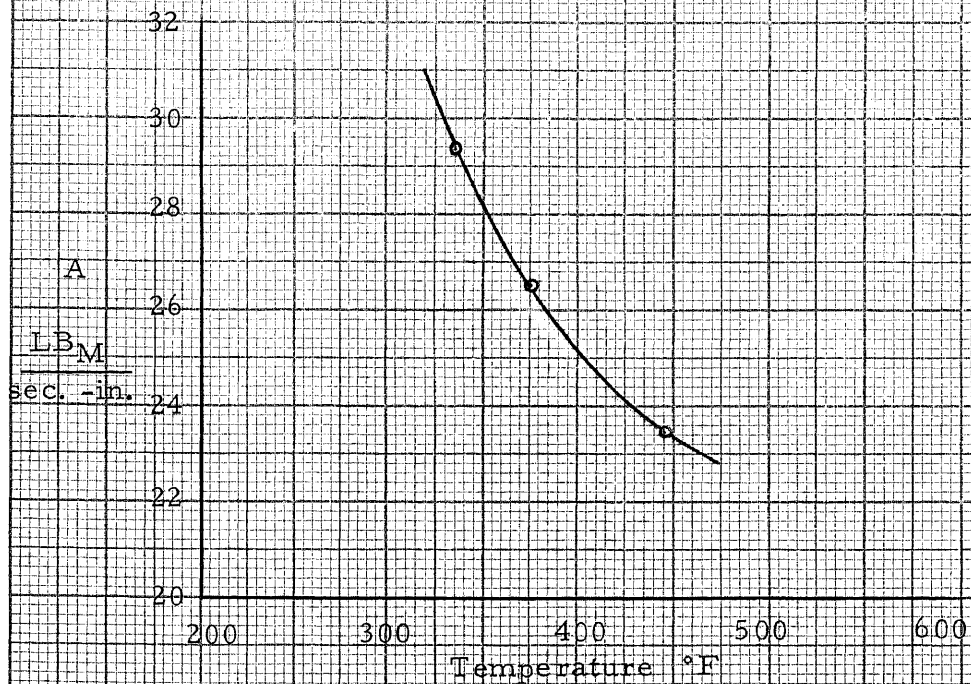
Figure VII

TEMPERATURE DEPENDENCE OF THE CONSTANT "B"
FOR TENITE POLYETHYLENE 856
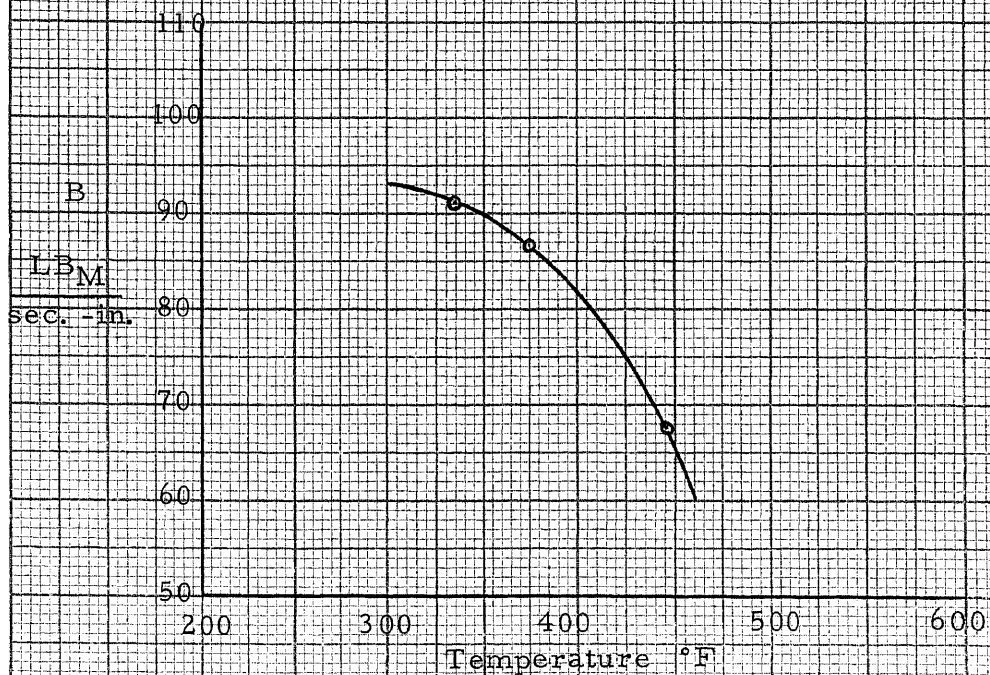
Figure VIII

TEMPERATURE DEPENDENCE OF THE CONSTANT "C"
FOR TENITE POLYETHYLENE 856
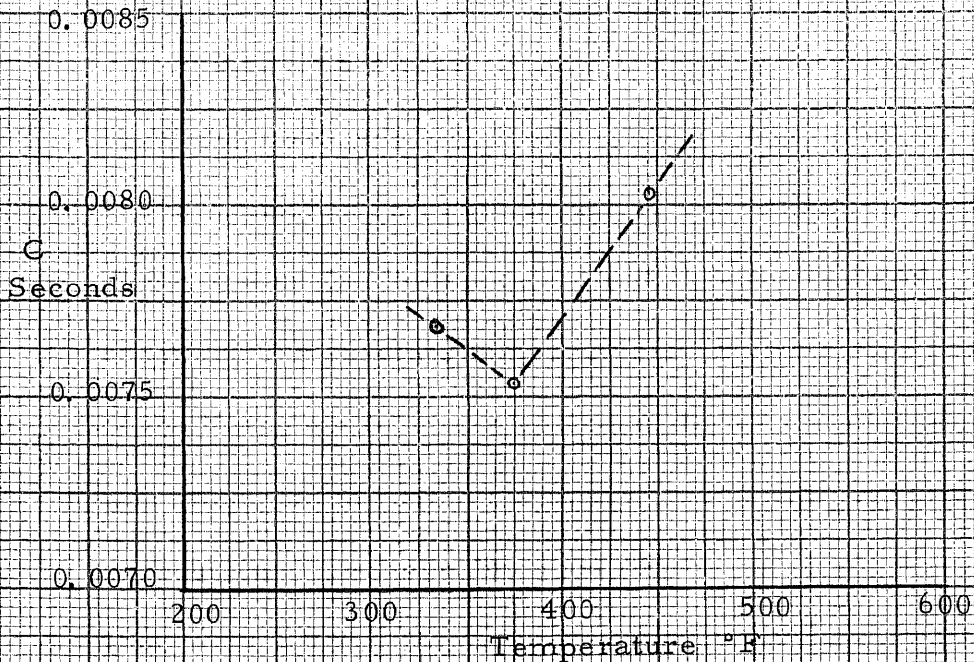
Figure IX

TEMPERATURE DEPENDENCE OF THE CONSTANT τ_0
FOR TENITE POLYETHYLENE 856
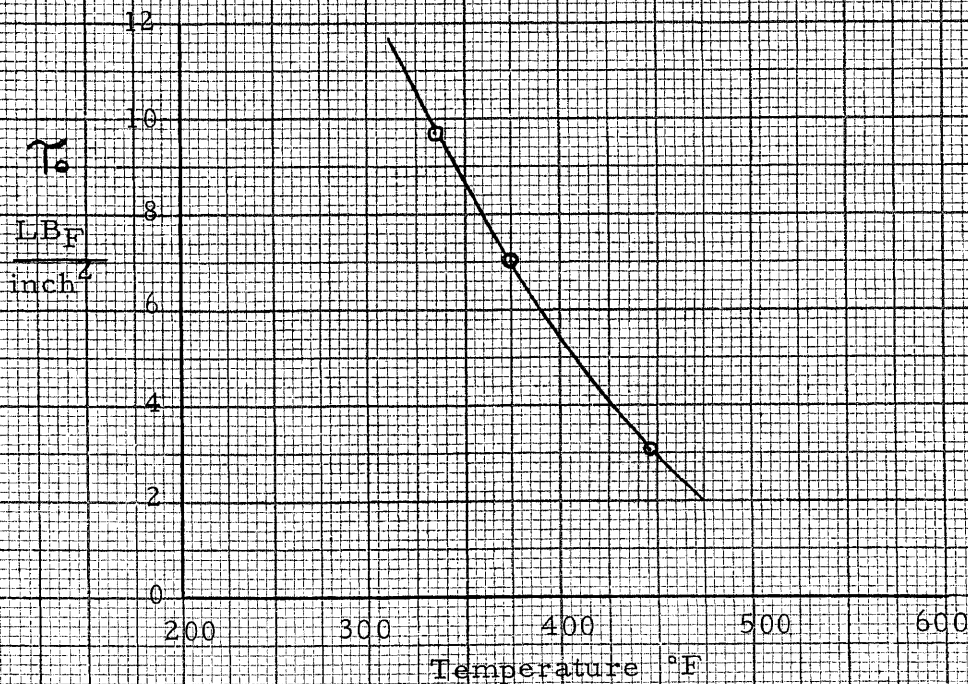
these constants. This method reverts to the use of flow curves rather than a preferred analytical expression.

Kowalski states "if data are not available at the temperature required, extrapolation or interpolation can be safely made over a 100°F temperature range by use of the Arrhenius equation $\mu = A e^{-E/RT}$ where $A =$ constant for the specific fluid, E = flow activation energy, R = gas constant, T = absolute temperature."[14] Since the constants A and B of the Huang equation are analogous to the constant μ, viscosity, it was attempted to fit the constants of the Huang equation to an Arrhenius expression. A reasonably good fit was obtained, as can be seen from Figures X - XIII. For a perfect fit, all points would fall on a straight line of slope = E and ordinate-intercept equal to lnK. The constants A and B can now be defined as temperature dependent parameters,

$$\text{XII} \qquad A = K_A e^{-E_A/T}, \quad B = K_B e^{-E_B/T}$$

Similarly, it was attempted to fit both T_o and C to an Arrhenius expression. A reasonably good fit was obtained for T_o (see Figure XIII.) However, the attempt to fit the constant C to an Arrhenius expression did not succeed (Figure XII). This is not surprising in light of the fact that, unlike the other constants of the Huang equation, C is not analogous to viscosity, its units being seconds. No analytical expression

14. R. C. Kowalski, "Introduction to Melt Rheology and Applications to Extrosion", SPE Journal, Vol. 24 (1968) p. 50.

Figure X

TEMPERATURE DEPENDENCE OF THE CONSTANT "A"
FOR TENITE POLYETHYLENE 856 - ARRHENIUS PLOT
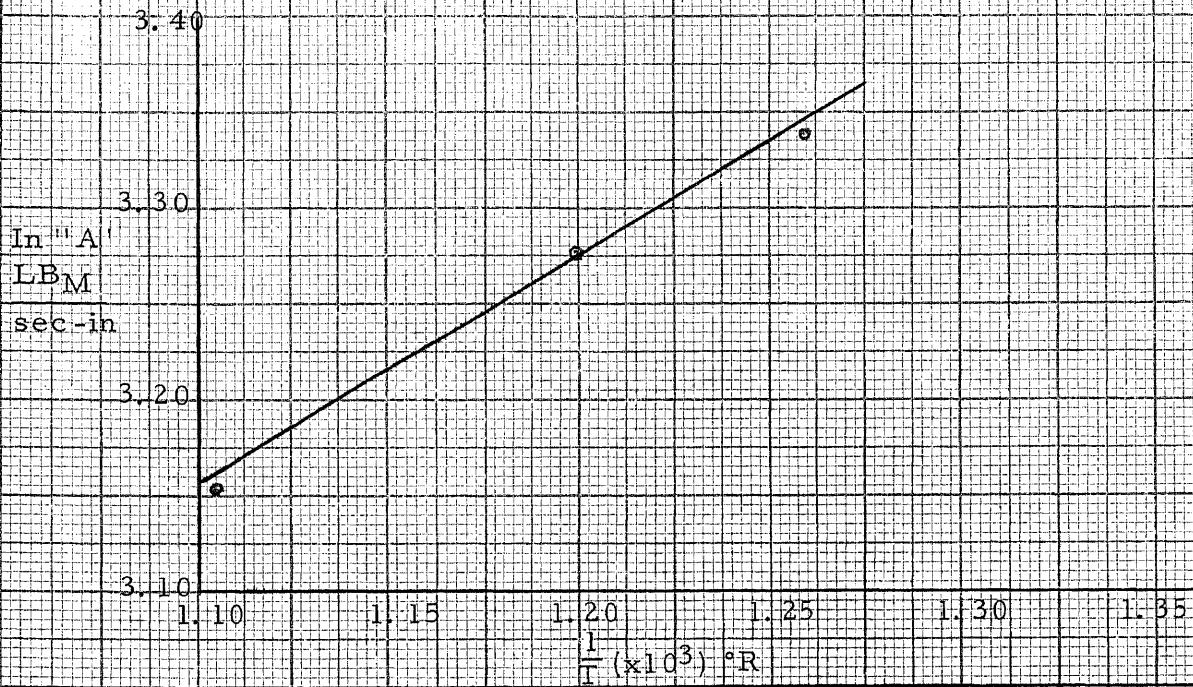
Figure XI

TEMPERATURE DEPENDENCE OF THE CONSTANT "B"
FOR TENITE POLYETHYLENE 856 - ARRHENIUS PLOT
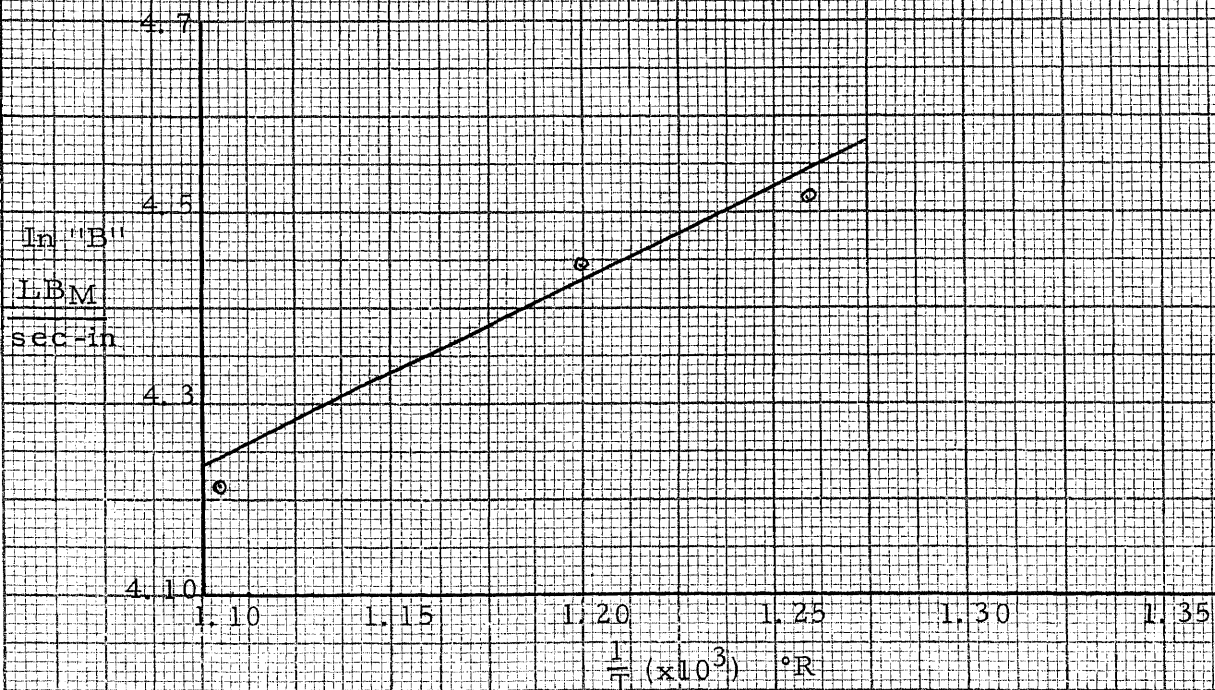
Figure XII

TEMPERATURE DEPENDENCE OF THE CONSTANT "C"
FOR TENITE POLYETHYLENE 856 - ARRHENIUS PLOT
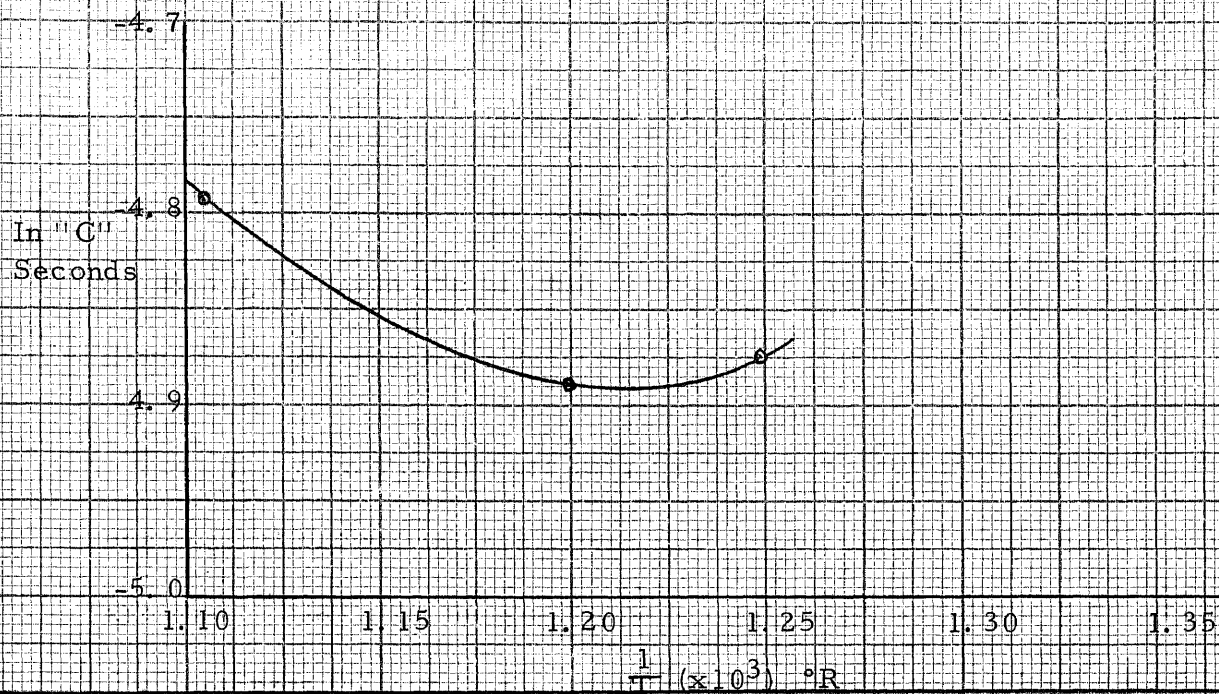
Figure XIII

TEMPERATURE DEPENDENCE OF THE CONSTANT T_o
FOR TENITE POLYETHYLENE 856 - ARRHENIUS PLOT
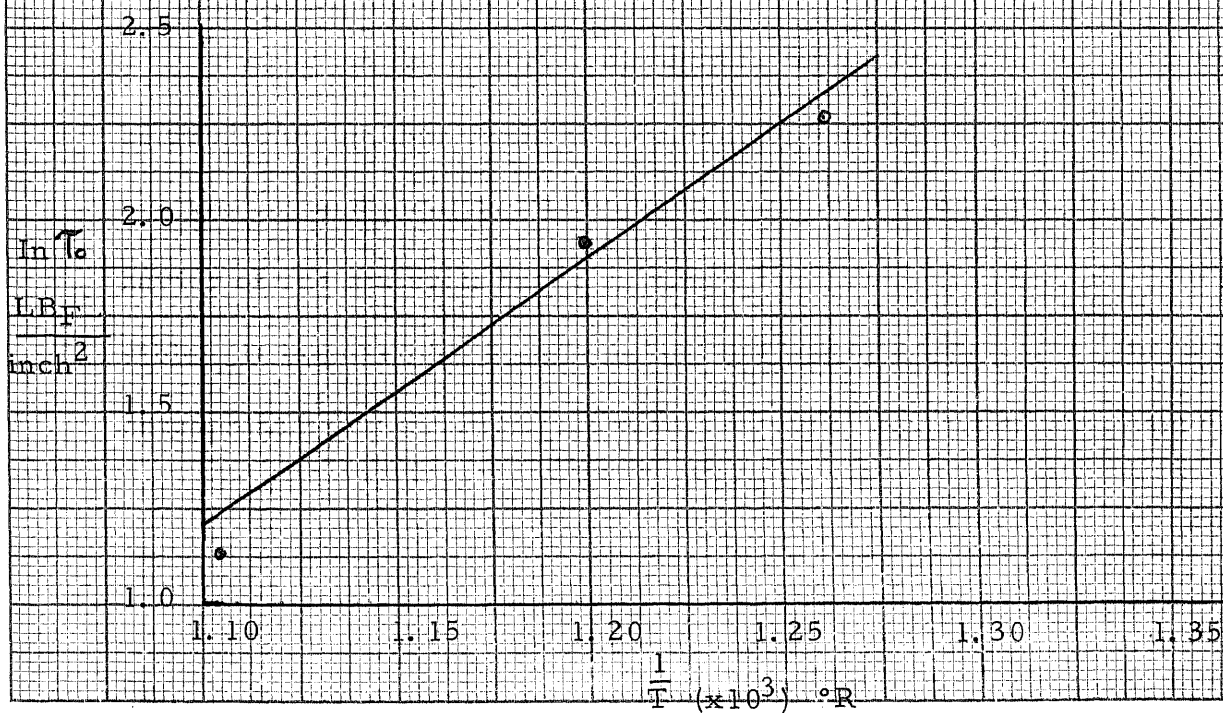
for the temperature dependence of C has yet been delineated. There-fore, data will have to be reported in the form of a curve, as in Figure XII.

The K and E values of A, B, and γ_o for Tenite Polyethylene 856 are given in Table III. These values, along with Figure XII and the Huang equation are all that is required to completely describe the flow of this material.

The above procedure may be applied to any thermoplastic whose rheological properties are known at three or more temperatures. Thus, and thermoplastic's rheological behavior can be completely described by six constants (K_A, K_B, K_{γ_o}, E_A, E_B, E_{γ_o}) and one curve (C as a function of temperature). It is hoped that manufacturers will adopt this procedure in reporting the rheological behavior of their products.

D. Molecular Weight Dependence

Although the rheological behavior of a particular thermoplastic can be predicted by both the Huang equation, once the values of the constants are known, and published flow curves, no accurate prediction of the be-havior of one material based solely on the flow curve of another is pos-sible. It is possible, however, that such predictions can be made by extrapolating or interpolating values of the Huang equation constants.

Table III

TEMPERATURE DEPENDENCY
OF THE CONSTANTS OF THE EQUATION
FOR TENITE POLYETHYLENE 856

<u>Arrhenius Expression</u>

$$X = K_x \, e^{-E_x/T}$$

X = Constant of the Equation
T = Extrusion Temperature, °R

Constant		K	E
A	$\dfrac{lbm}{second\text{-}inch}$	6.49	-1170
B	$\dfrac{lbm}{second\text{-}inch}$	8.28	-1930
τ_o	$\dfrac{lbf}{inch^2}$	0.00170	-6900

Rheological behavior is known to be a function of the molecular structure of thermoplastics.[15] It should be possible to relate the Huang equation constants to such characteristics as molecular weight and molecular weight distribution. R. G. King has stated that viscosity is a function of the molecular weight distribution of a thermoplastic, the wider molecular weight spread polymers showing a greater dependence of viscosity on shear rate.[16] Additionally, Kowalski has stated that the higher the molecular weight of a thermoplastic, the higher its position will be on a flow curve.[17]

The prediction of the rheological behavior of low density polyethylene (at 374°F) based on the material's molecular weight may be achieved by the use of Figures XIV - XVII and the Huang equation (equation VI). The Figures were derived from published rheological data on a series of polyethylenes at different molecular weights: Alathon 3, 10, and 17, E. I. DuPont de Nemours and Co. Table II in a previous section gives the values of the constants of the Huang equation at the molecular weights evaluated.

The values of the constants were found as described for the sample calculation in Appendix B. Although the correlations between

15. A. P. Metzger and J. R. Knox, "The Effect of Pressure Losses in the Barrel on Capillary Flow Measurements", Transactions of the Society of Rheology, Vol. 9 (1965) p. 13.

16. R. G. King, "A Rheological Measurement of Three Polyethylene Melts, Rheologica Acta, Vol. 5 (1966) p. 40.

17. R. C. Kowalski, op. cit.

Figure XIV

MOLECULAR WEIGHT DEPENDENCE OF THE
CONSTANT "A" FOR LOW-DENSITY POLYETHYLENE

Equation: $\tau_e = \tau_c + \frac{1}{\dot{\gamma}}\left[A(-\frac{dv}{dr}) + B(-\frac{dv}{dr})e^{-c(-\frac{dv}{dr})}\right]$

Material: ALATHON 3, 10 & 17
E. I. DuPont de Nemours

Molecular Weight ($\times 10^{-5}$)
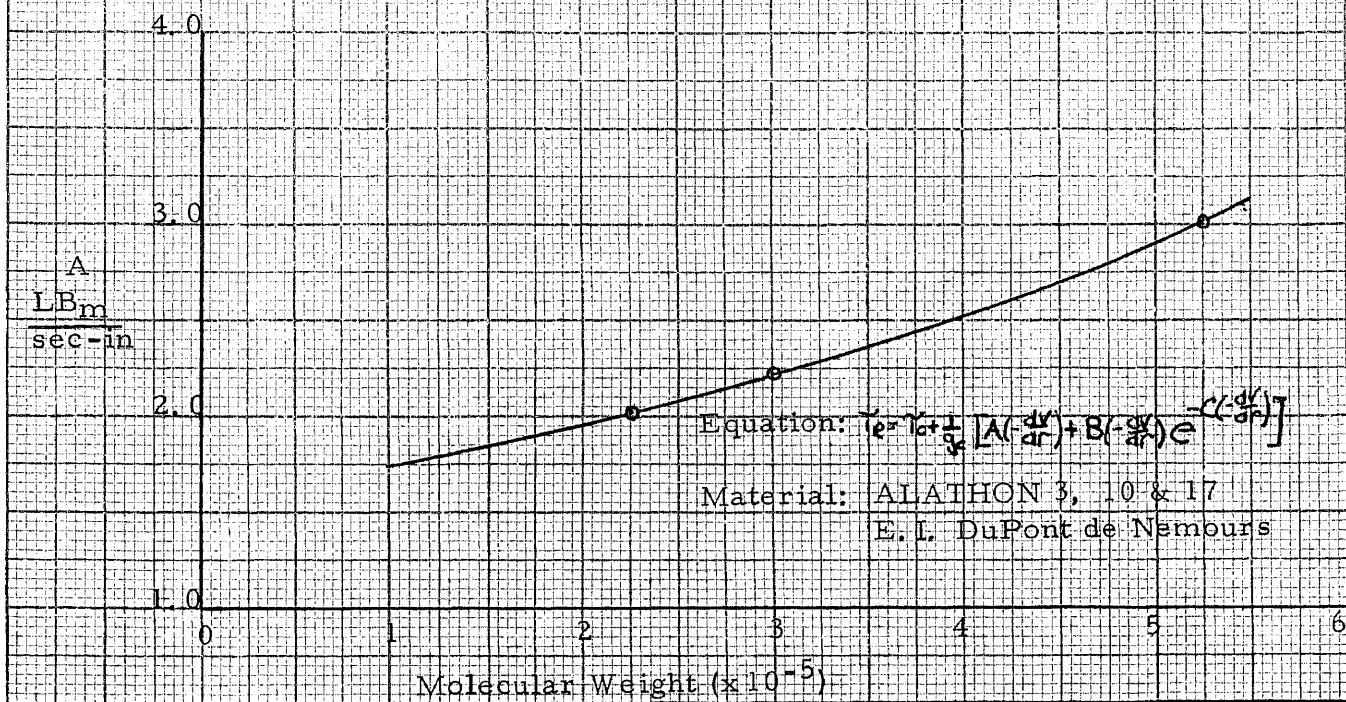
Figure XV

MOLECULAR WEIGHT DEPENDENCE OF THE
CONSTANT "B" FOR LOW-DENSITY POLYETHYLENE

Molecular Weight ($\times 10^{-5}$)

33
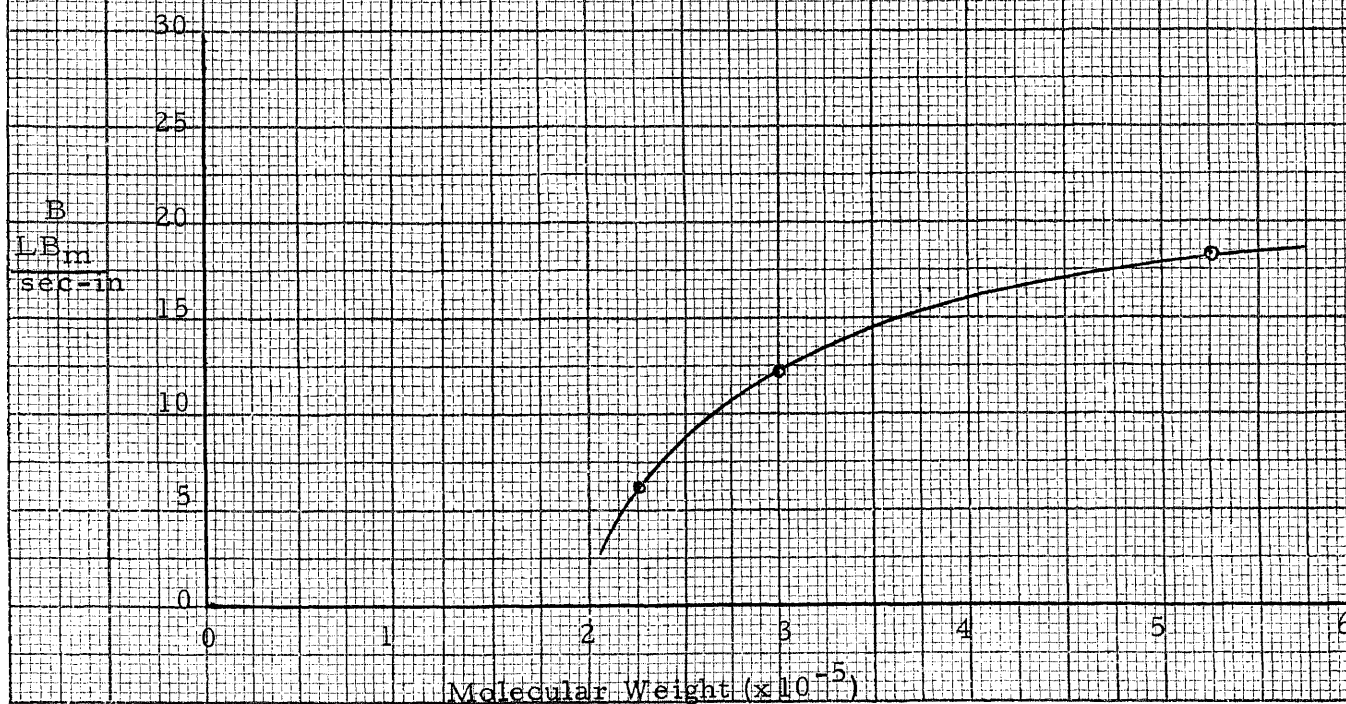
Figure XVI

MOLECULAR WEIGHT DEPENDENCE OF THE
CONSTANT "C" FOR LOW-DENSITY POLYETHYLENE

C
$(\times 10^4)$

seconds

Equation: $\tau_R = \tilde{\tau}_0 \frac{t}{t_0} \left[A\left(\frac{M}{M}\right) + B\left(\frac{M}{M}\right) e^{-C\left(\frac{M}{M}\right)} \right]$

Material: ALATHON 3, 10 & 17
E. I. DuPont De Nemours

Molecular Weight $(\times 10^{-5})$
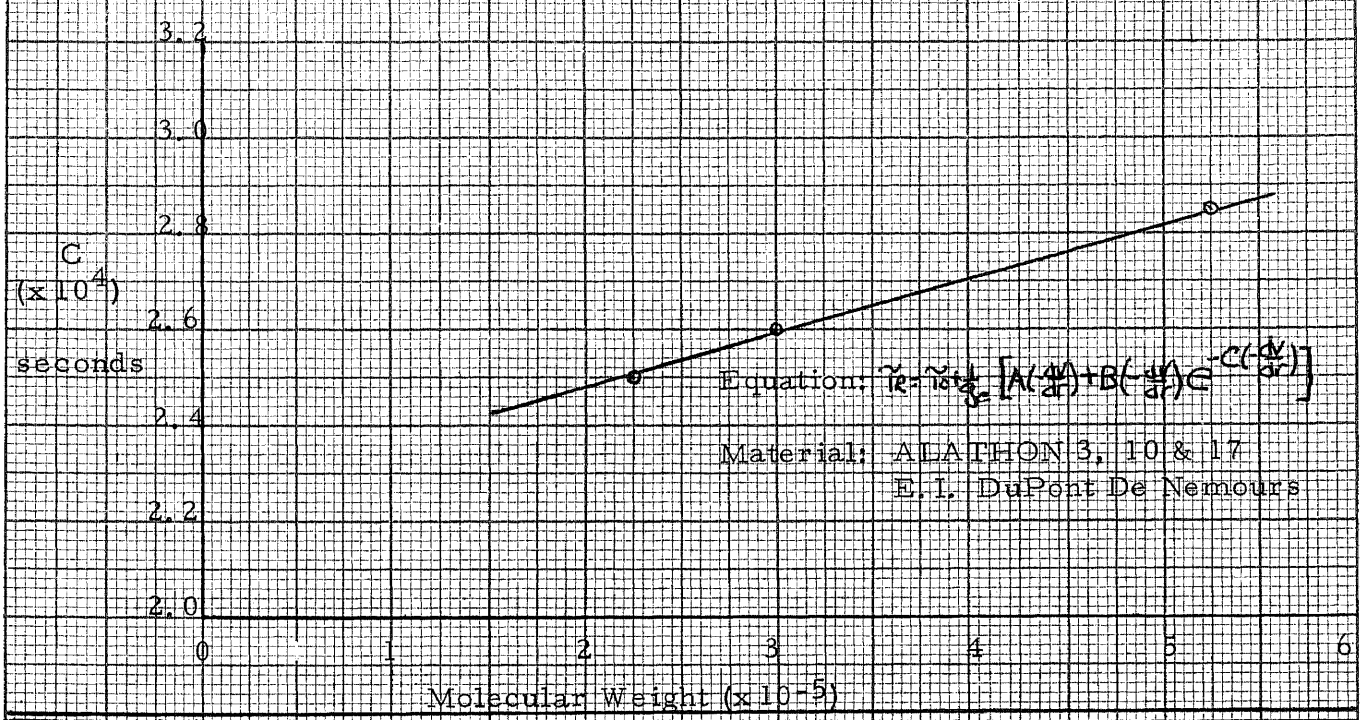
Figure XVII

MOLECULAR WEIGHT DEPENDENCE OF THE
CONSTANT "τ_0" FOR LOW-DENSITY POLYETHYLENE

τ_0

$\frac{LB_F}{INCH^2}$

Molecular Weight $(\times 10^{-5})$
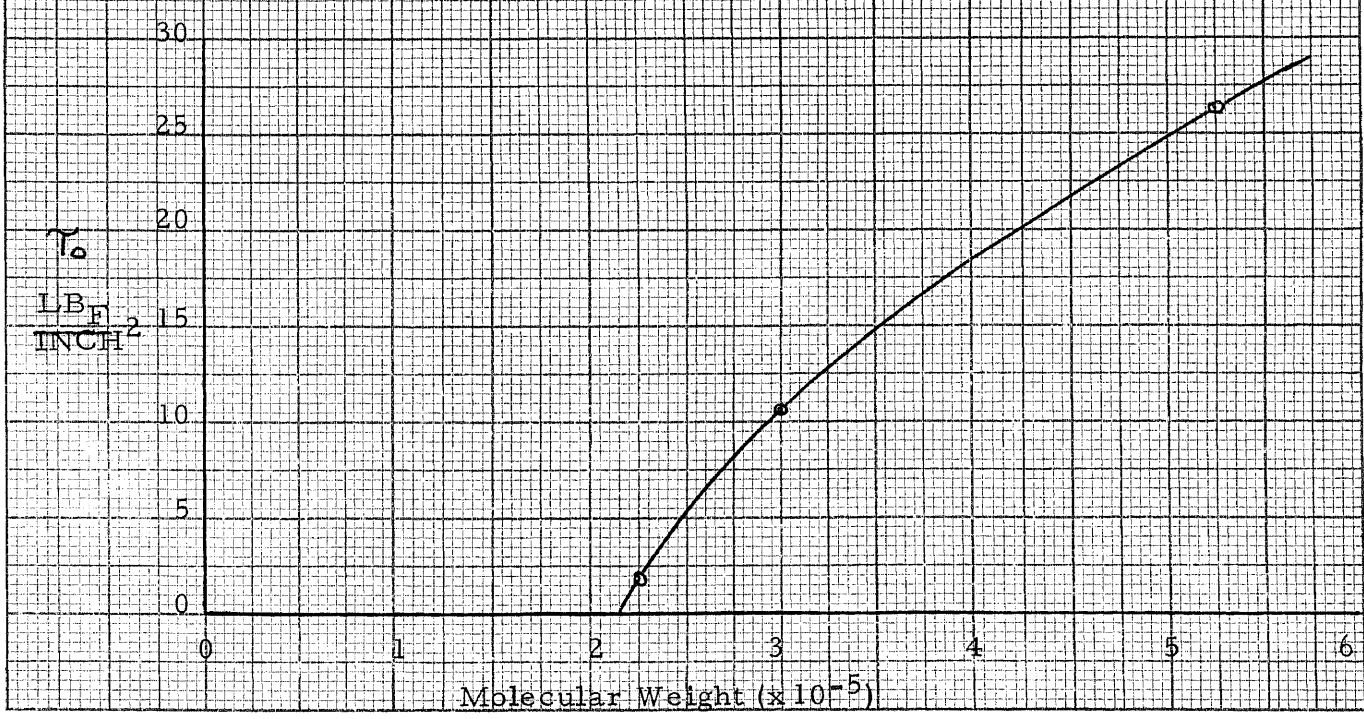
experimental and theoretical data was not as good as that achieved with Tenite 856, this may be explained in part by the much broader shear rate range fit by the constants for the Alathon series: 1 - 1000 seconds $^{-1}$ for the Alathon's compared to 1 - 400 seconds $^{-1}$ for Tenite 856.

Although based essentially on only one material (Alathon), the Huang equation should give a good first approximation of the rheology of all low density polyethylenes. The constants of Figures XIV - XVII should be used for such calculations. The procedure shown may be applied to additional thermoplastic rheological data for other materials. Also, it should be possible to relate the constants of the equation to other inherent thermoplastic properties, such as molecular weight distribution. Additional work in this area is felt to be justified.

APPENDIX A

ORIGINAL DATA (Literature)

Reported by R. F. Westover, "Processing Properties" in
E. C. Bernhardt, ed, Processing of Thermoplastic Materials, N. Y.,
1957, pp. 602 - 606, 610.

Figure XVIII

ORIGINAL DATA - TENITE POLYETHYLENE 856
334°F EXTRUSION TEMPERATURE
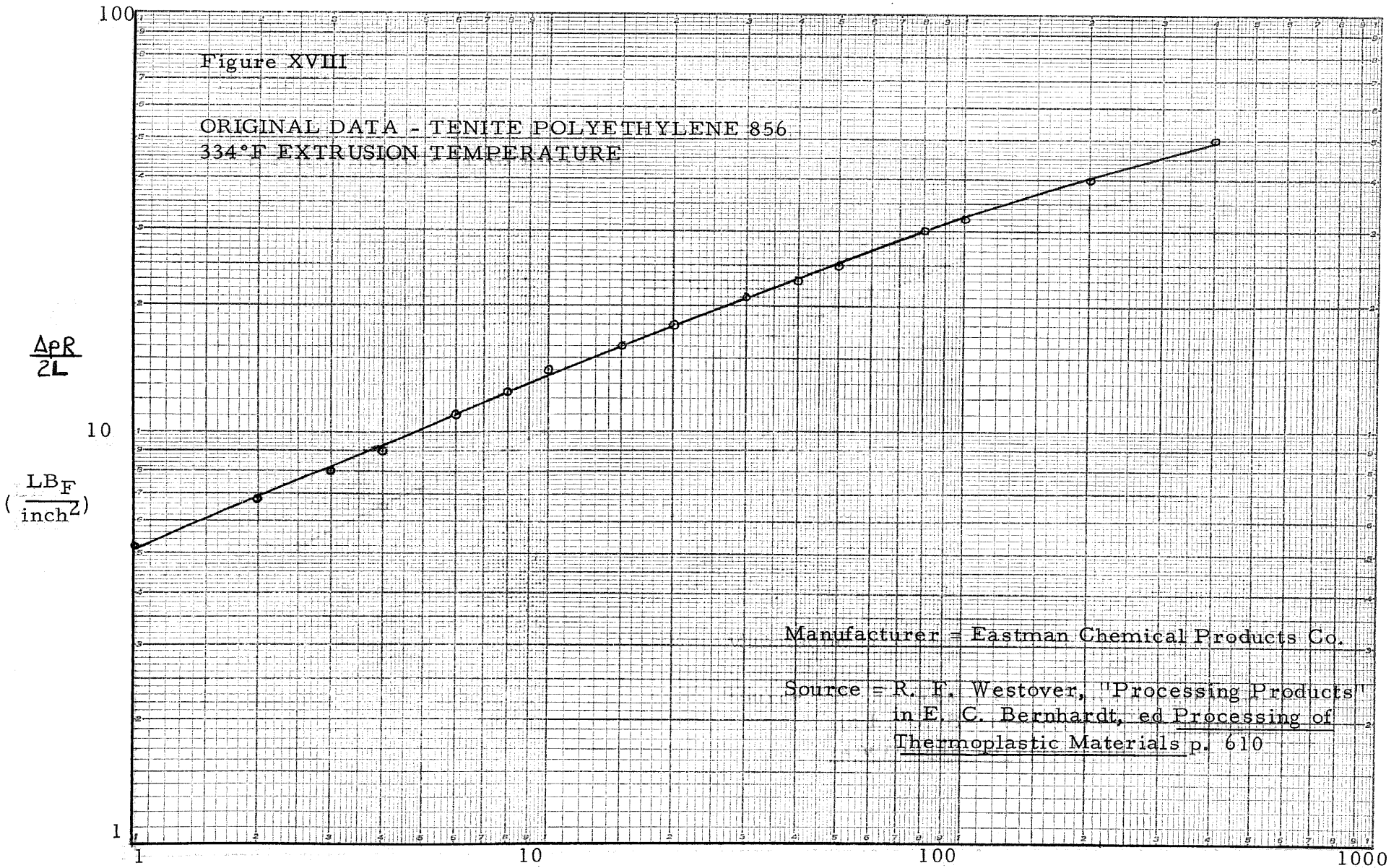
$\frac{\Delta PR}{2L}$

$(\frac{LB_F}{inch^2})$

Manufacturer = Eastman Chemical Products Co.

Source = R. F. Westover, "Processing Products"
in E. C. Bernhardt, ed Processing of
Thermoplastic Materials p. 610

Figure XIX

ORIGINAL DATA - TENITE POLYETHYLENE 856
374°F EXTRUSION TEMPERATURE

$\frac{\Delta_P R}{2L}$

$\frac{LB_F}{inch^2})$

Manufacturer = Eastman Chemical Products Co.

Source = R. F. Westover, "Processing Products"
in E. C. Bernhardt, ed Processing of
Thermoplastic Materials p. 610

$\frac{4Q}{\pi R^3}$ (SECONDS^{-1})
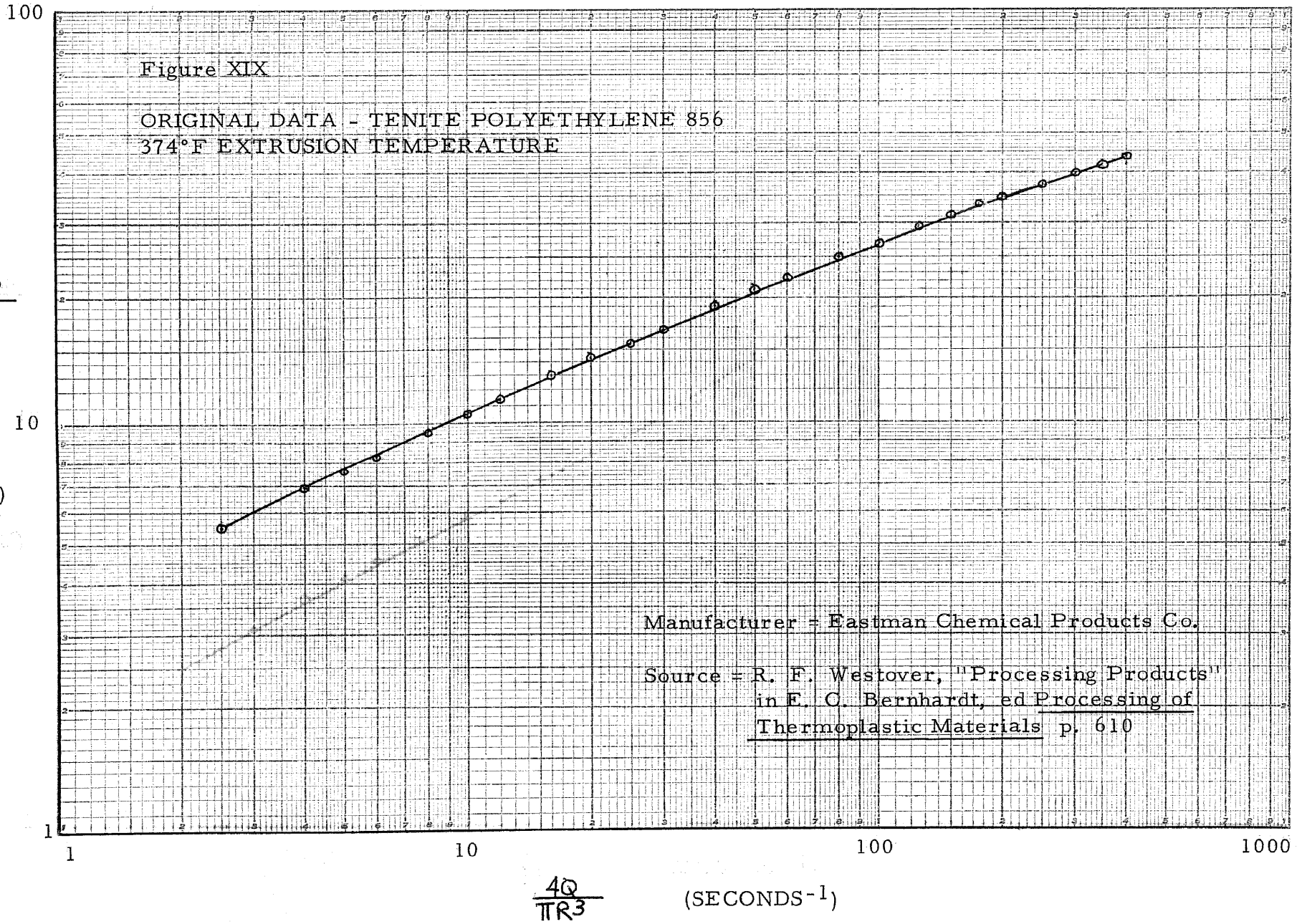
Figure XX

ORIGINAL DATA - TENITE POLYETHYLENE 856
446°F EXTRUSION TEMPERATURE

$\frac{\Delta P R}{2L}$

$\left(\frac{LB_F}{inch^2}\right)$

$\frac{4Q}{\pi R^3}$ (SECONDS $^{-1}$)
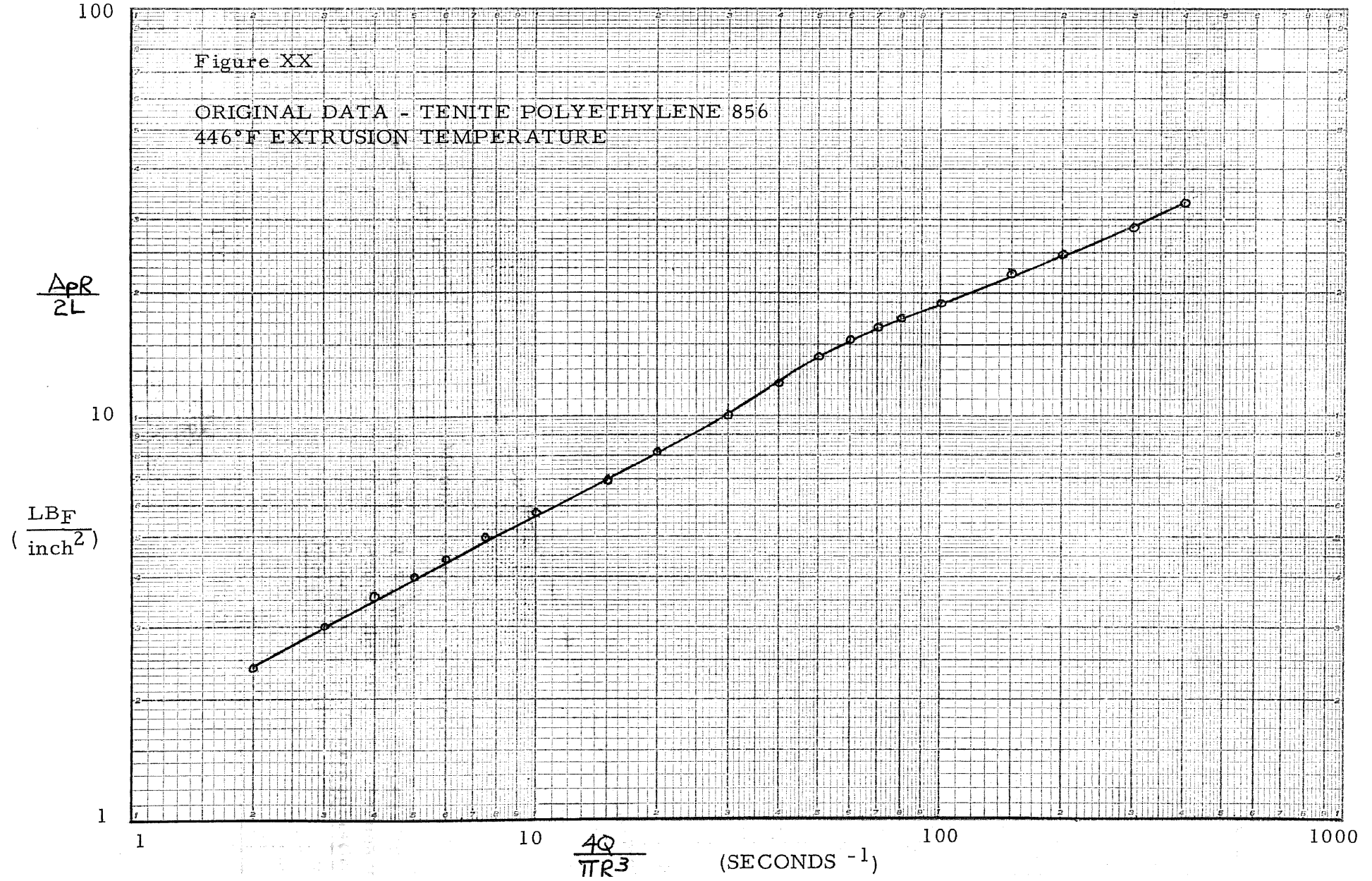
Figure XXI
ORIGINAL DATA - ALATHON 3 POLYETHYLENE
374°F EXTRUSION TEMPERATURE

$\dfrac{\Delta p R}{2L}$

$\left(\dfrac{LB_F}{inch^2}\right)$

Manufacturer: E. I. DuPont de Nemours

Source: R. F. Westover "Processing
Properties in E. C. Bernhardt
Processing of Thermoplastic
Materials p. 600

$\dfrac{4Q}{\pi R^3}$

(SECONDS^{-1})
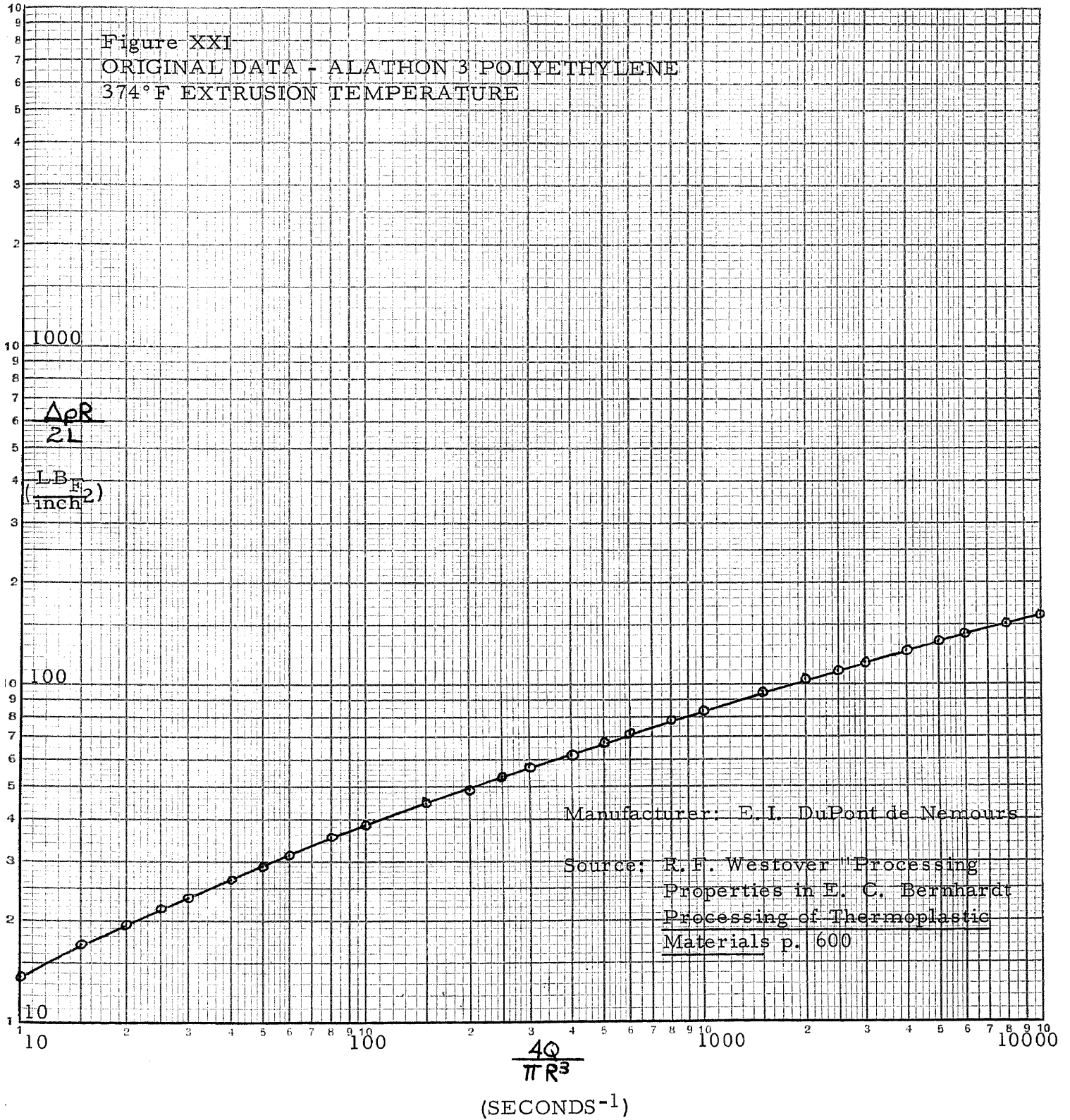
Figure XXII
ORIGINAL DATA – ALATHON-10 POLYETHYLENE
374°F EXTROSION TEMPERATURE

$\dfrac{\Delta \rho R}{2L}$

$(\dfrac{LB_F}{inch^2})$

Manufacturer: E. I. DuPont de Nemours

Source: R. F. Westover "Processing Properties"
in E. C. Bernhardts "Processing of
Thermoplastic Materials p. 602

$\dfrac{4Q}{\pi R^3}$

(SECONDS^{-1})
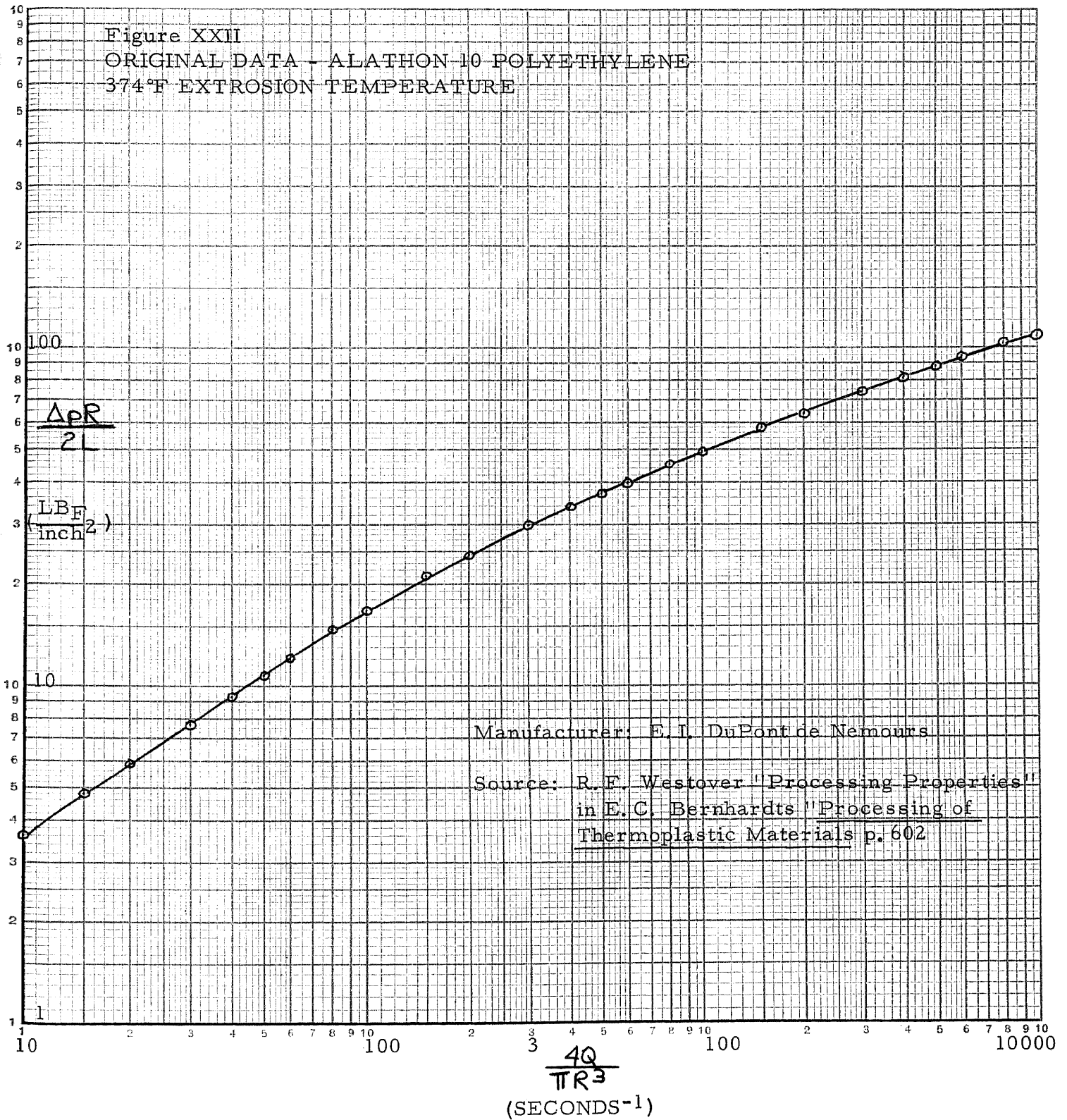
Figure XXIII
ORIGINAL DATA - ALATHON 17 POLYETHYLENE
374° F EXTRUSION TEMPERATURE

$\frac{\Delta p R}{2L}$

$(\frac{LBF}{inch^2})$

Manufacturer: E.I. DuPont de Nemours

Source: R.F. Westover: "Processing
Properties" in E.C. Bernhardt
Processing of Thermoplastic
Materials p. 604

$\frac{4Q}{\pi R^3}$

(SECONDS^{-1})
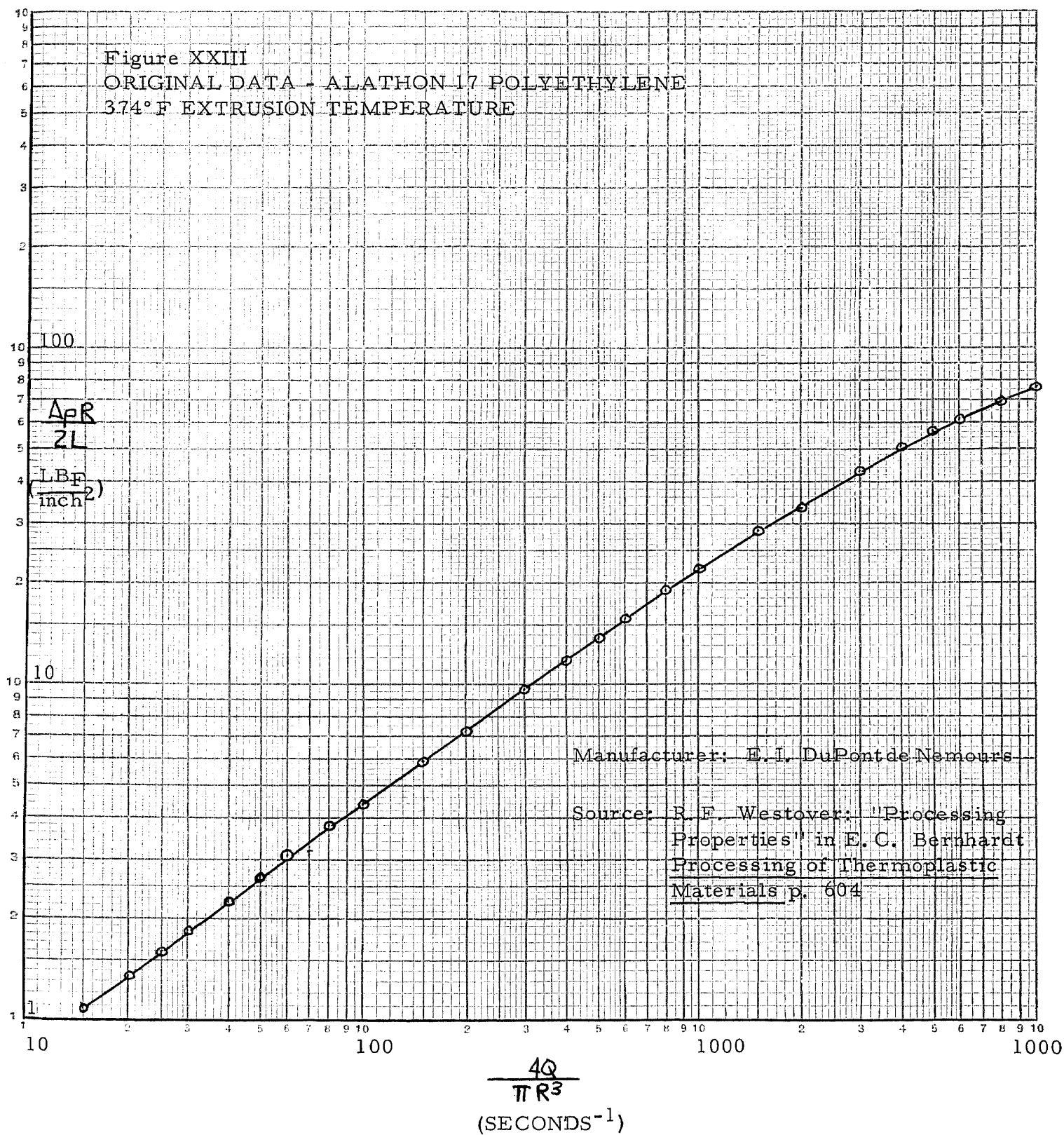
Appendix B
Sample Calculation

Data was taken from Westover's flow curves compiled in Bernhardt's book [18] for Tenite Polyethylene 856 at 374° F. The data originally was presented in the form of a logarithmic plot of $\frac{\Delta p R}{2L}$ versus $\frac{4Q}{\pi R^3}$. These parameters were labeled "maximum shear stress" and "apparent shear rate" respectively. These terms are misleading and will be ignored. The original flow curve for the sample calculation (replotted) is presented in Figure XIX, Appendix A.

In order to better interpolate the data, the original flow curve is replotted in rectangular coordinates. The results are presented in Figure XXIV.

The actual volumetric flow rate, Q, is found by dividing the reported $\frac{4Q}{\pi R^3}$ at each shear stress point by $\frac{4}{\pi R^3}$, where R is the capillary radius, 0.0095 inches. The values of $\frac{\Delta p R}{2L} = \gamma_R$, and the volumetric flow rate Q are tabulated for the sample calculation in Table IV. $\gamma_R Q$ is also found and tabulated in Table IV.

The value of $\frac{d(\gamma_R^3 Q)}{d\gamma_R}$ is determined at each value of γ_R and results presented in Table IV. This is accomplished by a numerical differentiation procedure whereby $\gamma_R^3 Q$ is plotted against γ_R and the slope of the tangent to the curve is evaluated at each shear stress.

18. R. F. Westover, op. cit.

Figure XXIV

UNCORRECTED FLOW CURVE

$\frac{\Delta \rho R}{2L}$

MATERIAL: TENITE POLYETHYLENE 856

SOURCE: BERNHARDT PROCESSING OF THERMO-
PLASTIC MATERIALS

EXTRUSION TEMPERATURE: 374°F

$\frac{4Q}{\pi R^3}$ SECONDS^{-1}

Table IV

SAMPLE CALCULATION
TENITE POLYETHYLENE 856 AT 374°F

$T_R = \dfrac{\Delta_p R}{2L}$ Shear Stress lb_F, Inch^2	$\dfrac{4Q}{\pi R^3}$ Seconds^{-1}	$Q = \dfrac{4Q/\pi R^3}{4/\pi R^3}$ Vol. Flow Rate Inch^3/Sec.	$T_R^3 Q$	$\dfrac{d(T_R^3 Q)}{dT_R}$	$-\dfrac{dv}{dr}\Big|_{r=R}$ Corrected Shear Rate Seconds^{-1}
5.5	2.5	1.68×10^{-6}	2.80×10^{-4}	–	
6.9	4.0	2.69×10^{-6}	8.85	5.70×10^{-4}	4.44
7.6	5.0	3.37×10^{-6}	1.48×10^{-3}	1.02×10^{-3}	6.54
8.3	6.0	4.04×10^{-6}	2.31×10^{-3}	1.65×10^{-3}	8.89
9.5	8.0	5.39×10^{-6}	4.62×10^{-3}	2.51×10^{-3}	10.3
10.4	10.0	6.74×10^{-6}	7.58×10^{-3}	3.87×10^{-3}	13.3
11.4	12.0	8.08×10^{-6}	1.20×10^{-2}	5.24×10^{-3}	15.5
12.3	14.0	9.43×10^{-6}	1.75×10^{-2}	7.31×10^{-3}	17.9
13.0	16.0	1.08×10^{-5}	2.37×10^{-2}	9.74×10^{-3}	21.4
13.7	18.0	1.21×10^{-5}	3.12×10^{-2}	1.21×10^{-2}	23.9
14.3	20.0	1.35×10^{-5}	3.94×10^{-2}	1.53×10^{-2}	27.9
14.8	22.0	1.48×10^{-5}	4.80×10^{-2}	1.89×10^{-2}	32.0
15.6	25.0	1.68×10^{-5}	6.39×10^{-2}	2.09×10^{-2}	31.9
16.2	27.0	1.82×10^{-5}	7.73×10^{-2}	2.58×10^{-2}	36.5
16.9	30.0	2.02×10^{-5}	9.75×10^{-2}	3.02×10^{-2}	39.3
17.4	32.0	2.15×10^{-5}	1.14×10^{-1}	3.52×10^{-2}	43.2
18.1	35.0	2.36×10^{-5}	1.40×10^{-1}	3.90×10^{-2}	44.2
18.6	37.0	2.49×10^{-5}	1.60×10^{-1}	4.62×10^{-2}	49.6
19.2	40.0	2.69×10^{-5}	1.91×10^{-1}	5.08×10^{-2}	51.2
19.7	42.0	2.83×10^{-5}	2.16×10^{-1}	6.17×10^{-2}	59.0
20.1	45.0	3.03×10^{-5}	2.46×10^{-1}	7.06×10^{-2}	64.9
20.5	47.0	3.16×10^{-5}	2.73×10^{-1}	7.30×10^{-2}	64.5
21.0	50.0	3.37×10^{-5}	3.19×10^{-1}	8.54×10^{-2}	71.9
21.8	55.0	3.70×10^{-5}	3.84×10^{-1}	9.89×10^{-2}	77.3
22.5	60.0	4.04×10^{-5}	4.60×10^{-1}	1.16×10^{-1}	85.1
23.2	65.0	4.38×10^{-5}	5.47×10^{-1}	1.28×10^{-1}	88.3
24.0	70.0	4.71×10^{-5}	6.52×10^{-1}	1.47×10^{-1}	94.7
24.6	75.0	5.05×10^{-5}	7.52×10^{-1}	1.82×10^{-1}	111.6
25.1	80.0	5.39×10^{-5}	8.52×10^{-1}	1.92×10^{-1}	113.1

Table IV (Con't.)

SAMPLE CALCULATION
TENITE POLYETHYLENE 856 AT 374°F

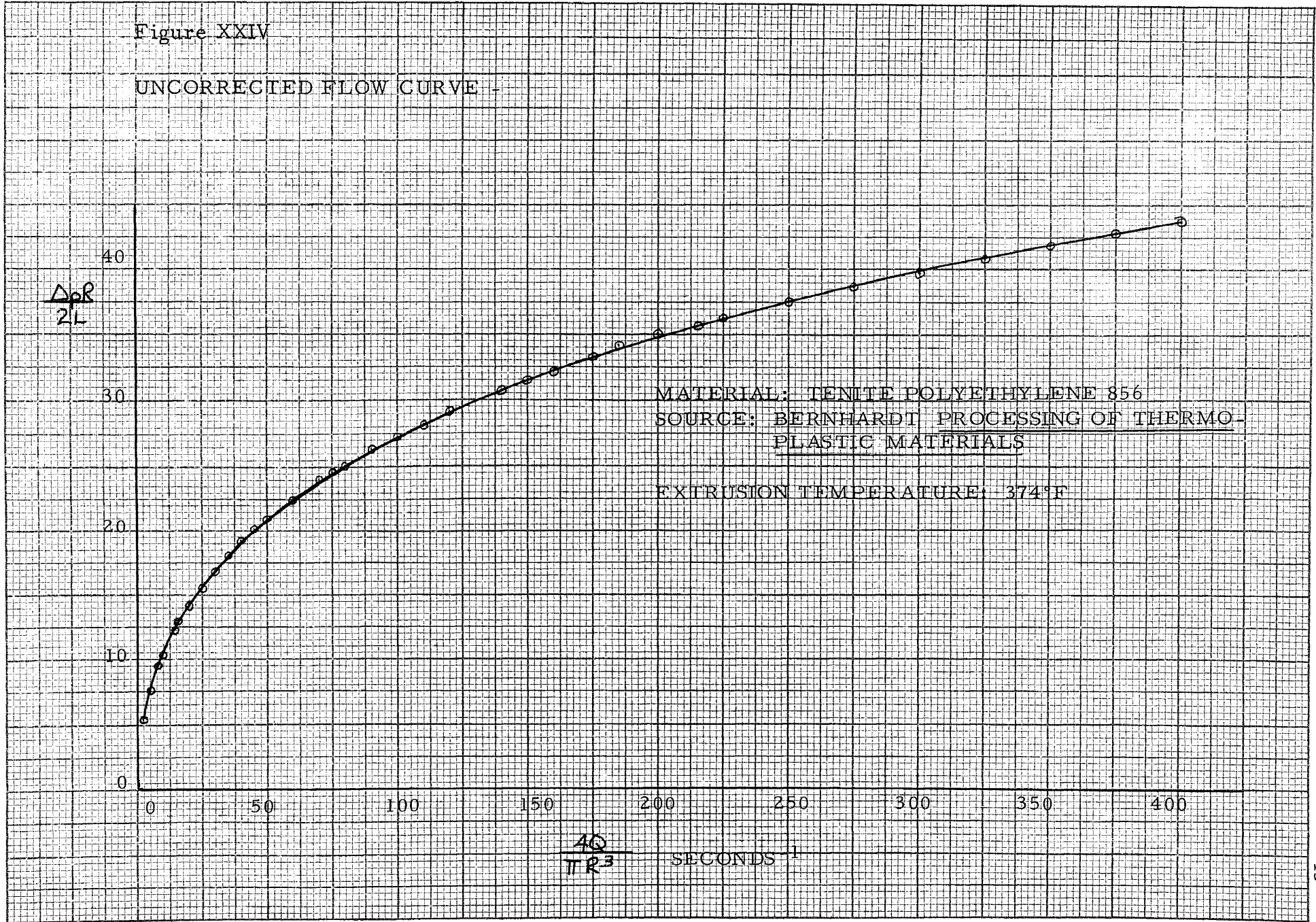| $T_R = \frac{\Delta p R}{2L}$	$\frac{4Q}{\pi R^3}$	$Q = \frac{4Q/\pi R^3}{4/\pi R^3}$	$T_R^3 Q$	$\frac{d(T_R^3 Q)}{dT_R}$	$-\frac{dv}{dr}\Big|_{r=R}$
Shear Stress lbF, Inch^2	Seconds^{-1}	Vol. Flow Rate Inch^3/Sec.			Corrected Shear Rate Seconds^{-1}
25.8	85.0	5.72×10^{-5}	9.83×10^{-1}	2.02×10^{-1}	112.7
26.4	90.0	6.06×10^{-5}	1.11×10^{0}	2.38×10^{-1}	126.8
26.9	95.0	6.40×10^{-5}	1.24×10^{0}	2.83×10^{-1}	145.2
27.3	100.0	6.73×10^{-5}	1.37×10^{0}	3.22×10^{-1}	160.4
27.7	105.0	7.07×10^{-5}	1.50×10^{0}	3.23×10^{-1}	156.3
28.2	110.0	7.41×10^{-5}	1.66×10^{0}	3.28×10^{-1}	153.1
28.7	115.0	7.74×10^{-5}	1.83×10^{0}	3.67×10^{-1}	165.4
29.1	120.0	8.08×10^{-5}	1.99×10^{0}	4.12×10^{-1}	180.6
29.5	125.0	8.42×10^{-5}	2.16×10^{0}	4.36×10^{-1}	186.0
29.9	130.0	8.75×10^{-5}	2.34×10^{0}	4.60×10^{-1}	191.0
30.3	135.0	9.09×10^{-5}	2.53×10^{0}	4.85×10^{-1}	196.1
30.7	140.0	9.43×10^{-5}	2.73×10^{0}	5.10×10^{-1}	200.9
31.1	145.0	9.76×10^{-5}	2.94×10^{0}	5.36×10^{-1}	204.4
31.5	150.0	1.01×10^{-4}	3.16×10^{0}	5.98×10^{-1}	228.7
31.8	155.0	1.04×10^{-4}	3.35×10^{0}	6.28×10^{-1}	230.5
32.2	160.0	1.08×10^{-4}	3.60×10^{0}	6.54×10^{-1}	234.2
32.5	165.0	1.11×10^{-4}	3.81×10^{0}	6.86×10^{-1}	241.1
32.9	170.0	1.14×10^{-4}	4.08×10^{0}	6.73×10^{-1}	230.8
33.3	175.0	1.18×10^{-4}	4.35×10^{0}	7.44×10^{-1}	249.0
33.6	180.0	1.21×10^{-4}	4.60×10^{0}	8.35×10^{-1}	274.6
33.9	185.0	1.25×10^{-4}	4.85×10^{0}	8.67×10^{-1}	280.1
34.2	190.0	1.28×10^{-4}	5.12×10^{0}	8.98×10^{-1}	285.6
34.5	195.0	1.31×10^{-4}	5.39×10^{0}	9.30×10^{-1}	296.1
34.8	200.0	1.35×10^{-4}	5.67×10^{0}	9.63×10^{-1}	295.2
35.1	205.0	1.38×10^{-4}	5.97×10^{0}	9.95×10^{-1}	299.8
35.4	210.0	1.41×10^{-4}	6.27×10^{0}	1.03×10^{0}	304.6
35.7	215.0	1.45×10^{-4}	6.59×10^{0}	1.06×10^{0}	310.2
36.0	220.0	1.48×10^{-4}	6.91×10^{0}	1.10×10^{0}	315.1
36.3	225.0	1.52×10^{-4}	7.25×10^{0}	1.24×10^{0}	349.4
36.5	230.0	1.55×10^{-4}	7.53×10^{0}	1.28×10^{0}	356.7
36.8	235.0	1.58×10^{-4}	7.89×10^{0}	1.20×10^{0}	329.0

Table IV(Con't.)

SAMPLE CALCULATION
TENITE POLYETHYLENE 856 AT 374°F

$\tilde{\tau}_R = \frac{\Delta p R}{2L}$	$\frac{4Q}{\pi R^3}$	$Q = \frac{4Q/\pi R^3}{4/\pi R^3}$	$\tilde{\tau}_R^3 Q$	$\frac{d(\tilde{\tau}_R^3 Q)}{d\tilde{\tau}_R}$	$\frac{dv}{dr}\big|_{r=R}$
Shear Stress b_F, Inch^2	Seconds^{-1}	Vol. Flow Rate Inch^3/Sec.			Corrected Shear Rate Seconds^{-1}
37. 1	240. 0	1.62×10^{-4}	8.25×10^{0}	1.35×10^{0}	364. 1
37. 3	245. 0	1.65×10^{-4}	8.56×10^{0}	1.39×10^{0}	370. 9
37. 6	250. 0	1.68×10^{-4}	8.95×10^{0}	1.42×10^{0}	372. 9
37. 8	255. 0	1.72×10^{-4}	9.27×10^{0}	1.64×10^{0}	426. 1
38. 0	260. 0	1.75×10^{-4}	9.61×10^{0}	1.68×10^{0}	431. 9
38. 2	265. 0	1.78×10^{-4}	9.95×10^{0}	1.53×10^{0}	389. 3
38. 5	270. 0	1.82×10^{-4}	1.04×10^{1}	1.57×10^{0}	393. 2
38. 7	275. 0	1.85×10^{-4}	1.07×10^{1}	1.82×10^{0}	451. 1
38. 9	280. 0	1.89×10^{-4}	1.11×10^{1}	1.85×10^{0}	453. 9
39. 1	285. 0	1.92×10^{-4}	1.15×10^{1}	1.88×10^{0}	456. 5
39. 3	290. 0	1.95×10^{-4}	1.18×10^{1}	1.74×10^{0}	418. 2
39. 6	295. 0	1.99×10^{-4}	1.23×10^{1}	1.78×10^{0}	421. 4
39. 8	300. 0	2.02×10^{-4}	1.27×10^{1}	2.00×10^{0}	468. 7
40. 0	305. 0	2.05×10^{-4}	1.31×10^{1}	2.05×10^{0}	475. 7
40. 2	310. 0	2.09×10^{-4}	1.36×10^{1}	2.13×10^{0}	489. 3
40. 4	315. 0	2.12×10^{-4}	1.40×10^{1}	1.94×10^{0}	441. 3
40. 7	320. 0	2.15×10^{-4}	1.45×10^{1}	1.96×10^{0}	439. 3
40. 9	325. 0	2.19×10^{-4}	1.50×10^{1}	2.25×10^{0}	499. 3
41. 1	330. 0	2.22×10^{-4}	1.54×10^{1}	2.30×10^{0}	505. 5
41. 3	335. 0	2.25×10^{-4}	1.59×10^{1}	2.33×10^{0}	507. 2
41. 5	340. 0	2.29×10^{-4}	1.64×10^{1}	2.40×10^{0}	517. 4
41. 7	345. 0	3.32×10^{-4}	1.69×10^{1}	2.45×10^{0}	523. 1
41. 9	350. 0	2.36×10^{-4}	1.73×10^{1}	2.86×10^{0}	604. 8
42. 0	355. 0	2.39×10^{-4}	1.77×10^{1}	2.93×10^{0}	616. 6
42. 2	360. 0	2.42×10^{-4}	1.82×10^{1}	2.55×10^{0}	531. 6
42. 4	365. 0	2.46×10^{-4}	1.87×10^{1}	2.60×10^{0}	536. 9
42. 6	370. 0	2.49×10^{-4}	1.93×10^{1}	2.67×10^{0}	546. 2
42. 8	375. 0	2.52×10^{-4}	1.98×10^{1}	2.70×10^{0}	547. 2
43. 0	380. 0	2.56×10^{-4}	2.03×10^{1}	3.75×10^{0}	552. 2
43. 2	385. 0	2.59×10^{-4}	2.09×10^{1}	3.26×10^{0}	648. 3
43. 3	390. 0	2.62×10^{-4}	2.13×10^{1}	3.30×10^{0}	653. 4
43. 5	395. 0	2.66×10^{-4}	2.20×10^{1}	2.90×10^{0}	568. 9
43. 7	400. 0	2.69×10^{-4}	2.25×10^{1}	-	

Although the numerical calculations were aided greatly by the use of

a Wang electronic calculator, the numerical differentiation procedure

could not be simplified and was found to be very time consuming. Ap-

proximately thirteen graphs and ninety data points are necessary for

each flow curve evaluated. Figure XXV, is an example of such a graph

used in the sample calculation.

Once the above calculations are completed the correct shear

rates are obtained at each shear stress value. This is achieved by

use of the Rabinowitsch correction, equation XI in this thesis. The

corrected shear rate is obtained by multiplying $\dfrac{d(\tau_R^3 Q)}{d\gamma_R} \times \dfrac{1}{\pi R^3 \tau_R^2}$,

obtaining $-\dfrac{dv}{dr}$. A tabulation of shear stress and corrected shear rate

for the sample calculation is presented in Table IV.

Shear stress and corrected shear rate are now plotted in the

form of a flow curve, as in Figure XXVI. A comparison of the original

data with the corrected data is also shown in Figure XXVI. Such a

comparison points out the fact that the shear rates reported in the original

data are, in some cases, in error by more than forty per cent. Thus, the

use of $\dfrac{4Q}{\pi R^3}$ as the shear rate is completely unjustified. Unfortunately,

this is a standard practice in industry.

Once the corrected shear stress - shear rate data are

determined, the procedure is to find the values of the Huang equation

such that the data can be generated by use of the equation. A trial

and error procedure for evaluation of the four constants in a
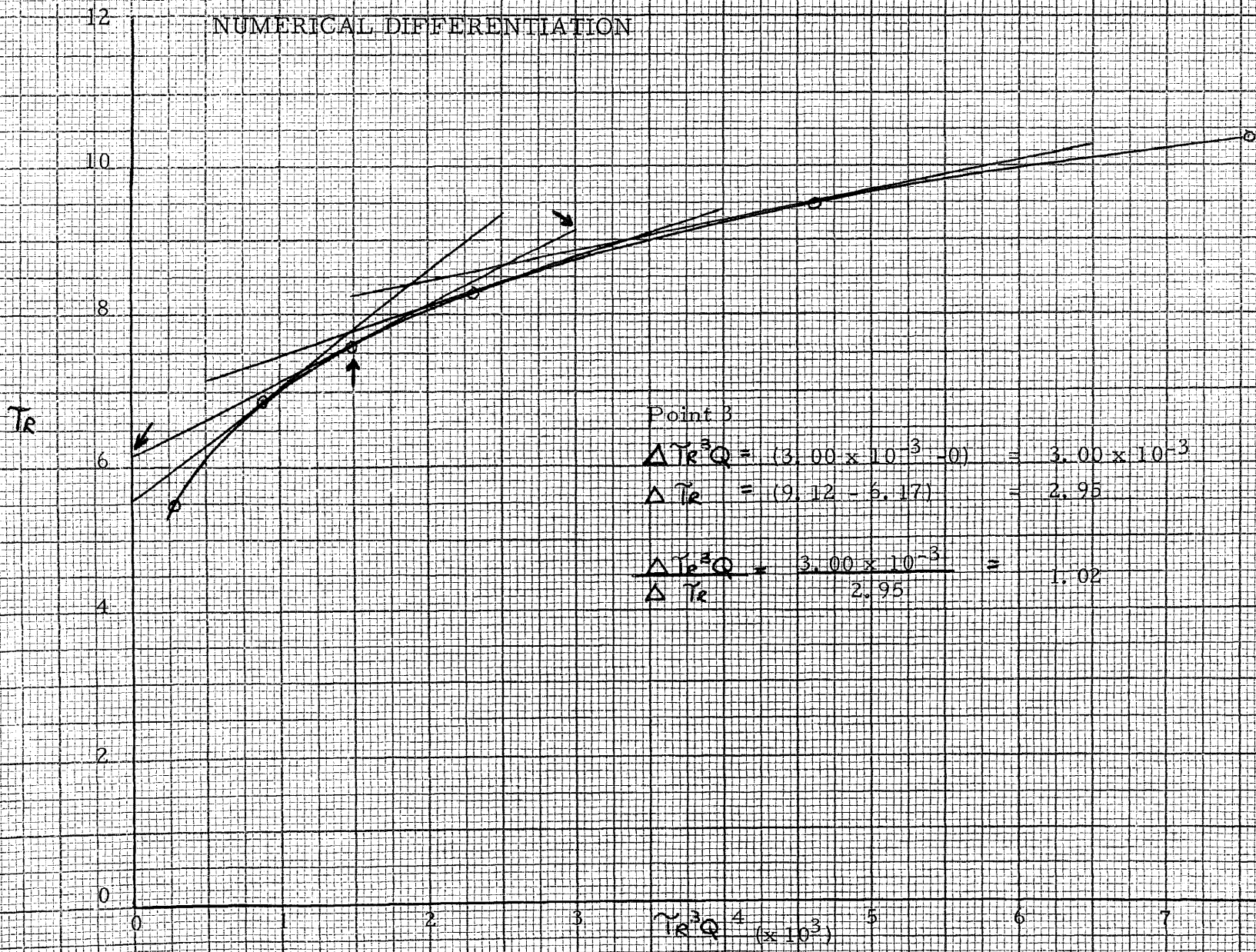
Figure XXV

NUMERICAL DIFFERENTIATION

Point 3

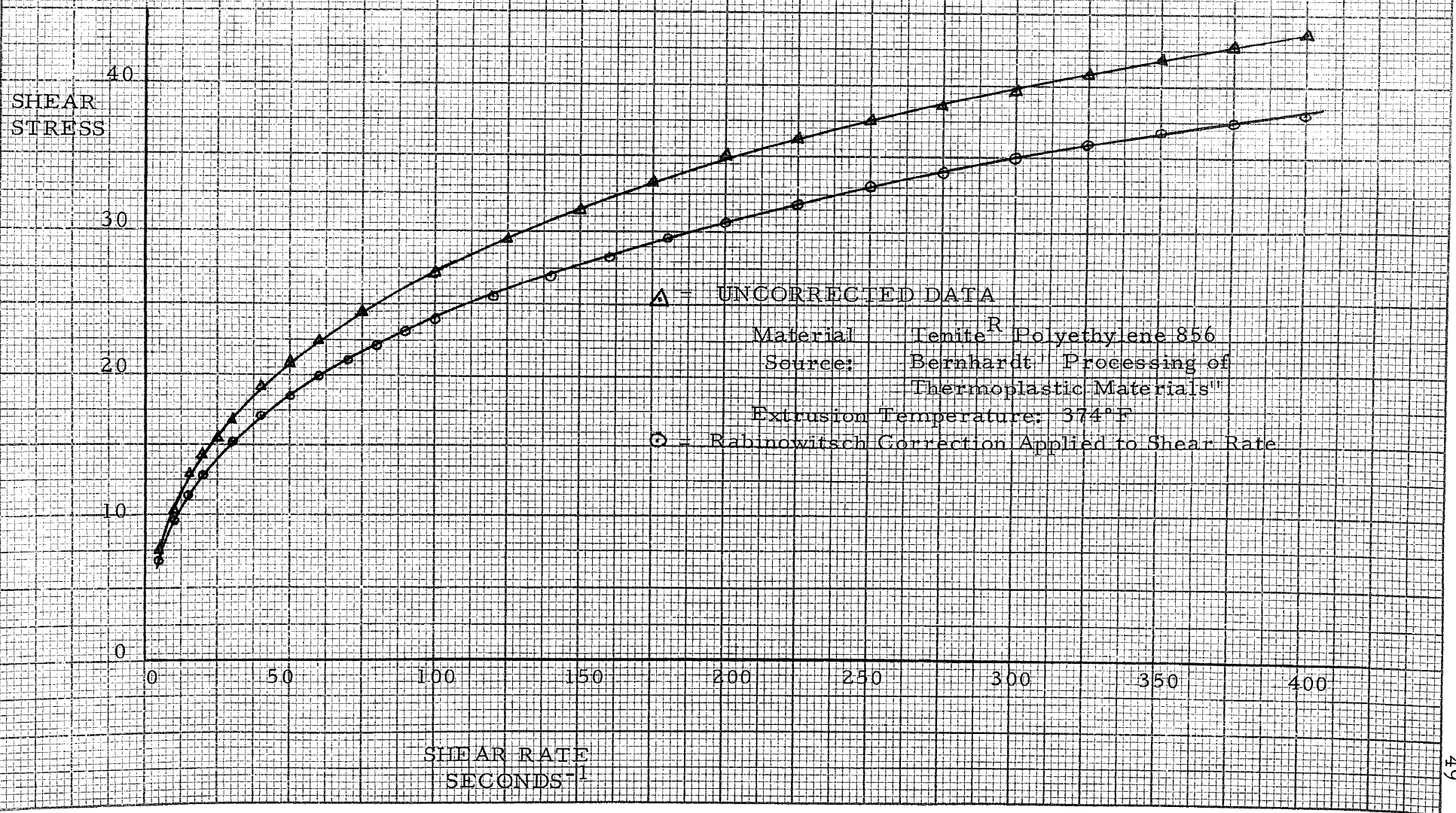$\Delta \tilde{T}_R{}^3 Q = (3.00 \times 10^{-3} - 0) = 3.00 \times 10^{-3}$

$\Delta \tilde{T}_R = (9.12 - 6.17) = 2.95$

$\dfrac{\Delta \tilde{T}_R{}^3 Q}{\Delta \tilde{T}_R} = \dfrac{3.00 \times 10^{-3}}{2.95} = 1.02$

$\tilde{T}_R{}^3 Q \quad (\times 10^3)$

T_R

Figure XXVI

EFFECT OF RABINOWITSCH CORRECTION TO UNCORRECTED FLOW CURVE

△ = UNCORRECTED DATA

Material: Tenite[R] Polyethylene 856
Source: Bernhardt "Processing of Thermoplastic Materials"
Extrusion Temperature: 374°F
⊙ = Rabinowitsch Correction Applied to Shear Rate

SHEAR STRESS

SHEAR RATE SECONDS⁻¹

non-linear equation is a difficult, if not impossible task to accomplish

by hand. However, this computation was made possible by the use of

an IBM 1130 computer.

The computer program utilized is a modified standard IBM

program for the evaluation of the best fit of the constants by non-

linear least squares. The program is coded in Fortran IV.

In principle, the program minimizes the sum of the squares

of the differences between the experimental and the computer calculated

values by a combination of statistical methods. The necessary input

to the program consists of: the equation to be fit (the Huang equation,

equation VI); the data, shear stress τ_R and corrected shear rate $\frac{-dv}{dr}$

in this case; initial guesses of the values of the constants of the

equation as determined by the procedure outlined below; and the size

of each iteration.

Initial estimates of the constants of the Huang equation may

be determined through a plot of $\frac{\tau_R}{-dv/dr}$ against $\frac{-dv}{dr}$. Figure XXVII is

such a plot, with data of the sample calculation. At very high values

of $\frac{-dv}{dr}$, $e^{-c\left(-\frac{dv}{dr}\right)}$ is very small, and $\frac{\tau_R}{-dv/dr}$ reduces to the constant A

of the Huang equation. At very low values of the corrected shear

rate $e^{-c\left(-dv/dr\right)}$ is essentially equal to unity, and $\frac{\tau_R}{-dv/dr}$ is approxi-

mately equal to the constants A plus B. For the sample calculation

the estimated value of A as determined from Figure XXVII closely

approximates the final correct value.

Figure XXVII

INITIAL ESTIMATES OF CONSTANTS

$A \approx 0.7$

$\dfrac{\tau_R}{\left(-\dfrac{dV}{dr}\right)}$

$\left(-\dfrac{dV}{dr}\right)$
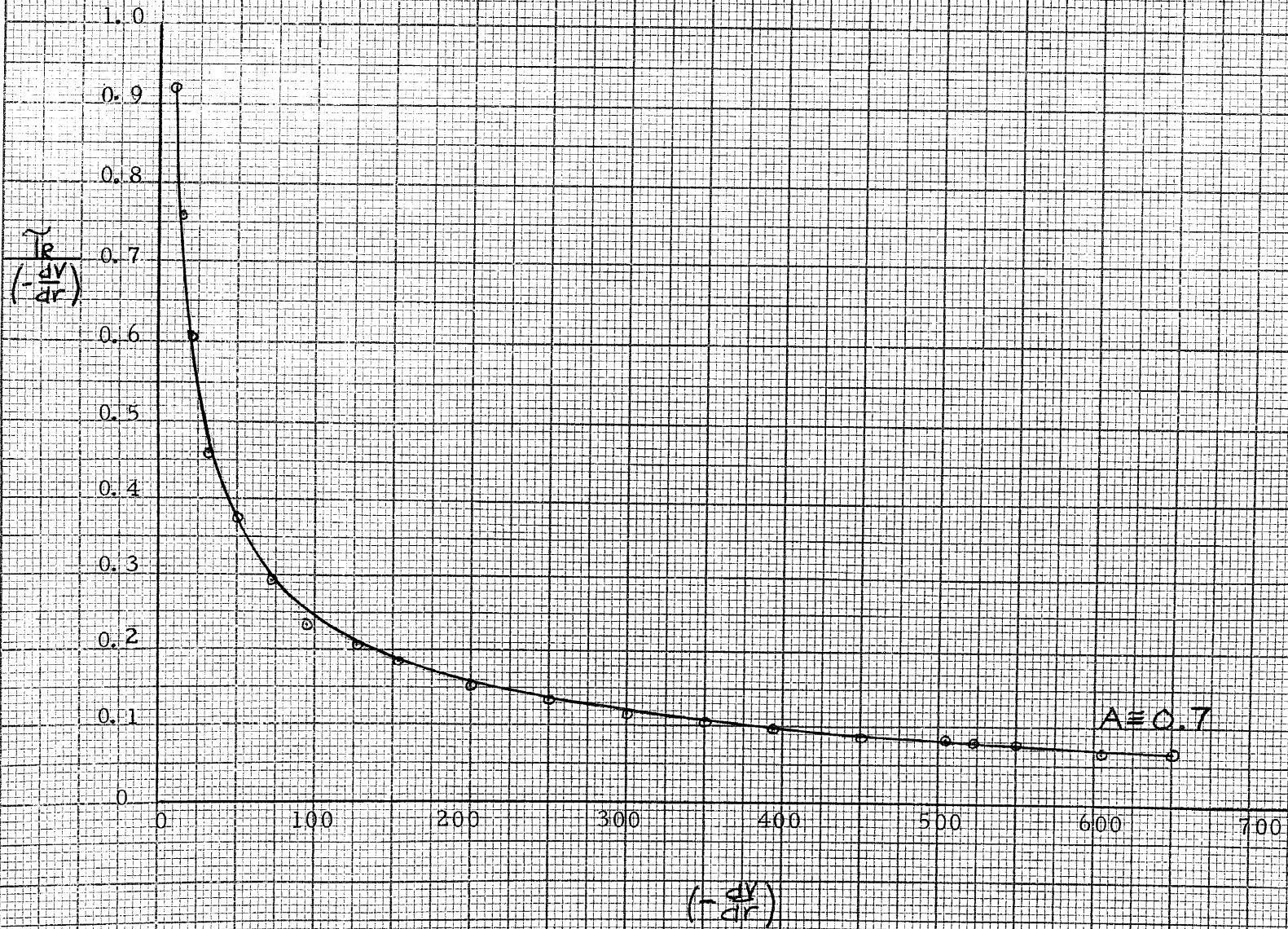
The constants of the Huang equation are determined, as shown for the sample calculation, for Eastman Chemical Products Tenite Polyethylene 856 at temperatures of 334°F, 374°F, and 446°F, and for Alathon 3, 10 and 17 (DuPont) at 374°F. The constants A and B of the equation, obtained from the computer analysis, must be corrected for the gravitational constant g_c before they can be used in the Huang equation. The corrected values of the constants are presented in Tables I and II in this thesis.

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