New Jersey Institute of Technology
Digital Commons @ NJIT

Theses | Electronic Theses and Dissertations

Spring 5-31-1970

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

Jeffrey N. Goldstein
New Jersey Institute of Technology

Follow this and additional works at: https://digitalcommons.njit.edu/theses

 Part of the Chemical Engineering Commons

Recommended Citation

Goldstein, Jeffrey N., "The application of a non-Newtonian rheological equation to low-density polyethylene" (1970). *Theses*. 1497.
https://digitalcommons.njit.edu/theses/1497

This Thesis is brought to you for free and open access by the Electronic Theses and Dissertations at Digital Commons @ NJIT. It has been accepted for inclusion in Theses by an authorized administrator of Digital Commons @ NJIT. For more information, please contact digitalcommons@njit.edu.

Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a, user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #" on the print dialog screen

NJIT New Jersey's Science & Technology University

The Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

THE APPLICATION OF A NON-NEWTONIAN RHEOLOGICAL EQUATION TO LOW-DENSITY POLYETHYLENE

BY

JEFFREY N. GOLDSTEIN

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

AT

NEWARK COLLEGE OF ENGINEERING

This thesis is to be used only with due regard to the rights of the author. Bibliographical references may be noted, but passages must not be copied without permission of the College and without credit being given in subsequent written or published work.

Newark, New Jersey
1970

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

THE APPLICATION OF A

NON-NEWTONIAN RHEOLOGICAL EQUATION

TO LOW-DENSITY POLYETHYLENE

BY

JEFFREY N. GOLDSTEIN

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

_____

_____

Newark, New Jersey

June, 1970

ACKNOWLEDGEMENT

The author wished to gratefully acknowledge the invaluable guidance of Dr. C. R. Huang. The generosity of the Cities Service Oil Company is also greatly appreciated.

TABLE OF CONTENTS

	Page
Abstract	i
Approval of Thesis	ii
Acknowledgement	iii
List of Figures	v
List of Tables	vi
Nomenclature	vii
I. Introduction	
A. Purpose	1
B. Theoretical Background	2
II. Presentation of the Equation	9
III. Experimentation	
A. Experimental Background	11
B. Experimental Data (Literature)	13
C. Correction of Experimental Data	14
IV. Results and Discussion of Results	
A. Verification of the Equation	17
B. Constants of the Equation	17
C. Temperature Dependence	21
D. Molecular Weight Dependence	29
Appendix A - Original Data (Literature)	35
Appendix B - Sample Calculation	42
Bibliography	53

LIST OF FIGURES

		Page
Figure I	Flow Behavior of Molten Thermoplastics.....	4
Figure II	Typical Thermoplastic Flow Curve.....	6
Figures III-V	Prediction of Experimental Data by Huang Equation	
III	334°F Extrusion Temperature.....	18
IV	374°F Extrusion Temperature.....	19
V	446°F Extrusion Temperature.....	20
Figures VI-IX	Temperature Dependence of the Constants for Tenite Polyethylene 856	
VI	Constant "A".....	24
VII	Constant "B".....	24
VIII	Constant "C".....	25
IX	Constant "T_o".....	25
Figures X-XIII	Temperature Dependence of the Constants For Tenite Polyethylene 856-Arrhenius Plot	
X	Constant "A".....	27
XI	Constant "B".....	27
XII	Constant "C".....	28
XIII	Constant "T_o".....	28
Figures XIV-XVII	Molecular Weight Dependence of the Constants For Low-Density Polyethylene	
XIV	Constant "A".....	32
XV	Constant "B".....	32
XVI	Constant "C".....	33
XVII	Constant "T_o".....	33
Figures XVIII-XXIII	Appendix A - Original Data (Literature)	
XVIII	Tenite Polyethylene 856 - 334°F.....	36
XIX	Tenite Polyethylene 856 - 374°F.....	37
XX	Tenite Polyethylene 856 - 446°F.....	38
XXI	Alathon 3 Polyethylene - 374°F.....	39
XXII	Alathon 10 Polyethylene - 374°F.....	40
XXIII	Alathon 17 Polyethylene - 374°F.....	41
Figures XXIV-XXVII	Appendix B - Sample Calculation	
XXIV	Uncorrected Flow Curve.....	43
XXV	Numerical Differentiation.....	48
XXVI	Effect of Rabinowitsch Correction to Uncorrected Flow Curve.....	49
XXVII	Initial Estimates of Constants.....	51

LIST OF TABLES

		Page
TABLE I	Constants of the Equation for Tenite Polyethylene 856.....	22
TABLE II	Constants of the Equation for Alathon 3, Alathon 10, Alathon 17, at 374°F Extrusion Temperature.....	23
TABLE III	Temperature Dependency of the Constants of the Equation for Tenite Polyethylene 856.....	30
TABLE IV	Sample Calculation - Tenite Polyethylene 856 at 374°F.....	44

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)	
$\mathcal{B}^{ij}$	Molecular Arrangement Parameter Tensor At Equilibrium Conditions	
$\dot{\gamma}$	Rate of Shear Tensor	
Δ_P	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	
$\mathcal{Y}$	Constant = Equation VI-A (Huang)	

1. INTRODUCTION

A. Purpose

For the last several years the flow behavior of molten thermoplastics (rheology) has been the object of extensive research. Considerable 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 empirically 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 properties at new or extrapolated conditions, including different temperatures. 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 behavior is quite practical. Thermoplastics are commonly utilized industrially 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. Successive layers of fluid will be sheared with resultant decreases in velocity 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, τ. 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 cylindrical 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.

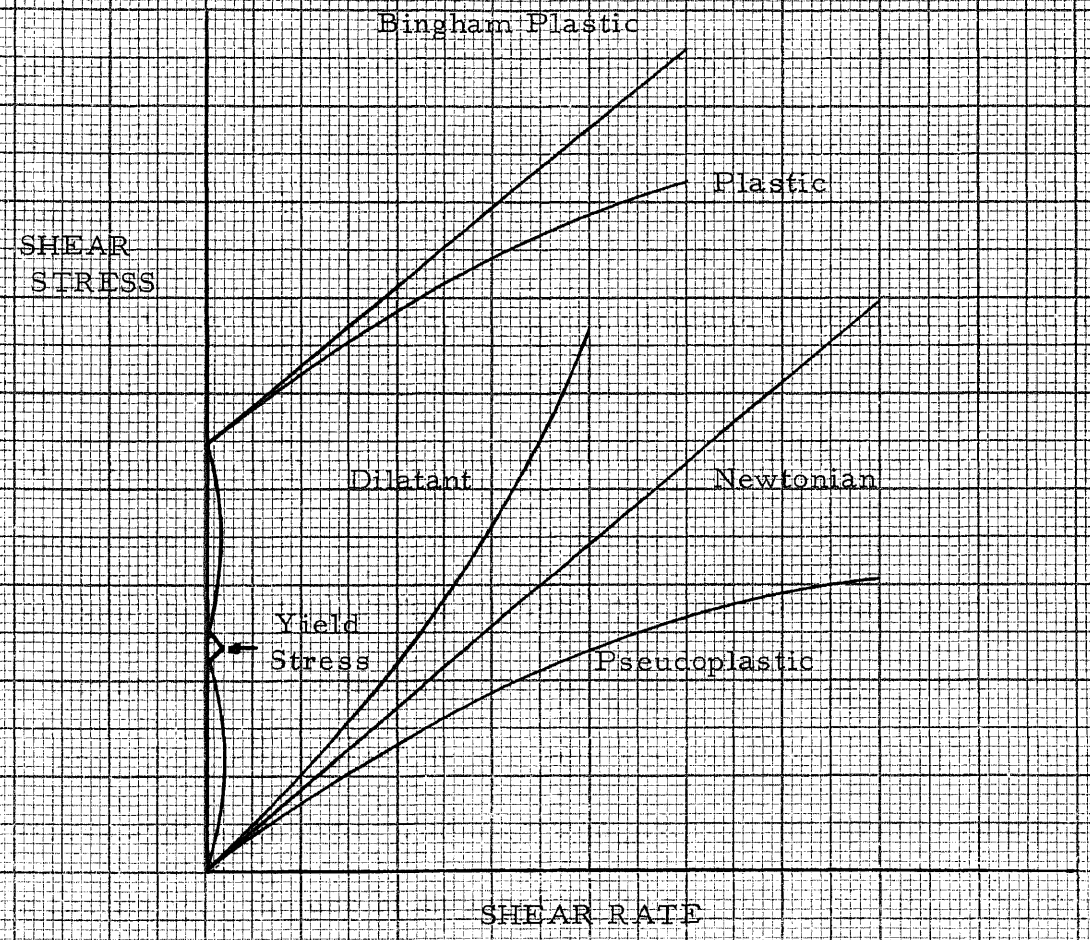
A fluid that obeys equation I is termed a Newtonian fluid. Few materials and essentially no thermoplastics obey this equation; hence, molten thermoplastics are known as non-Newtonian fluids.

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



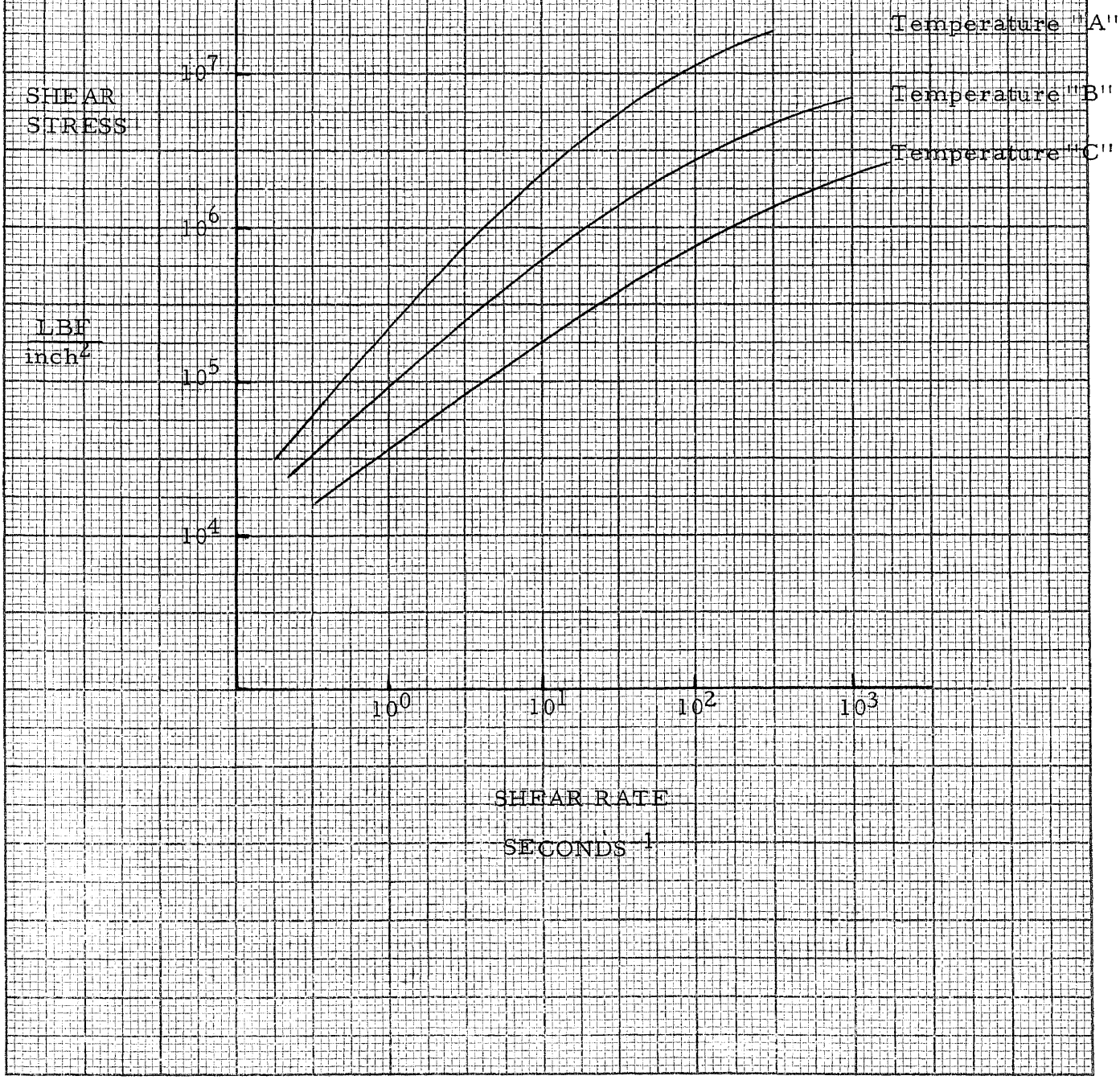
shear stress is directly proportional to the shear rate, as in Newtonian flow. Pseudoplastic behavior is marked by a disproportionate gain in shear rate for each increment of shear stress. This type of behavior is common among thermoplastics. Plastic and pseudoplastic behavior are equivalent, except 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 analytical 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:

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

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 thermoplastic material. However, K and n have been found to vary considerably 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 literature is the Eyring-Powell equation.[3]

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

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:

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

and the Reiner-Philippoff model:[5]

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

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 developed 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]

$$\text{VI} \quad \tau = \tau_0 + \left[A\left(-\frac{dv}{dr}\right) + B\left(-\frac{dv}{dr}\right) e^{-C\left(-\frac{dv}{dr}\right)}\right]\left[\frac{1}{g_c}\right]$$

where τ_0, A, B, C are temperature dependent constants empirically determined 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.

VI-A $$\tau^{ij} - \frac{\tau_o}{\sqrt{\frac{1}{2}\tau^{ij}\tau_{ij}}}\tau^{ij} = \left(\mu - c_3 J \beta^{ij} e^{-c_3 \delta^{ij} \ln q t_o \frac{|\dot{\gamma}^{ij}|}{\dot{\gamma}^{ij}}}\right)\dot{\gamma}^{ij}$$

μ, c_3, J, t_o = 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 τ and $C=0$ equation VI reduces to the Newtonian equation I. Additionally A and B may be considered viscosity terms, and τ_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 $\frac{\Delta p R}{2L}$ 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 MATERIALS.[9] Severs has called this collection of flow curves the greatest ever compiled.[10] All data were obtained in capillary rheometers by the manufacturer of the thermoplastics.

Low density polyethylene is the thermoplastic chosen for experimental 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 calculation 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]

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

where R equals capillary radius and L equals capillary length. Rearranging and, in the limit, letting $dP = \Delta P$ and $dL = L$, we obtain

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

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 $\frac{\Delta PR}{2L}$ and $\frac{dV}{dr}$ as $\frac{4Q}{\pi R^3}$, and plot $\frac{\Delta PR}{2L}$ 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 $\frac{\Delta PR}{2L}$ 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 correction 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

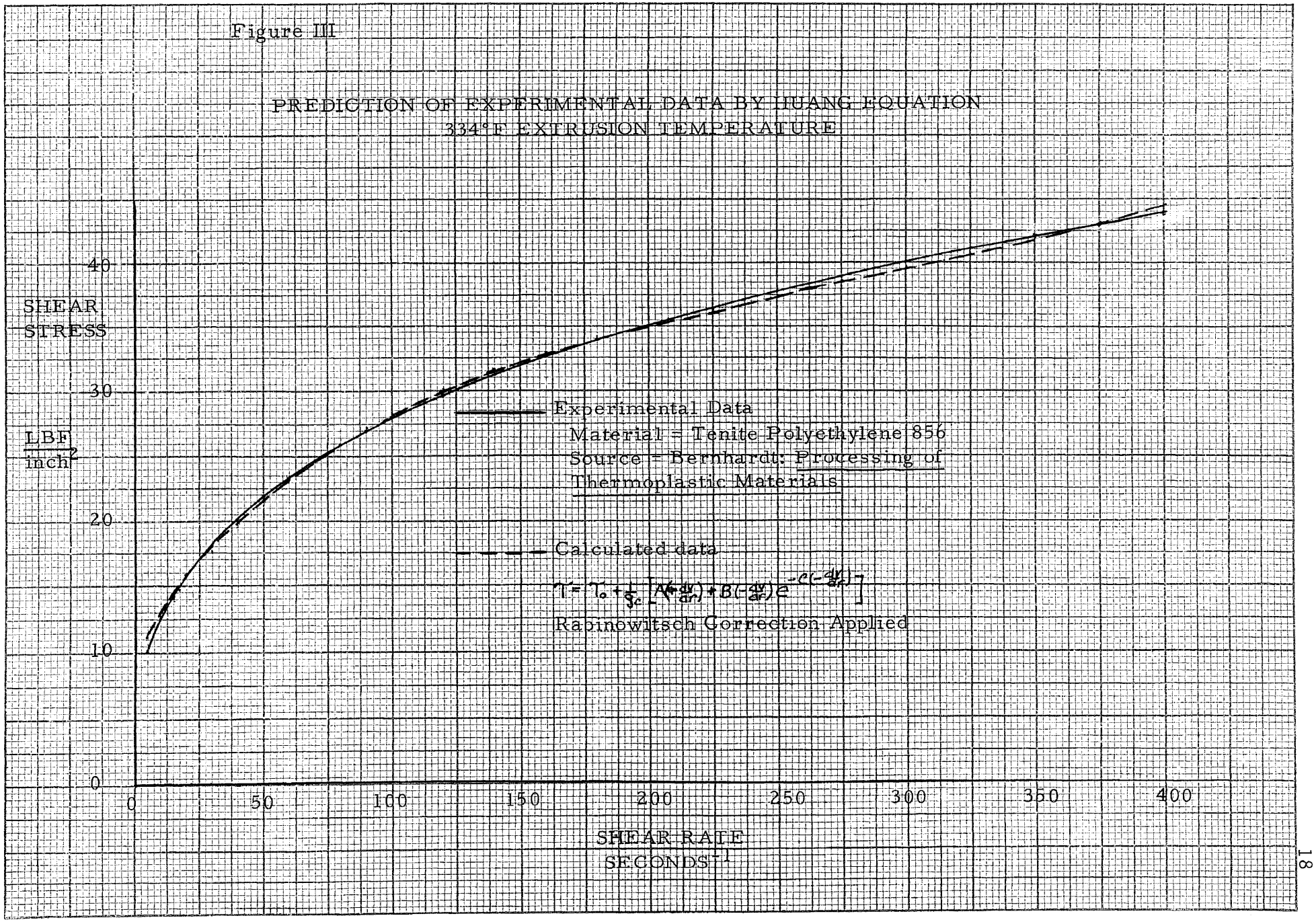


Figure IV

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

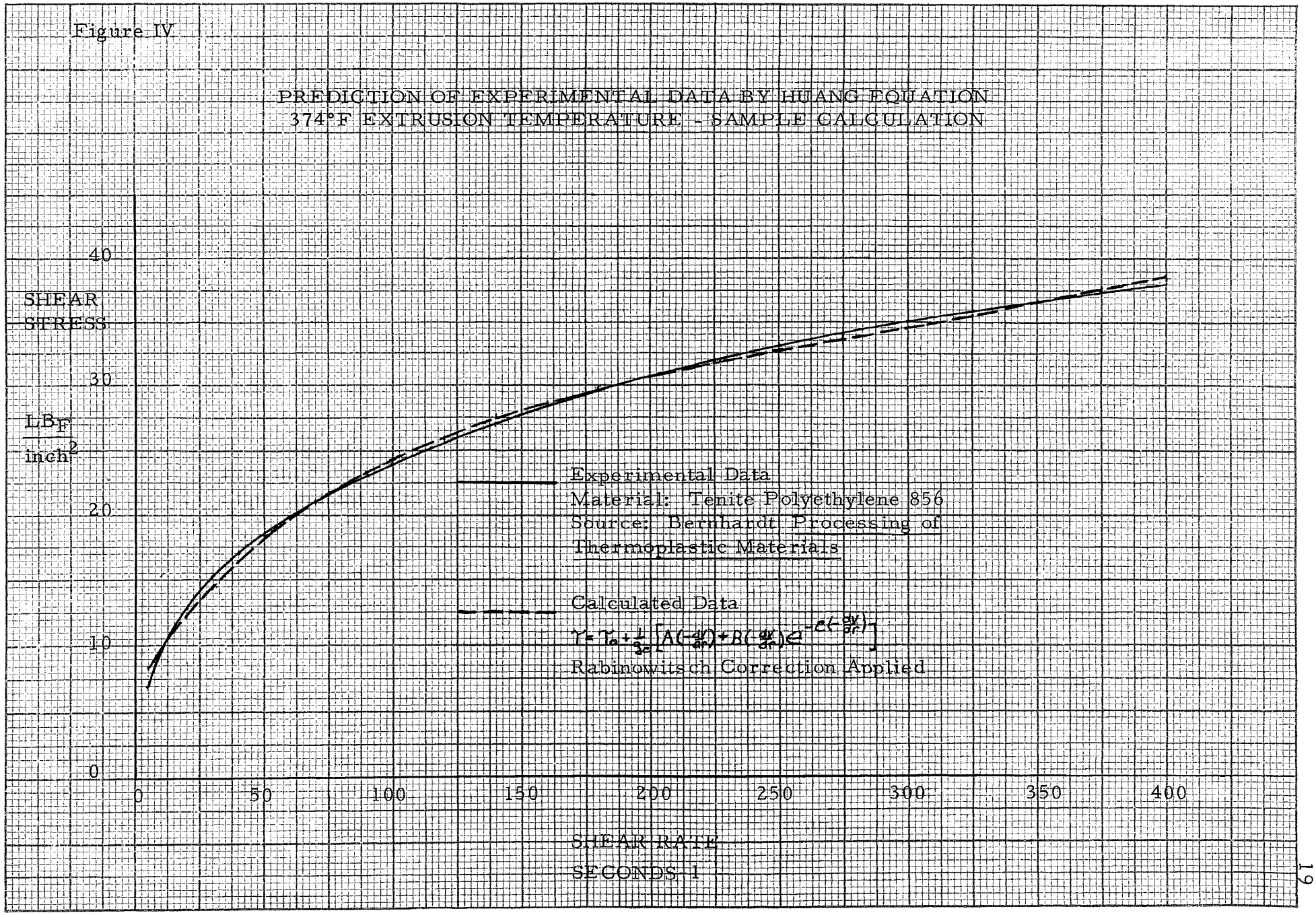
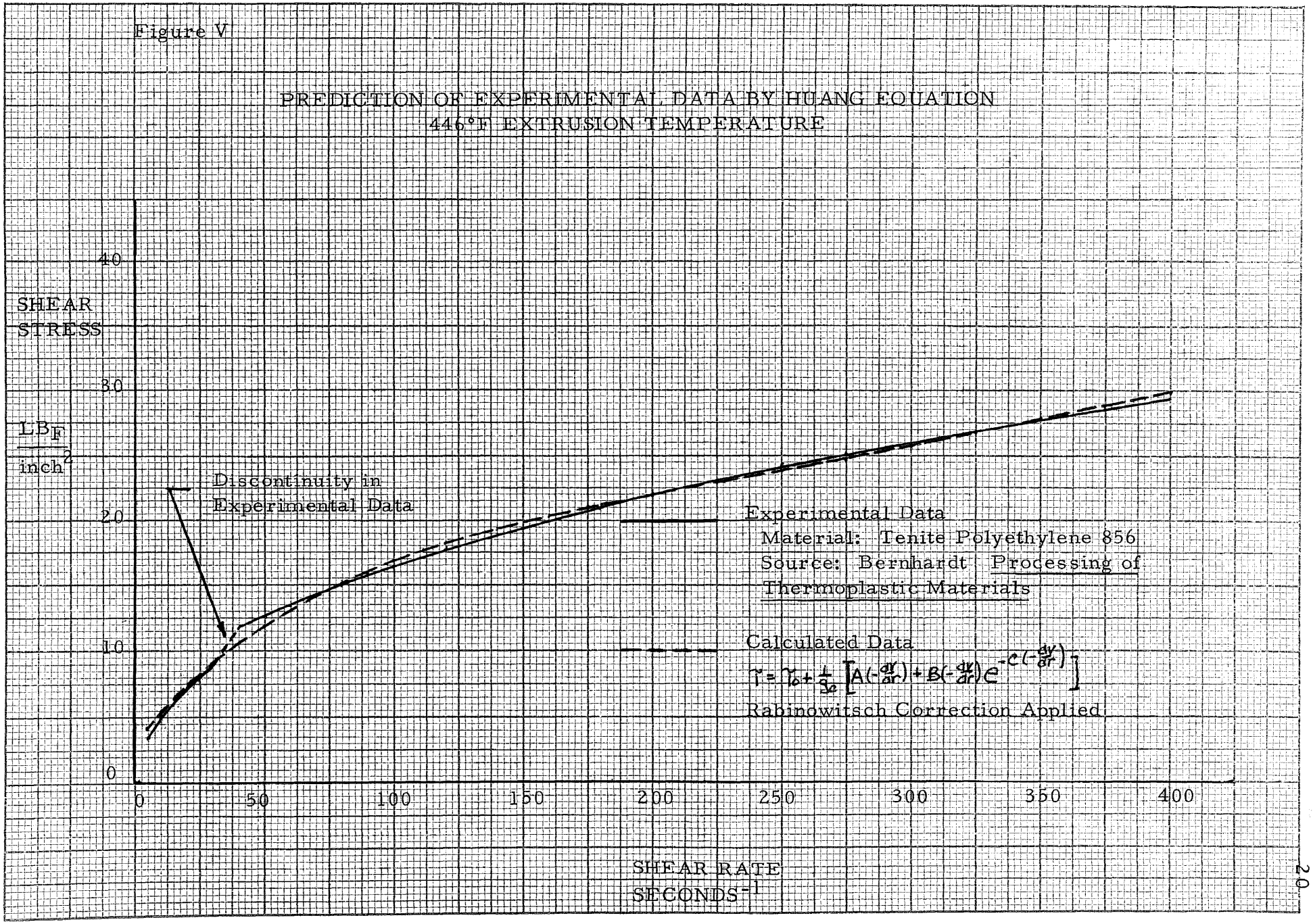


Figure V

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



Tenite Polyethylene 856 at 334°F, 374°F and 446°F. Results are presented in Table I. The method of obtaining the constants is outlined 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 equation, 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 τ_0 from Figures VI - IX and evaluates the Huang equation with

Table I

CONSTANTS OF THE EQUATION
FOR TENITE POLYETHYLENE 856

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

τ_R = lbf/inch^2
$-dv/dr$ = seconds
g_c = 386.09 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
τ_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
τ_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: $\tau_R = \tau_0 + \frac{1}{g_c}\left[A\left(-\frac{dv}{dr}\right) + B\left(-\frac{dv}{dr}\right)e^{-C\left(-\frac{dv}{dr}\right)}\right]$

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

Material	Weight Average Molecular Weight	A $\frac{\text{lbm}}{\text{second-inch}}$	B $\frac{\text{lbm}}{\text{second-inch}}$	C seconds	τ_0 $\frac{\text{lbf}}{\text{inch}^2}$
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

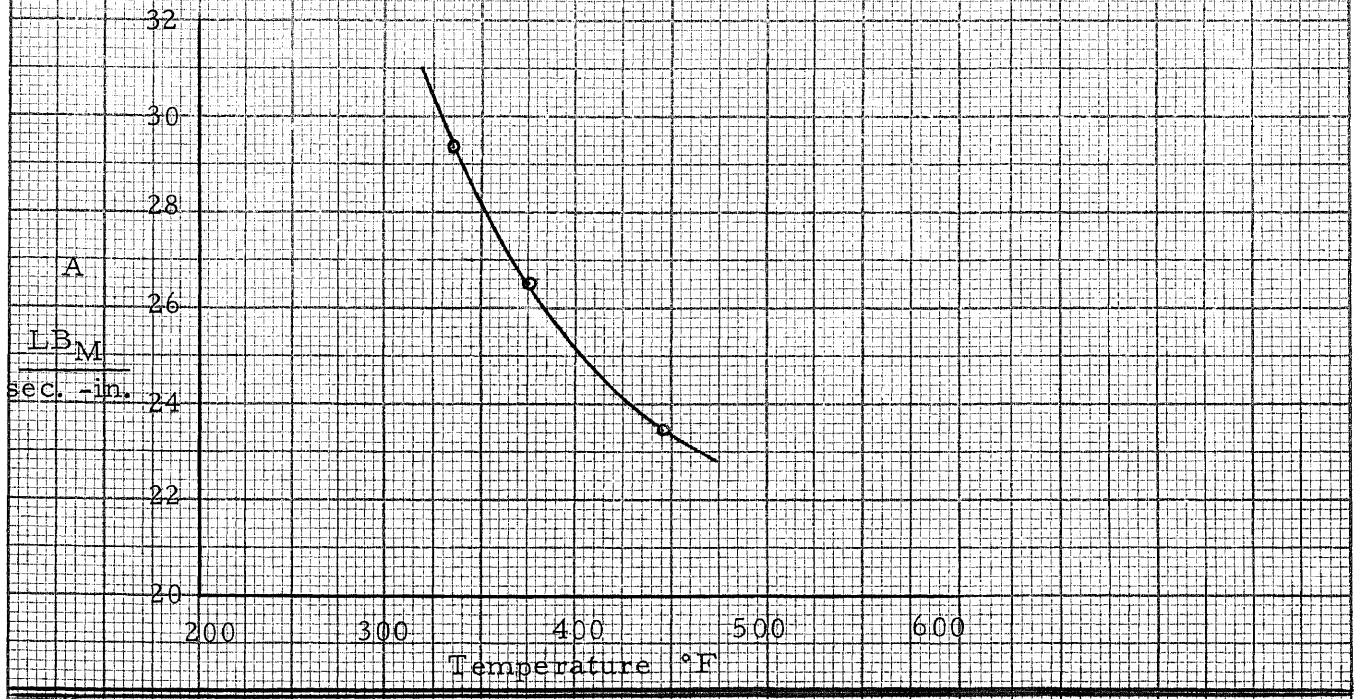


Figure VII

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

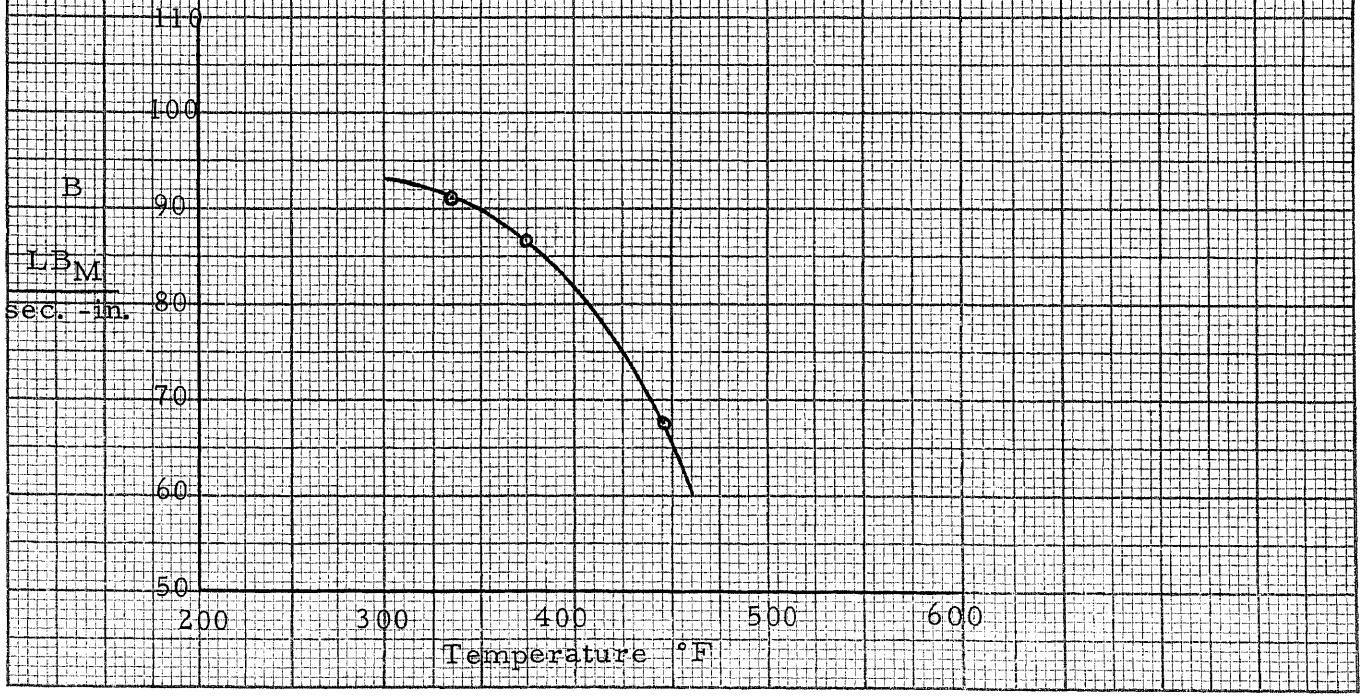


Figure VIII

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

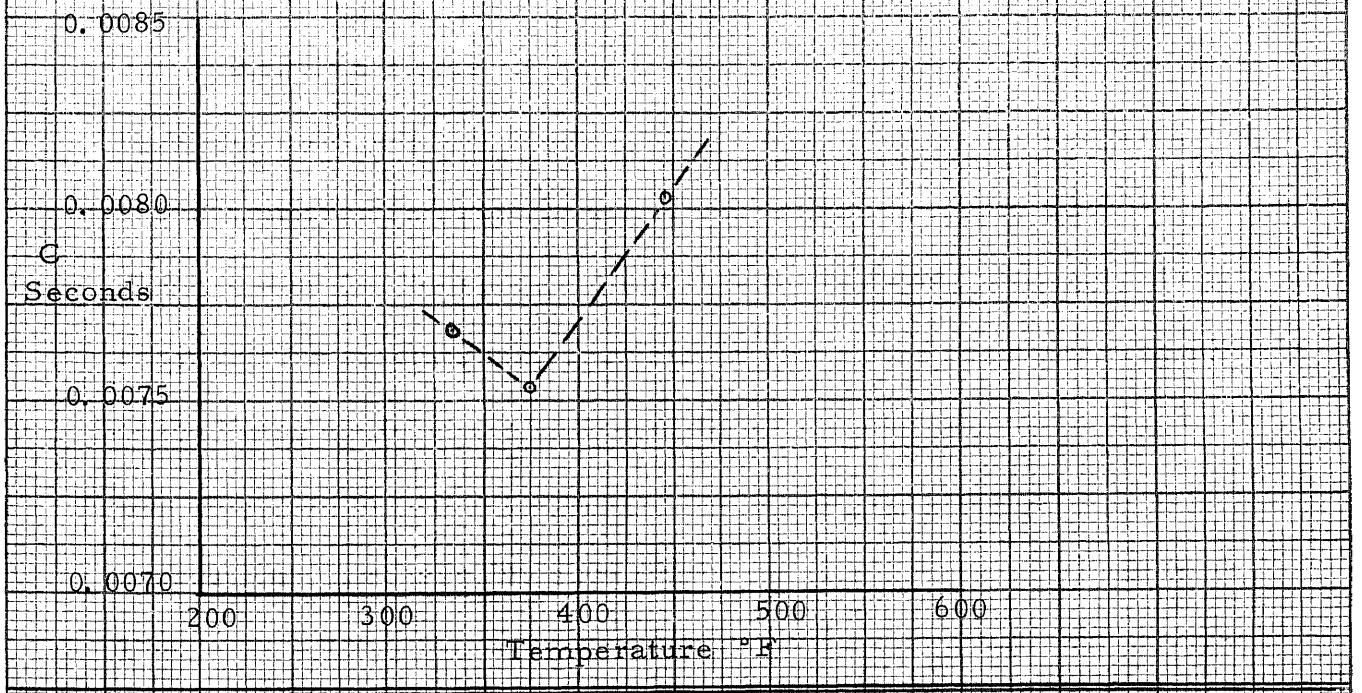
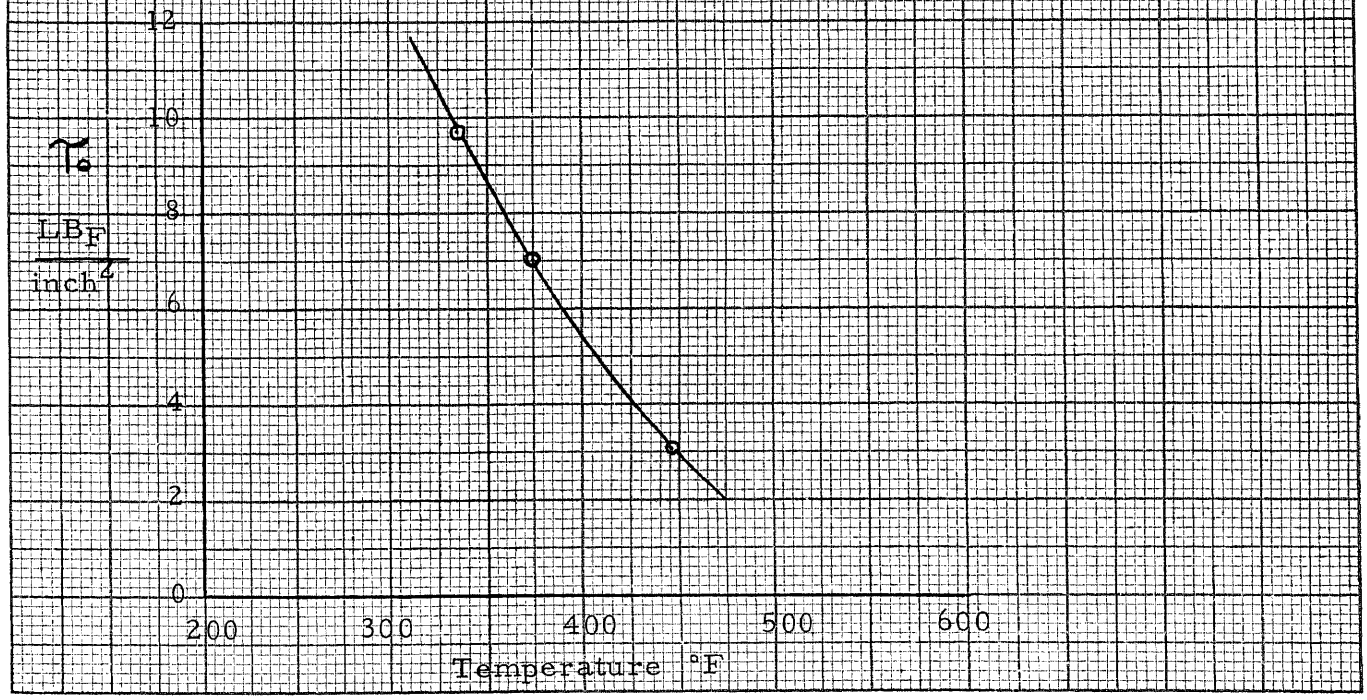


Figure IX

TEMPERATURE DEPENDENCE OF THE CONSTANT τ_o
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 $\mu = Ae^{-E/RT}$ 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,

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

Similarly, it was attempted to fit both τ_0 and C to an Arrhenius expression. A reasonably good fit was obtained for τ_0 (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

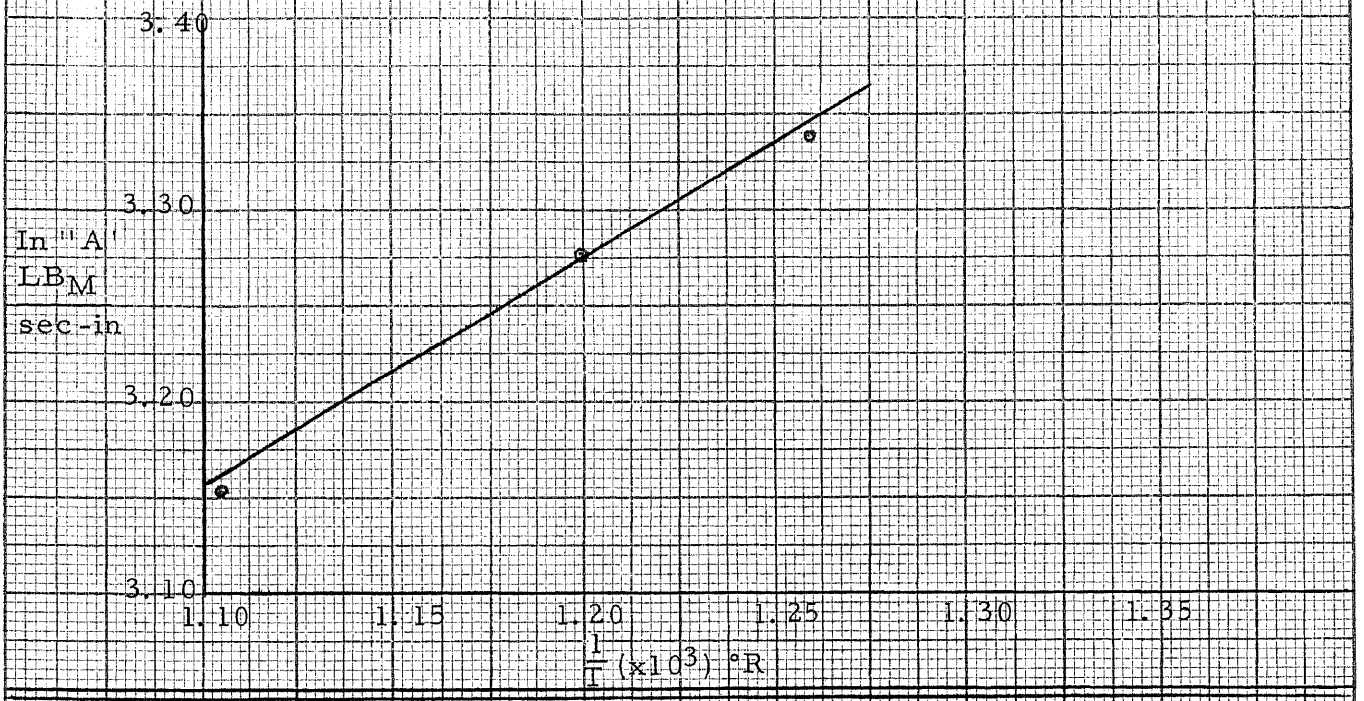


Figure XI

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

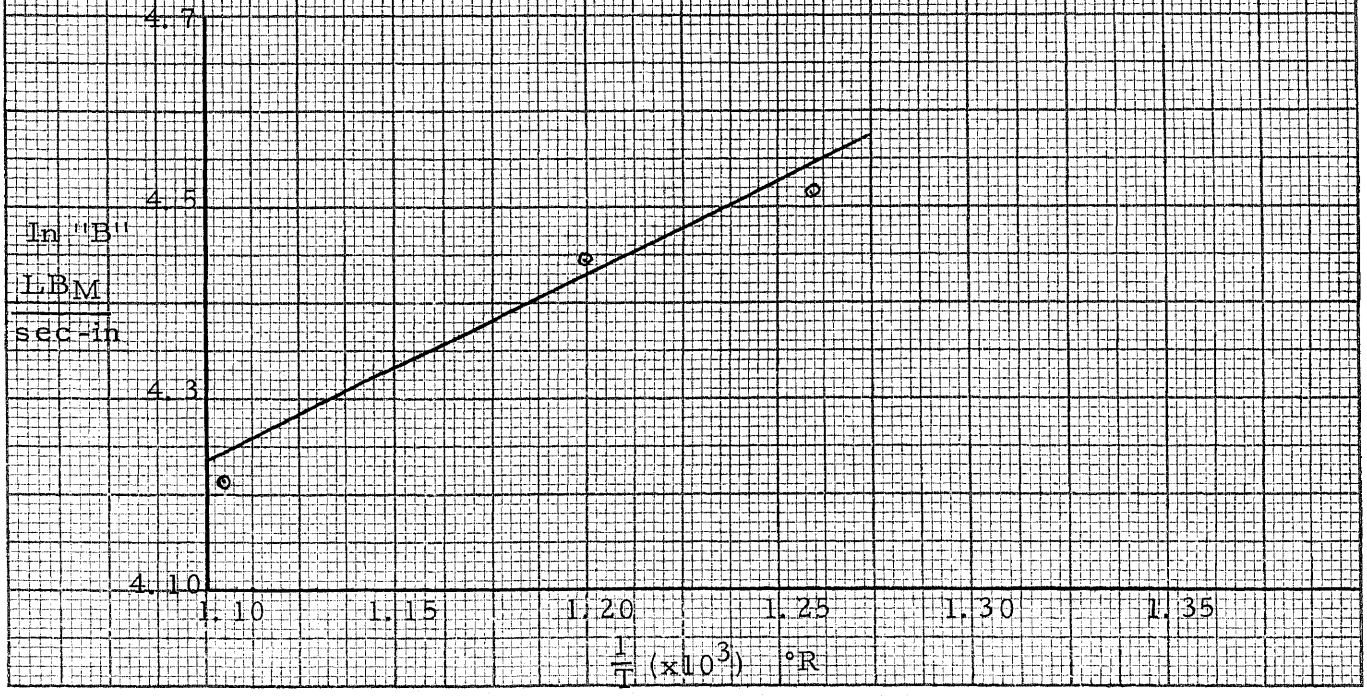


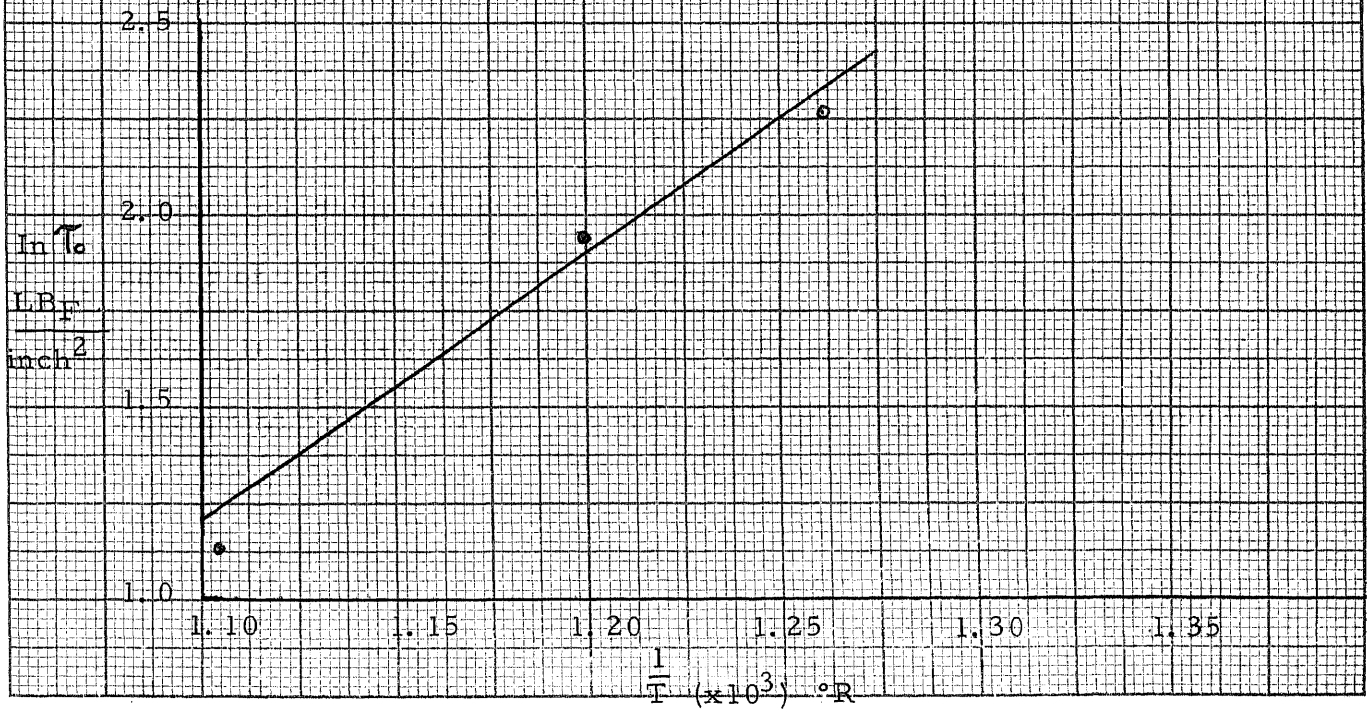
Figure XII

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



Figure XIII

TEMPERATURE DEPENDENCE OF THE CONSTANT "To"
FOR TENITE POLYETHYLENE 856 - ARRHENIUS PLOT



for the temperature dependence of C has yet been delineated. Therefore, 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 τ_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_{τ_o}, E_A, E_B, E_{τ_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 behavior of one material based solely on the flow curve of another is possible. 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

Arrhenius Expression

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

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

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

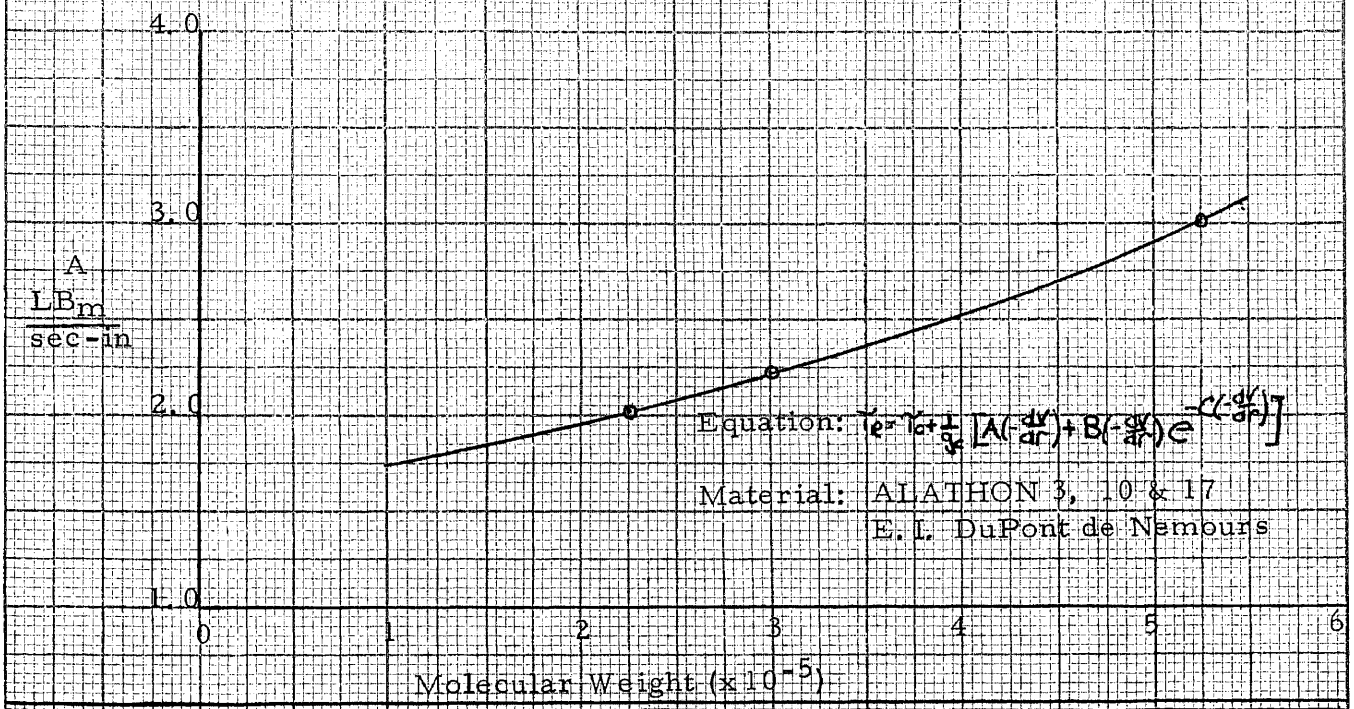


Figure XV
MOLECULAR WEIGHT DEPENDENCE OF THE
CONSTANT "B" FOR LOW-DENSITY POLYETHYLENE

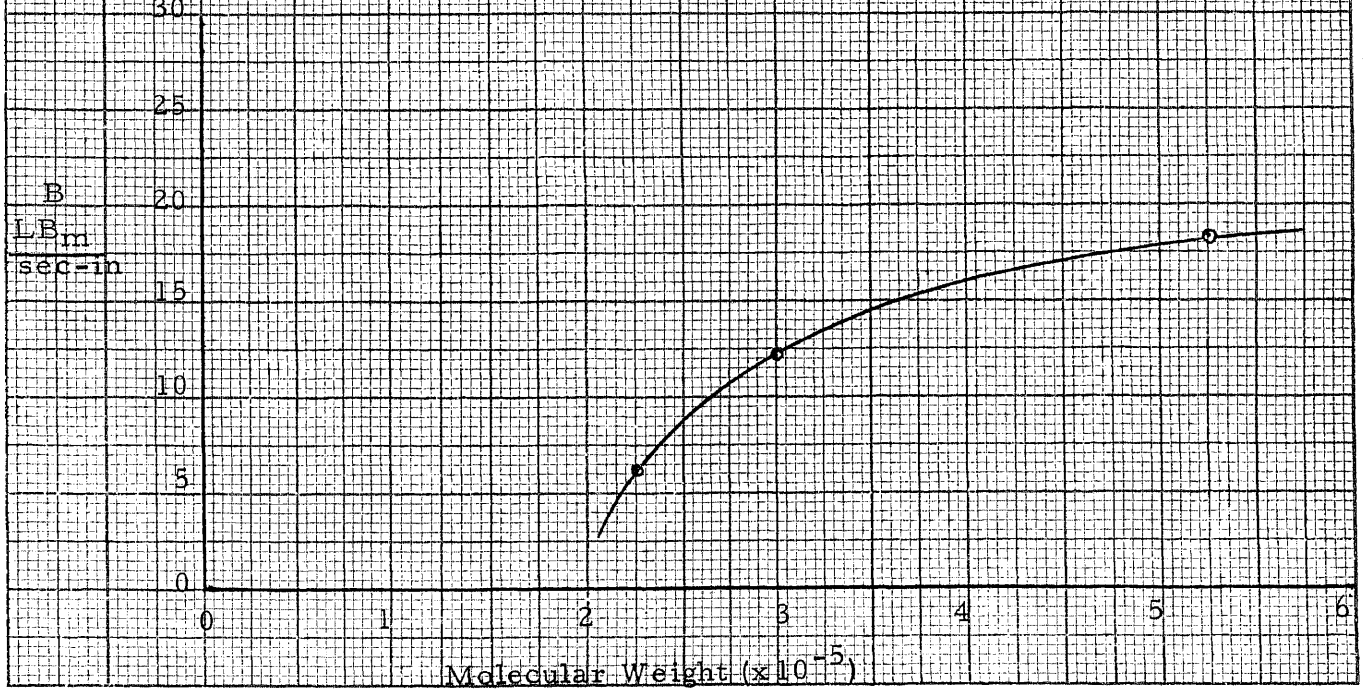


Figure XVI
MOLECULAR WEIGHT DEPENDENCE OF THE
CONSTANT "C" FOR LOW-DENSITY POLYETHYLENE

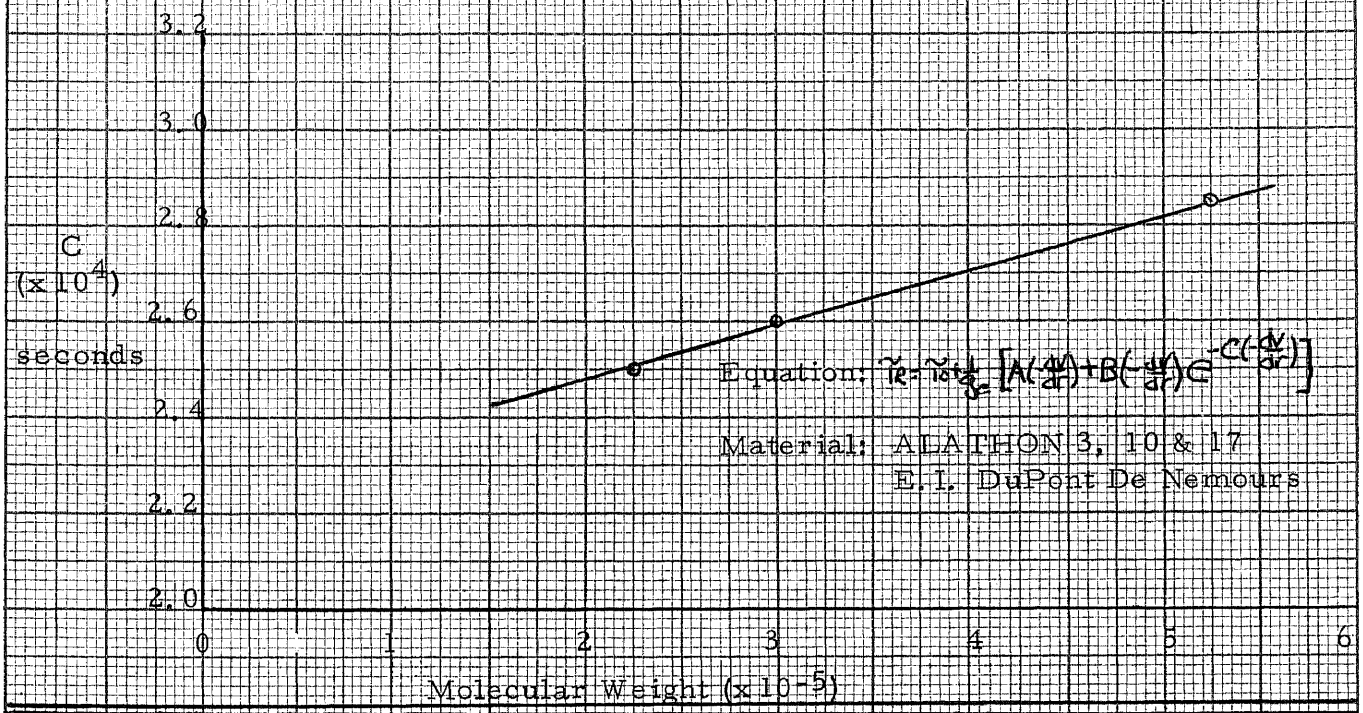
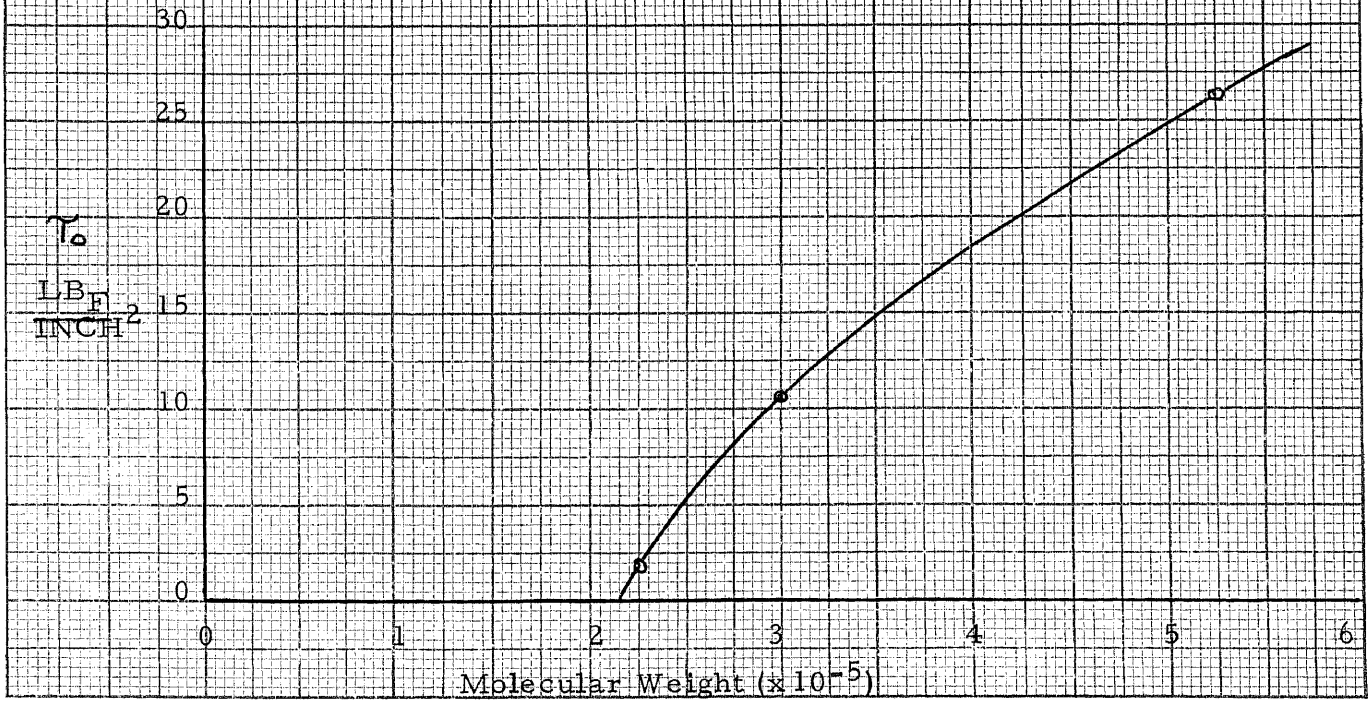


Figure XVII
MOLECULAR WEIGHT DEPENDENCE OF THE
CONSTANT "T_o" FOR LOW-DENSITY POLYETHYLENE



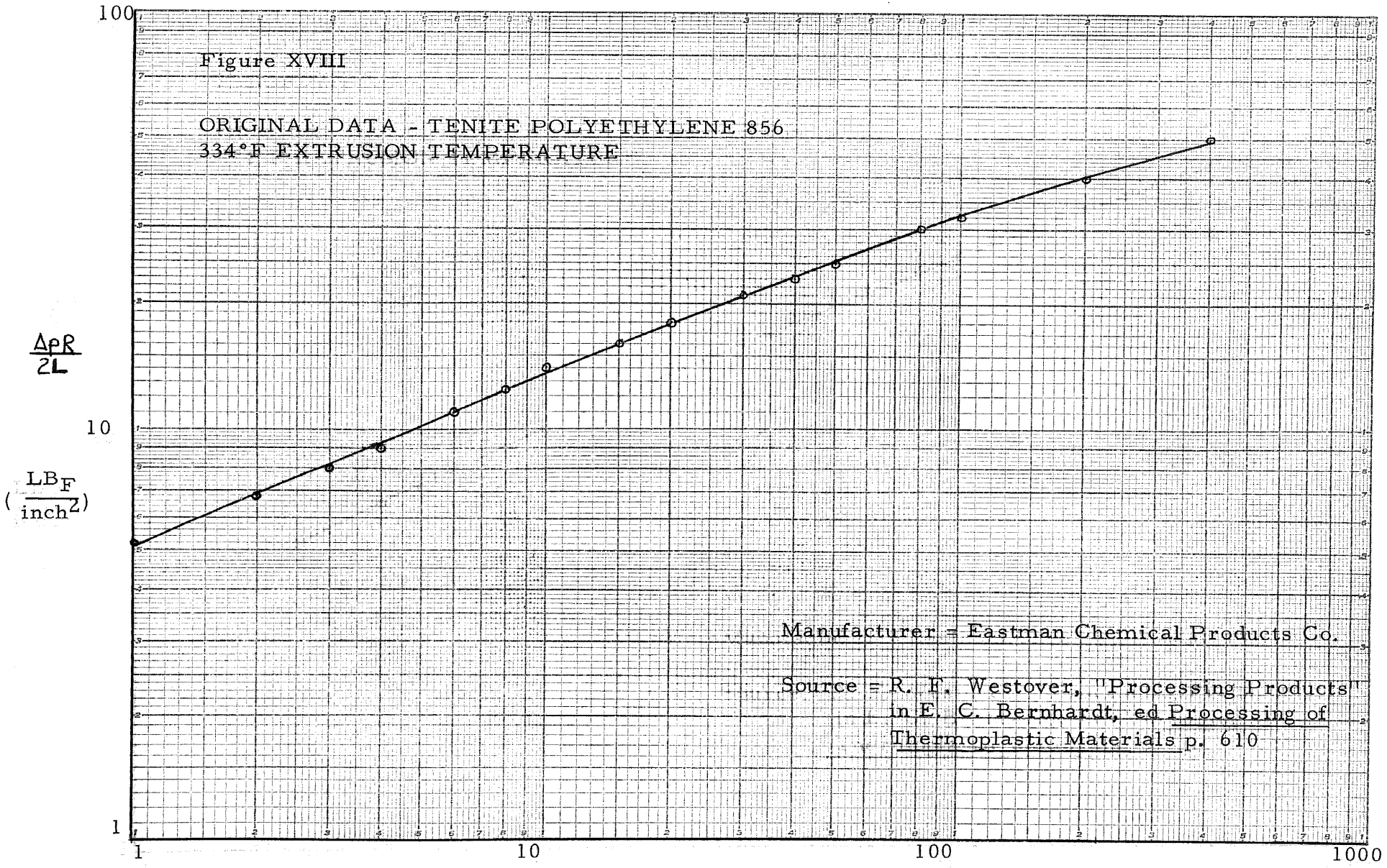
experimental and theoretical data was not as good as that achieved with Tenite 856, this may be explained in part by the much broader shear rate range fit by the constants for the Alathon series: 1 - 1000 seconds $^{-1}$ for the Alathon's compared to 1 - 400 seconds $^{-1}$ for Tenite 856.

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
$\frac{\Delta P R}{2L}$
$\left(\frac{LB_F}{inch^2}\right)$
100
10
1
1
10
100
1000
Manufacturer = Eastman Chemical Products Co.
Source = R. F. Westover, "Processing Products" in E. C. Bernhardt, ed Processing of Thermoplastic Materials p. 610

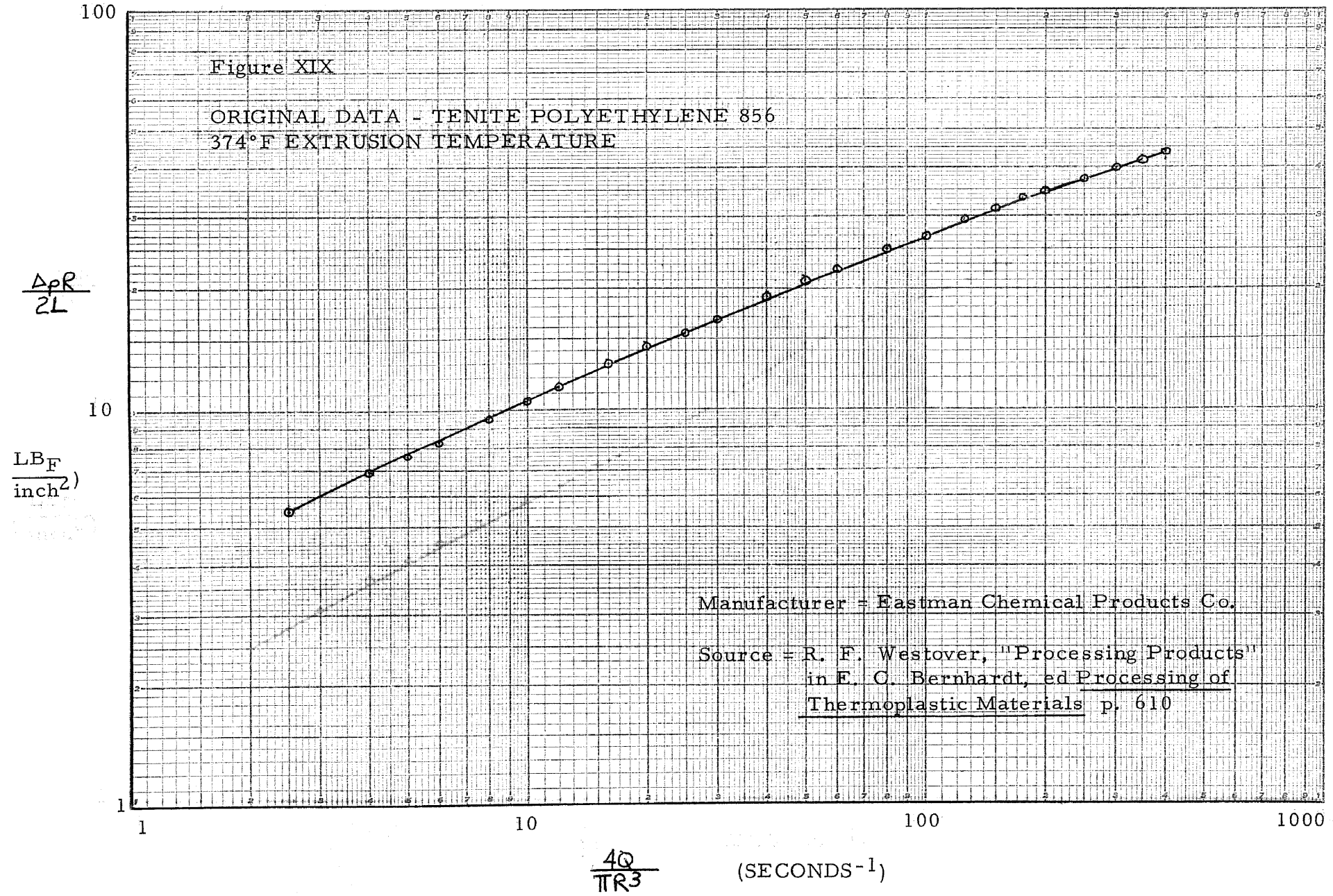

Figure XIX
ORIGINAL DATA - TENITE POLYETHYLENE 856
374°F EXTRUSION TEMPERATURE
100
10
1
1
10
100
1000
ΔpR/2L
LB_F/inch^2)
4Q/πR^3
(SECONDS^-1)
Manufacturer = Eastman Chemical Products Co.
Source = R. F. Westover, "Processing Products" in E. C. Bernhardt, ed Processing of Thermoplastic Materials p. 610

Figure XX

ORIGINAL DATA - TENITE POLYETHYLENE 856
446°F EXTRUSION TEMPERATURE

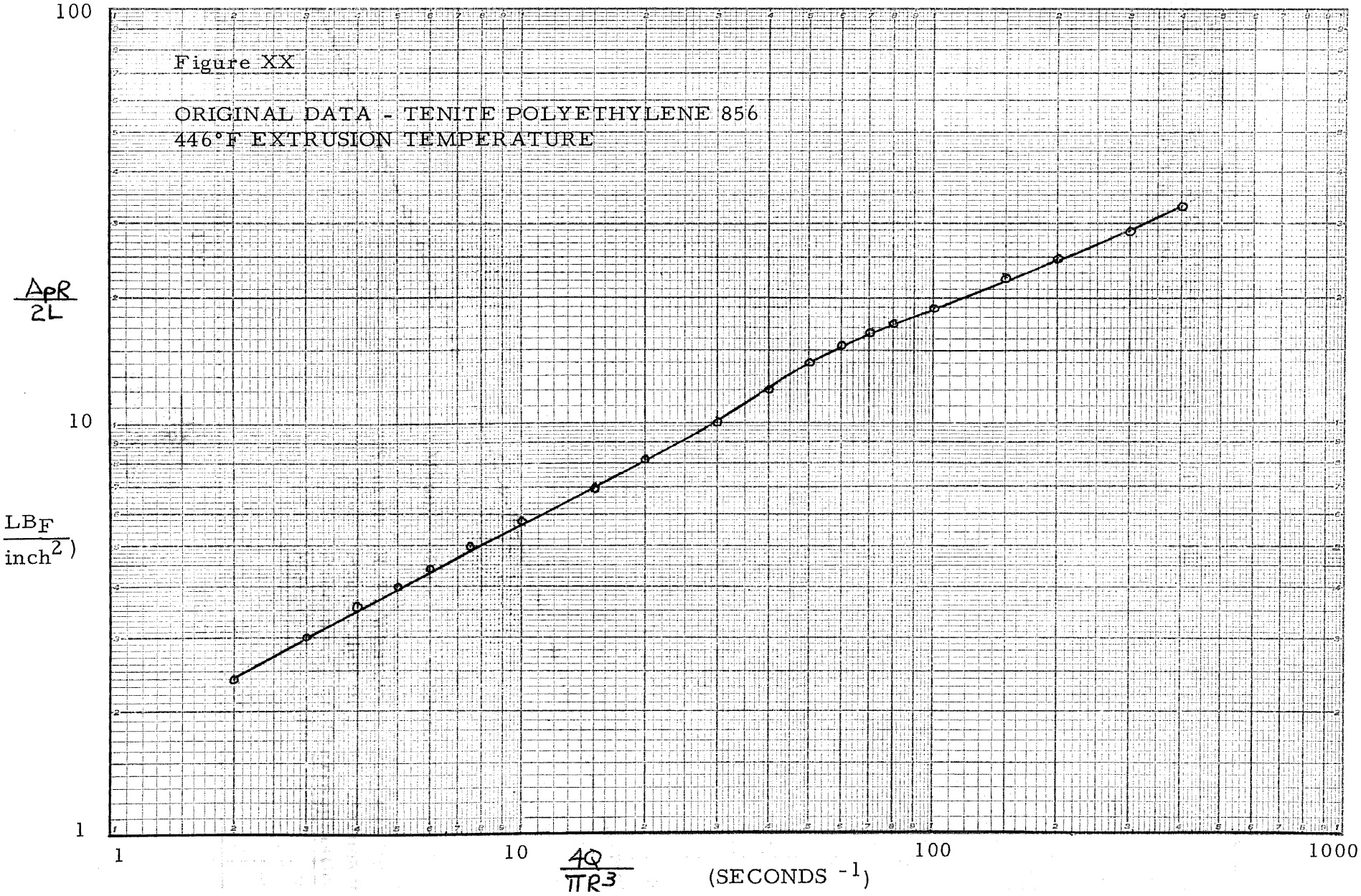


Figure XXI
ORIGINAL DATA - ALATHON 3 POLYETHYLENE
374°F EXTRUSION TEMPERATURE

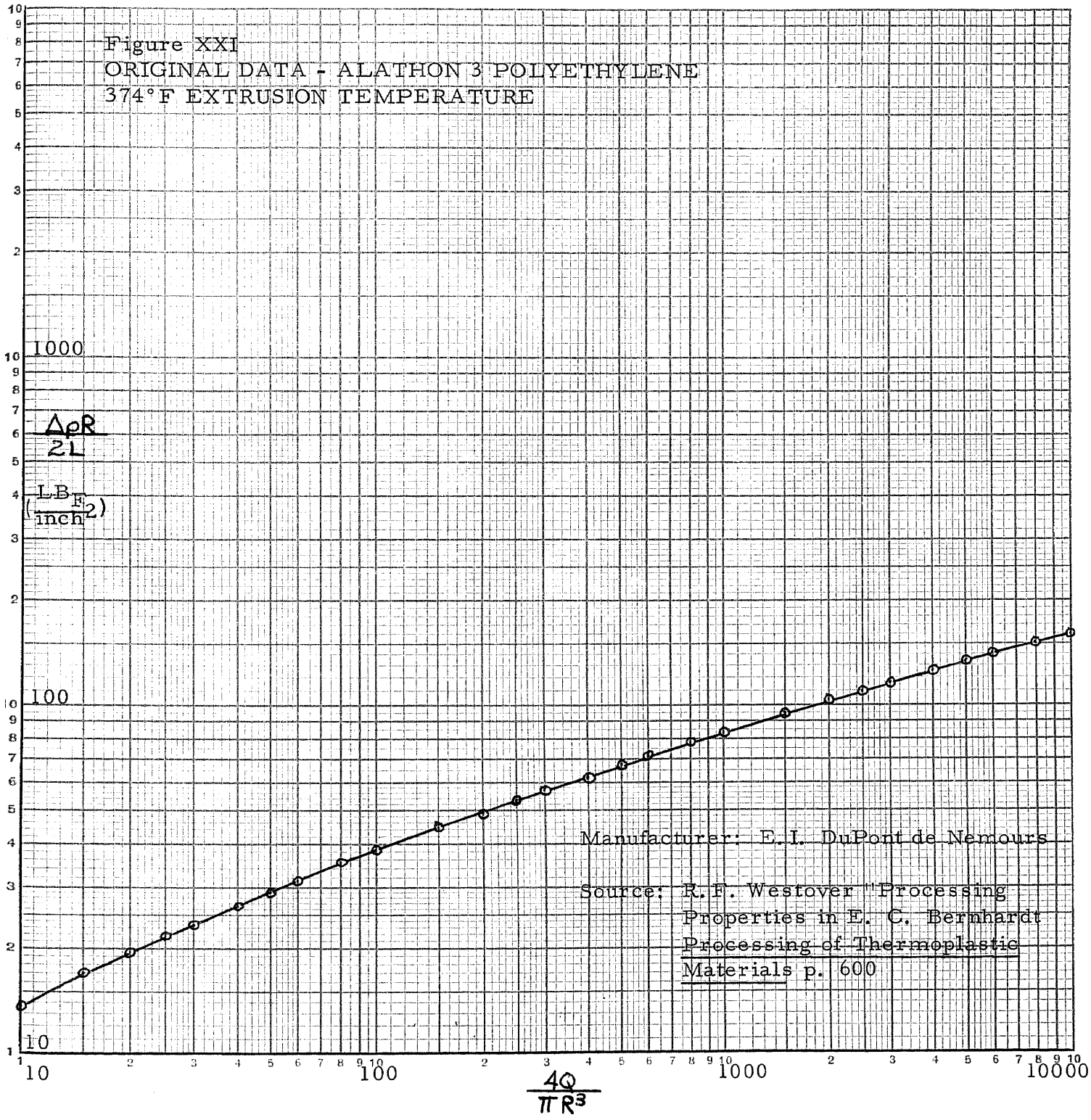
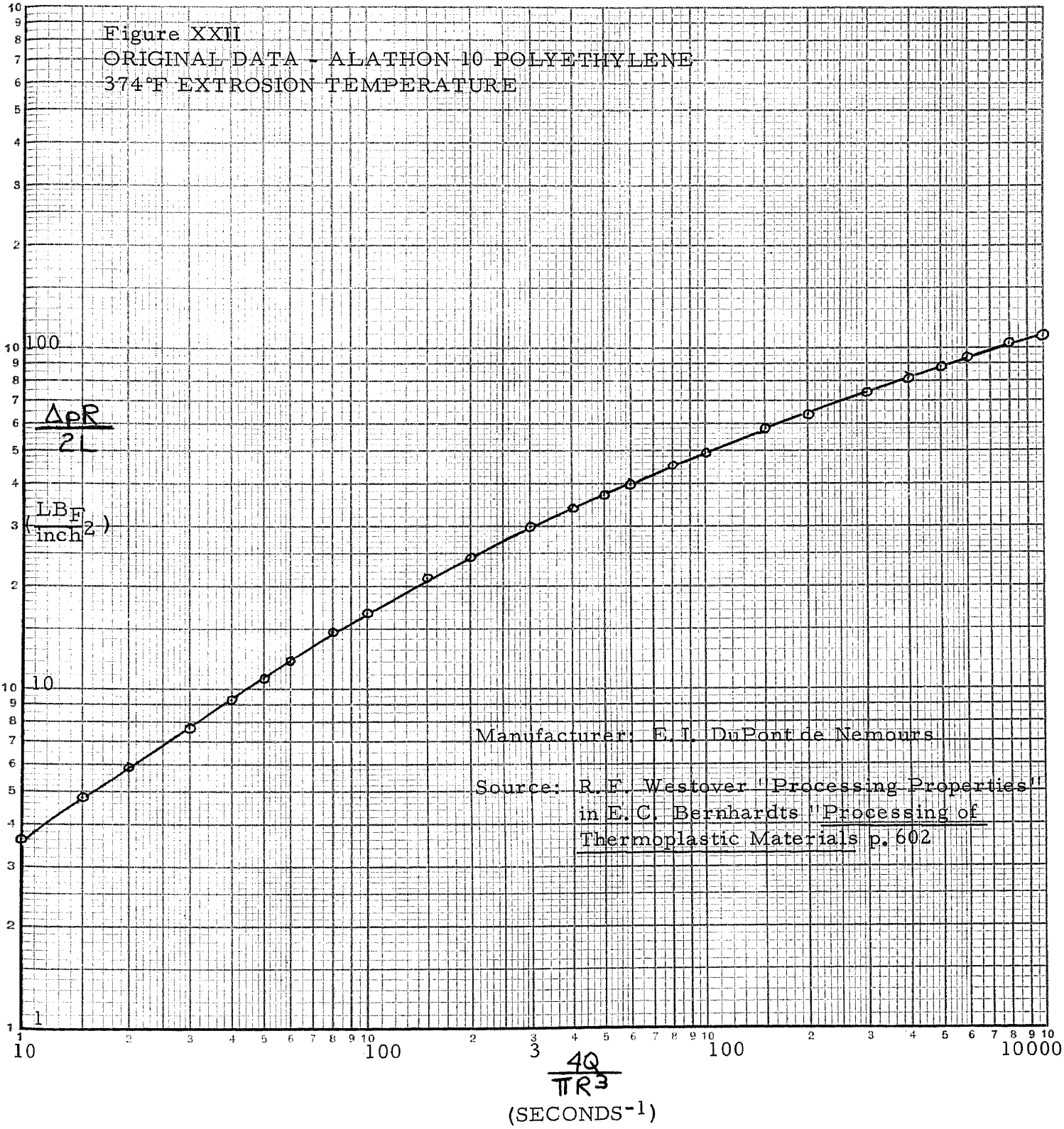


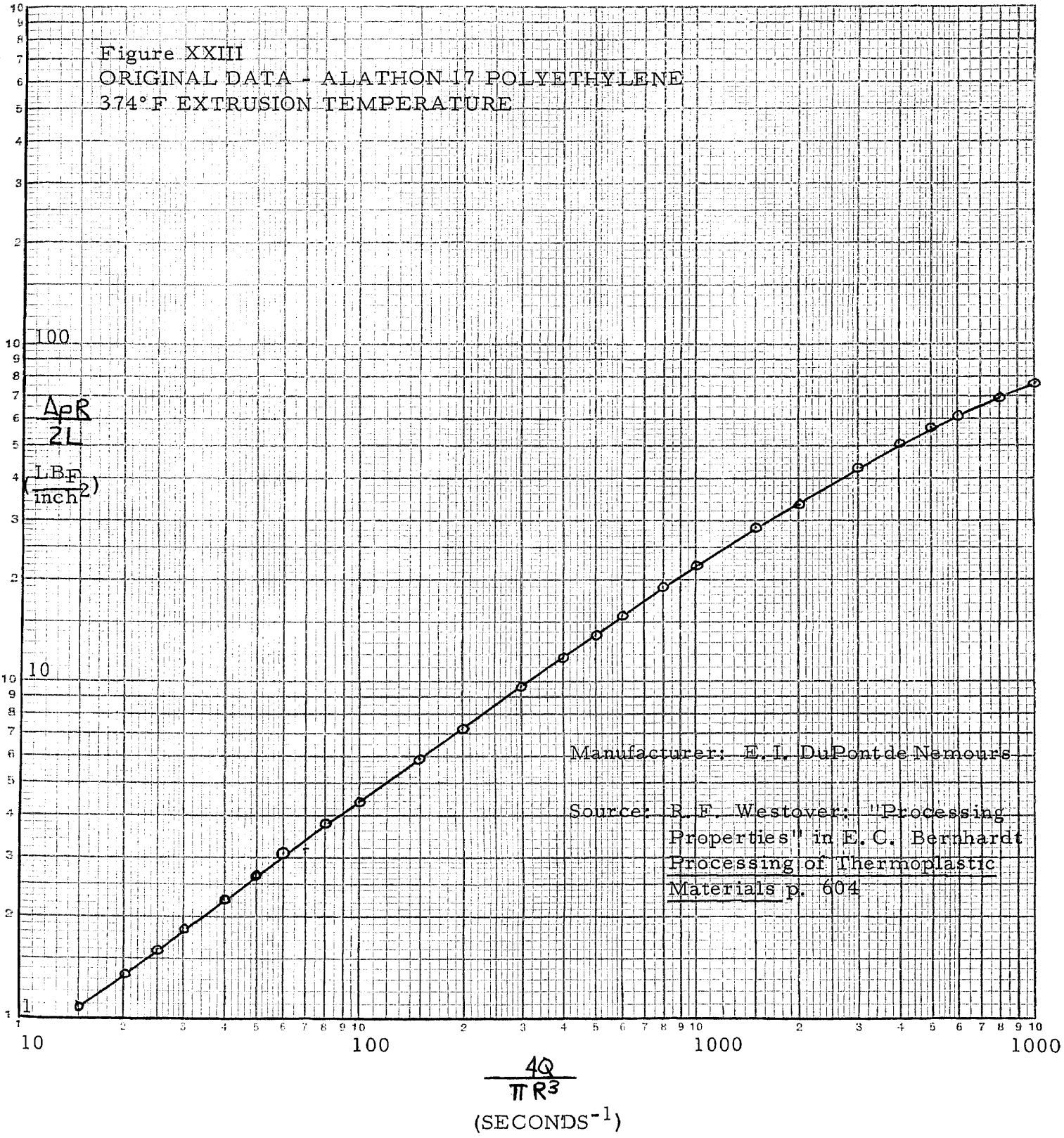
Figure XXII
ORIGINAL DATA - ALATHON-10 POLYETHYLENE
374°F EXTROSION TEMPERATURE



Manufacturer: E. I. DuPont de Nemours

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

Figure XXIII
ORIGINAL DATA - ALATHON 17 POLYETHYLENE
374° F EXTRUSION TEMPERATURE



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 $\frac{\Delta p R}{2L} = \tau_R$, and the volumetric flow rate Q are tabulated for the sample calculation in Table IV. $\tau_R Q$ is also found and tabulated in Table IV.

The value of $\frac{d(\tau_R^3 Q)}{d\tau_R}$ is determined at each value of τ_R and results presented in Table IV. This is accomplished by a numerical differentiation procedure whereby $\tau_R^3 Q$ is plotted against τ_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 -

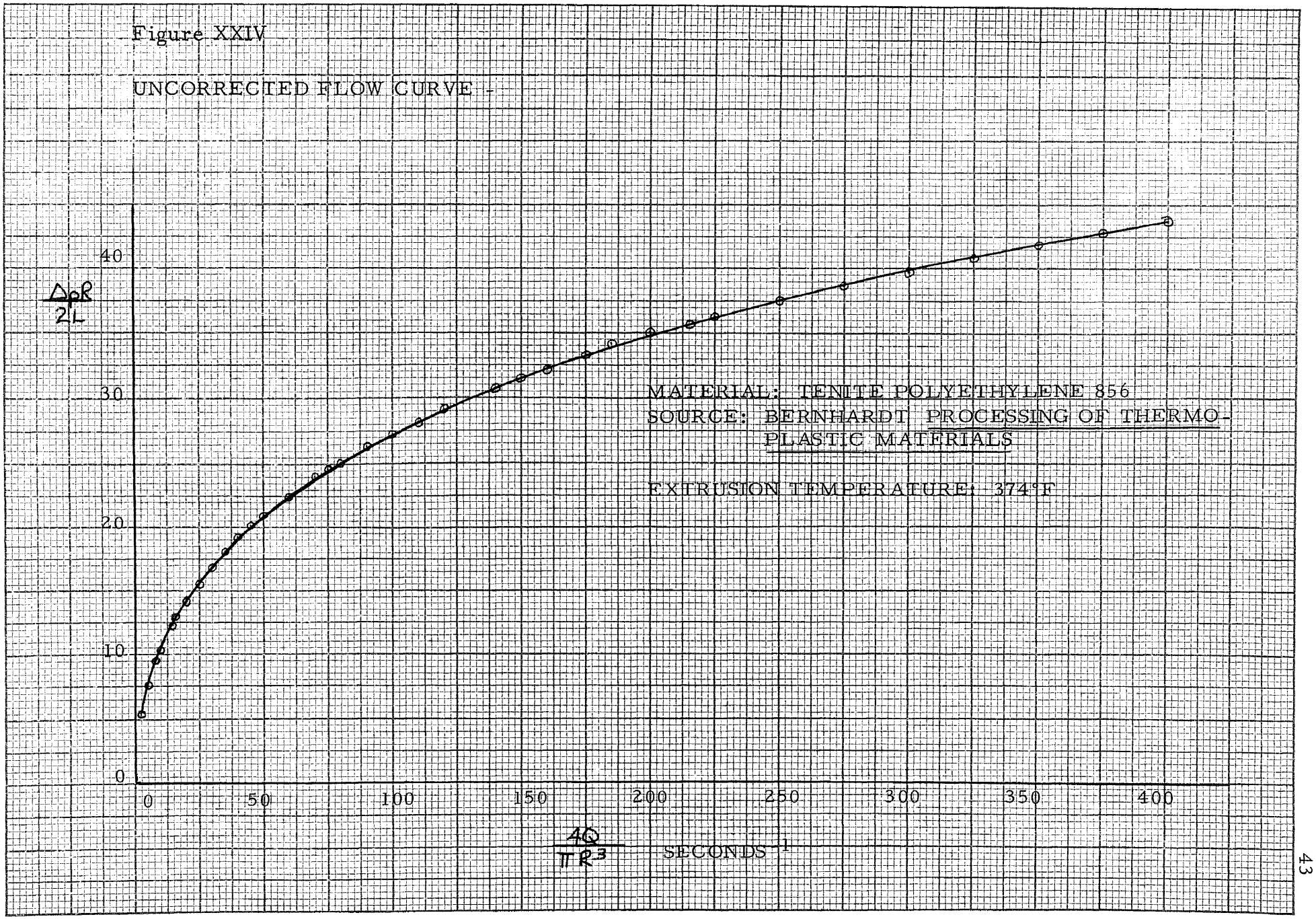


Table IV

SAMPLE CALCULATION
TENITE POLYETHYLENE 856 AT 374°F

$\tau_R = \frac{\Delta_p R}{2L}$	$\frac{4Q}{\pi R^3}$	$Q = \frac{4Q/\pi R^3}{4/\pi R^3}$	$\tau_R^3 Q$	$\frac{d(\tau_R^3 Q)}{d\tau_R}$	$-\frac{dv}{dr}\Big\|_{r=R}$
Shear Stress lb_F, $Inch^2$	$Seconds^{-1}$	Vol. Flow Rate $Inch^3/Sec.$			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

$\tau_R = \frac{\Delta p R}{2L}$	$\frac{4Q}{\pi R^3}$	$Q = \frac{4Q/\pi R^3}{4/\pi R^3}$	$\tau_e^3 Q$	$\frac{d(\tau_e^3 Q)}{d\tau_R}$	$-\frac{dv}{dr}\Big\|_{r=R}$
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

$\tau_R = \frac{\Delta p R}{2L}$	$\frac{4Q}{\pi R^3}$	$Q = \frac{4Q/\pi R^3}{4/\pi R^3}$	$\tau_R^3 Q$	$\frac{d(\tau_R^3 Q)}{d\tau_R}$	$\frac{dv}{dr}\Big\|_{r=R}$
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. Approximately 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.

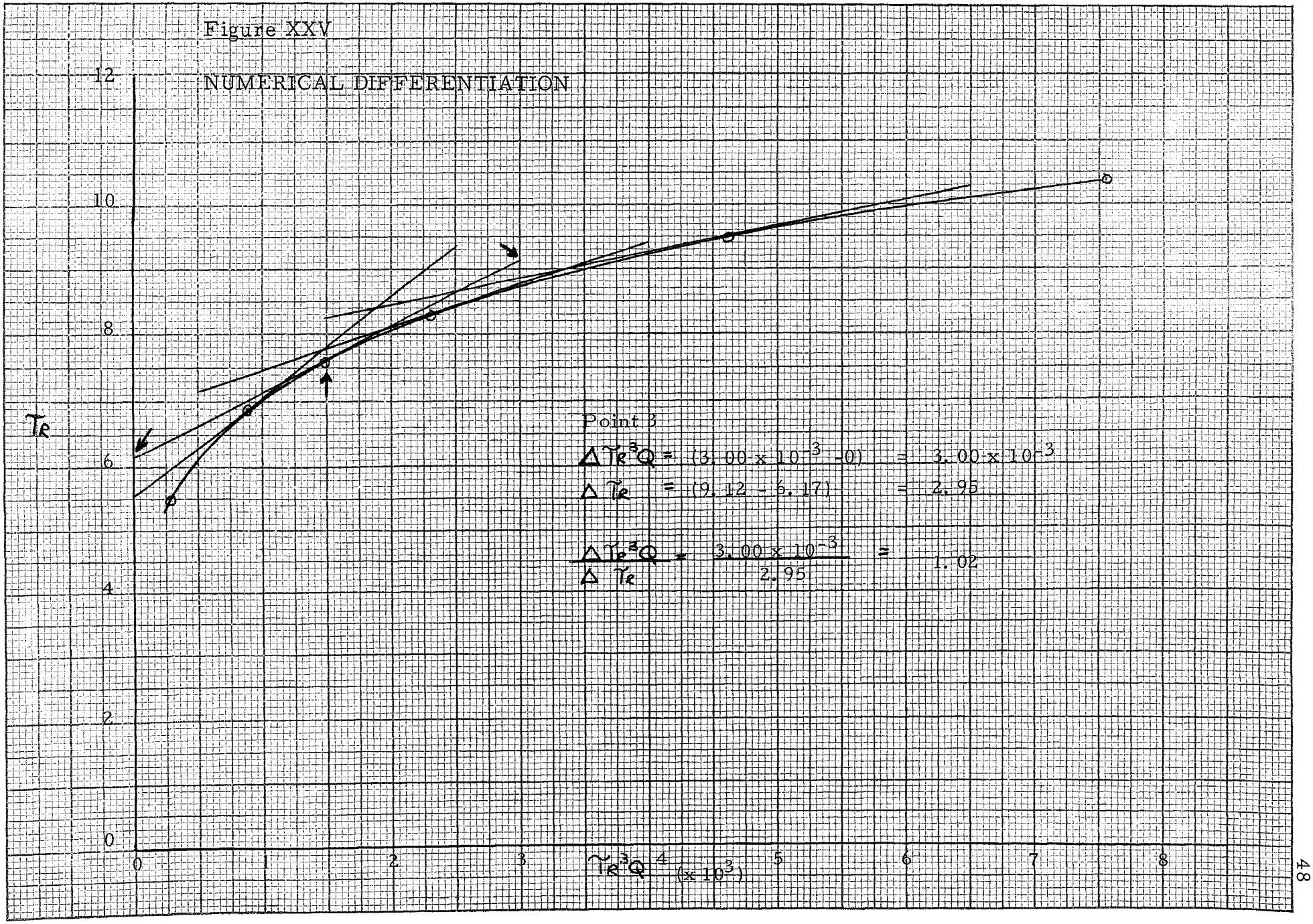
Once the above calculations are completed the correct shear rates are obtained at each shear stress value. This is achieved by use of the Rabinowitsch correction, equation XI in this thesis. The corrected shear rate is obtained by multiplying $\frac{d(\tau_R^3 Q)}{d\tau_R} \times \frac{1}{\pi R^3 \tau_R^2}$, obtaining $-\frac{dv}{dr}$. 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 $\frac{4Q}{\pi R^3}$ 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

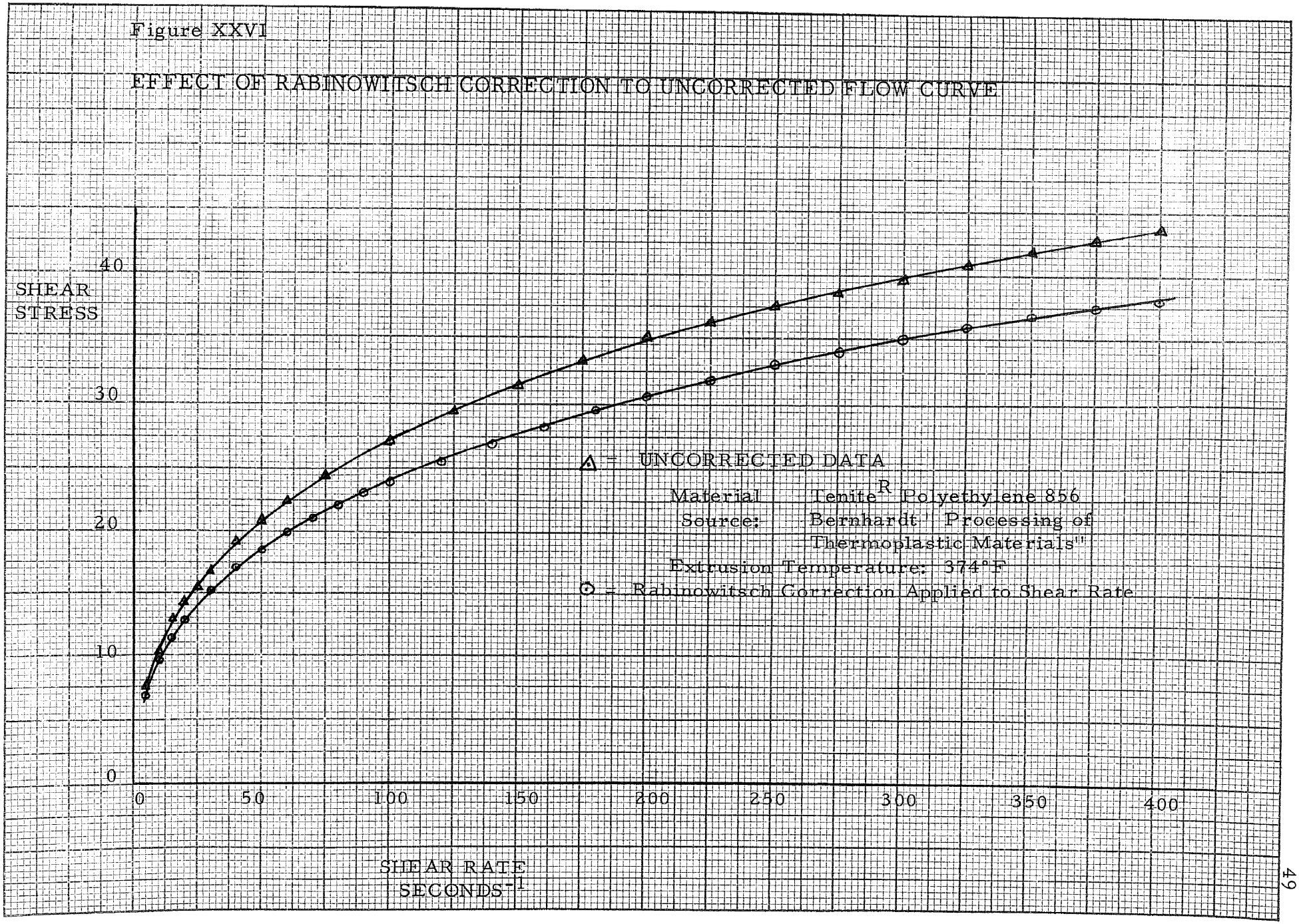
$\Delta \tilde{\gamma}_R{}^3Q = (3.00 \times 10^{-3} - 0) = 3.00 \times 10^{-3}$

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

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

Figure XXVI

EFFECT OF RABINOWITSCH CORRECTION TO UNCORRECTED FLOW CURVE



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.

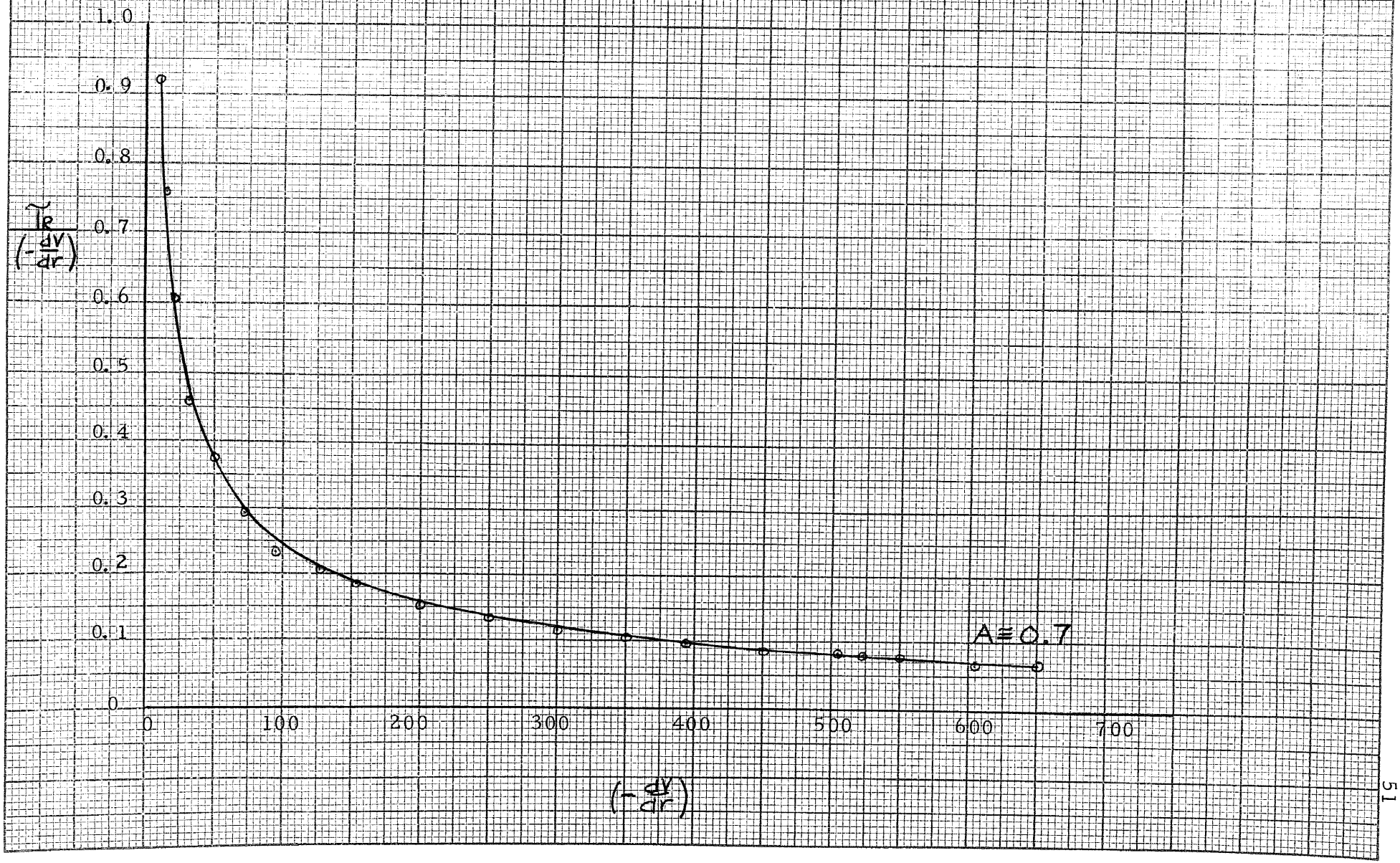
The computer program utilized is a modified standard IBM program for the evaluation of the best fit of the constants by non-linear least squares. The program is coded in Fortran IV.

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



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 Bof 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.

BIBLIOGRAPHY

Bagley, E. B. "End Corrections in the Capillary Flow of Polyethylene" Journal of Applied Physics 28 (5) 624-627 (1957)

Best, D. M. and Rosen, S. L. "A Simple, Versatile and Inexpensive Rheometer For Polymer Melts" Polymer Engineering and Science 8 (2) 116 - 125 (1968)

Duvdevani, I. J. and Klein, I. "Analysis of Polymer Melt Flow in Capillaries Including Pressure Effects" SPE Journal 23 (12) 41 - 45 (1967)

Kataoka, T. and Ueda, S. "Flow Properties of Polyethylene Melt" Journal of Applied Polymer Science 12 939 - 953 (1968)

King, R. G. "A Rheological Measurement of Three Polyethylene Melts" Rheologica Acta 5 (1) 35 - 41 (1966)

Kowalski, R. C. "Introduction to Melt Rheology and Applications to Extrusion" SPE Journal 24 (3) 47 - 51 (1968)

Lenk, R. S. "A Generalized Flow Theory" Journal of Applied Polymer Science 11 1033 - 1042 (1967)

Lupton, J. M., and Regester, J. W. "Melt Flow of Polyethylene At High Rates" Polymer Engineering and Science 5 (4) (10/1965)

Merz, E. and Colwell, R. E. "High Shear Rate Capillary Rheometer For Polymer Melts" ASTM Bulletin 232 63 - 67 (1958)

Metzger, A. P. and Brodkey, R. S. "Measurement of The Flow of Molten Polymers Through Short Capillaries" Journal of Applied Polymer Science 7 399 - 410 (1963)

Metzger, A. P. and Hamilton, C. W. "Melt Flow Properties of Linear Polyethylenes" SPE Tech. Papers 6 83 - 1, 83 - 4

Metzger, A. P. and J. R. Know, "The Effect of Pressure Losses in the Barrel on Capillary Flow Measurements", Transactions of the Society of Rheology, 9 (1) 13 - 25 (1965)

Metzner, A. B. "Flow Behavior of Thermoplastics" Bernhardt E. C., ed. Processing of Thermoplastic Materials Reinhold Publishing Co., N. Y. 1957

BIBLIOGRAPHY (Con't.)

Metzner, A. B. "Non-Newtonian Fluid Flow" Industrial and Engineering Chemistry 49 (9) 1429 - 1432 (1957)

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

Pearson, J. R. A. Mechanical Principles of Polymer Melt Processing Permagon Press, Oxford, 1966, pp 32 - 38

Pezzin, Giovanni "Rheology of Molten Polymers" Materie Plastiche Ed Elastomeri (1962) Reprinted and translated in Instron Application Series p 12 Instron Corp., Canton, Ohio

Porter, R. S. and Johnson, J. F. "The Status of Non-Newtonian Polymer Flow" SPE Transactions 3 (1) 18 - 20 (1963)

Ryder, L. B. "The Significant Flow Properties of Thermoplastics" 15th SPE Tech. Conf. 46 - 1 -- 46 - 6

Severs, E. T. Rheology of Polymers Reinhold Publishing Company, N. Y., 1962

Tordella, J. P. "Capillary Flow of Molten Polyethylene-A Photographic Study of Melt Fracture" Transactions of the Society of Rheology 1 203 - 212 (1957)

Tordella, J. P. and Jolly, R. E. "Melt Flow of Polyethylene" Modern Plastics 31 (2) 146 ff (1953)

Westover, R. F. "Processing Properties", Bernhardt, E. C., ed. Processing of Thermoplastic Materials Reinhold Publishing Company, New York, 1957

Wohl, Martin H. "Rheology of Non-Newtonian Materials", Chemical Engineering (February 12, 1968)

Wohl, Martin H. "Instruments for Viscometry", Chemical Engineering (March 25, 1968)