

REPORT

A COMPARISON OF TECHNIQUES FOR MEASURING THE FLOW PROPERTIES OF ONE COMPONENT FILLED EPOXY ADHESIVES

A. OLUSANYA

June 1996

CMMT(A)19

NPL 
National Physical Laboratory

**MTS Adhesives Project 5
Measurements For Optimising Adhesives Processing
Report 1**

**A Comparison of Techniques for Measuring
the Flow Properties of One Component
Filled Epoxy Adhesives**

A OLUSANYA

This report represents the deliverable for Task 3a. - Rheology

June 1996

A Comparison of Techniques for Measuring the Flow Properties of One Component Filled Epoxy Adhesives

A OLUSANYA

Centre for Materials Measurement and Technology
National Physical Laboratory
Teddington
Middlesex, UK, TW11 0LW

ABSTRACT

This report compares the data obtained by a range of instruments which can be operated in various modes. Use is made of the Cox-Merz relationship to compare data obtained by laboratory instruments at relatively low strains to data obtained by capillary extrusion measurements which can achieve shear rates similar to those occurring in processing. Modifications were made to the commercial constant stress rheometry instrument in order to eliminate the experimental errors due to the non-parallelism of the test geometries used. Discrepancies attributable to the data processing techniques were also found and are commented upon.

© Crown copyright 1996
Reproduced by permission of the Controller of HMSO

ISSN 1361-4061

National Physical Laboratory
Teddington, Middlesex, UK, TW11 0LW

No extracts from this report may be reproduced without
the prior written consent of the Managing Director
National Physical Laboratory; the source must be acknowledged

Approved on behalf of Managing Director, NPL, by Dr M K Hossain,
Director, Centre for Materials Measurement and Technology

CONTENTS

	Page
1 INTRODUCTION	1
2 MATERIALS	2
3 EXPERIMENTAL AND DISCUSSION	2
3.1 Equipment	2
3.2 Calibration	3
3.3 Adhesives Testing	5
3.3.1 Rotational Rheometry	5
3.3.2 Capillary Extrusion Rheometry	9
3.3.3 Oscillatory Rheometry	10
4 CONCLUSIONS	10
5. REFERENCES	12
6. LIST OF FIGURES	12

1 INTRODUCTION

Adhesives are used in a multiplicity of manufacturing sectors, enabling the joining of various materials. Despite the advanced nature of modern adhesives and the penetration of these materials into wide ranging markets, the availability of basic data pertaining to their processing properties is still at a low level. This project "Measurements for Optimising Adhesive Processing", (ADH5), is one of five within the research programme, Tests and Measurement Methods on the Performance of Adhesive Joints, sponsored by the Department of Trade and Industry. This project, ADH5, is specifically aimed at providing measurement methods which are required by manufacturing industries to aid production and, thus increase the confidence of users and potential users of adhesives.

Single component heat-curing epoxy adhesives have a widespread use particularly in automotive manufacturing processes. These adhesives generally consist of liquid epoxy resins combined with reinforcing fillers, curing agents, modifying agents and plasticisers. They are relatively stable at room temperatures for extended periods and are processed as pumpable pastes or liquids. For optimising of the dispensing process, characterisation of the flow behaviour is required. Typical shear rates for adhesive dispensing in automotive applications are of the order $5 - 150 \text{ s}^{-1}$. Processing performance is affected by the inherent properties of the adhesive for example viscosity and yield stress and the process variables, including flow rate and application temperature.

The complex composition of these adhesives means that their rheological properties deviate significantly from Newtonian behaviour, ($\text{stress} = \text{strain rate} \times \text{viscosity}$). Therefore characterisation of the flow properties is essential in understanding and modelling the adhesive application process. The use in industry of a wide range of differing measuring instruments poses a problem. In principle, there should be no variability in the reported properties of a material from correctly maintained and measurement instruments, however differences in operating procedures have lead to difficulties in the interpretation of data from the various sources.

2 MATERIALS

Three high temperature curing one component epoxy adhesives were used in this study. These adhesives have been designed for semi-structural applications. A major user is the automotive sector, where adhesives are used in the bonding of strengthening members for car bonnets and in conjunction with weld bonding for door panels. Typical cure cycles are given in Table 1.

Table 1: Basic cure properties of the test adhesives.

Adhesive	Type	Cure Temperature (°C)	Curing Time (min)
Ciba-Geigy XB5315	Toughened Epoxy	180	30
PPG 3289Y5000	Polybutadiene/Epoxy	190	20
3M Scotchweld 7823G	Corrosion resistant epoxy	120/180	180/30

3 EXPERIMENTAL AND DISCUSSION

3.1 Equipment

Flow curves were obtained for the three test adhesives using

- i) Contraves Rheomat 30 rotational rheometer (Figure 1)
- ii) TA Instruments (formerly Carrimed) 500 CSL controlled stress rheometer, (Figure 2)
- iii) Carter-Baker Enterprises/NPL RACER capillary die extrusion rheometer (Figure 3).

Flow curves were obtained by use of the Contraves and TA instruments using cone and plate, parallel plate and concentric cylinder (cup and bob) geometries.

3.2 Calibration

A calibration procedure using PTB certified reference oils in range 0.71Pa.s - 12Pa.s was conducted to establish the conversion coefficients for the Contraves instrument. This procedure related the rotational speed of the instrument with the measured torque for a given reference oil of certified viscosity and measurement geometry. The range of reference oils was selected to cover the anticipated viscosity of the adhesives to be tested. For this series of measurements the geometries employed were concentric cylinders and cone and plate. The TA constant stress rheometer was checked by using PTB reference oils with certified viscosities in the range 1 - 13Pa.s. Flow curves for the adhesives were then obtained (Figures 4, 5 and 6). The hysteresis effect seen for the "up" and "down" flow curves and for repeat experiments carried out shortly after the initial testing is attributed to the reduction in viscosity due to work applied to the sample.

The accuracy of measurement of rotational rheometry at high shear rates can be impaired by expulsion of material from the gap for the parallel plate and cone and plate methods, and by creep of material up the shaft when using the concentric cylinder method.

The constant stress rheometer can be operated in three basic modes and each was assessed individually:

- i) Measurement directly on the peltier plate.
- ii) Using the High Temperature System attachment (Figure 7)
- iii) Using a disposable plate system for use with adhesives and similar materials (Figure 8).

The data obtained from the reference oils using modes i and ii gave good agreement with the quoted values. However, there was a large discrepancy with the viscosity values obtained using the disposable plate system as can be seen from the data presented in Figure 9. The discrepancy could be attributed to variations in the measurement gap between the "parallel" plates caused by poor alignment of the measurement system.

The error due to poor parallel alignment has a greater influence at small gaps. The angle of deviation from parallel is constant, thus at ever decreasing measurement gaps the relative error in measurement will increase. This can be more easily seen from the constitutive equations.

For example, for the case of a parallel plate geometry with a radius, D and a measurement gap, d , the shear stress measured at d is given by equation 1:

$$\sigma = \frac{2}{\pi D^3} \tau \quad (1)$$

where σ = shear stress and τ = torque

$$\gamma = \frac{D}{d} \omega \quad (2)$$

where γ = shear rate and ω = angular displacement

When d is small, the error in γ caused by errors in d is relatively large. Deviations from parallel are shown in Figure 10. These deviations were measured by a dial gauge attached to the air bearing shaft rotating through a single revolution. Modifications based upon the design of the high temperature system were made which would allow better alignment of the measurement system. These modifications were produced by TA Instruments to the specification submitted by NPL. However, due to the delays in delivery, measurements reported here were made using the high temperature system or directly on the peltier plate (normally protected by a flat polished cover plate).

3.3 Adhesives Testing

3.3.1 Rotational Rheometry

Following calibration, the next stage was to assess the flow characteristics of the adhesives to be used in subsequent studies. Li, Masich and Dickie⁽¹⁾ used constant shear stress and constant shear rate rheometry methods to generate flow curves of one component paste adhesives. An adhesive which had similar characteristics to one of those reported was obtained from Ciba-Geigy, adhesive XB 5315.

The experimental flow curves for adhesive XB5315, (Figures 11,12 and 13) show similar trends to those reported⁽¹⁾ for the similar adhesive, XB3131 obtained using similar stress and shear rate procedures. The data was analysed using the Casson equation, (Equation 3).

$$\sigma = (\sigma_y^{1/2} + K^{1/2} * \gamma^{1/2})^2 \quad (3)$$

where:

σ = stress

σ_y = yield stress

K = Casson viscosity coefficient

and

γ = shear rate

The Casson equation proved a good model to describe the data, however there was concern over differences between the results obtained using the analytical software supplied with the rheometer and the parameters calculated using alternative commercial mathematical packages. Typical values are given in Table 2 from data presented in Figures 11-13.

Table 2: Computed values of yield stress and the Casson viscosity at various temperatures

Material: Ciba Geigy XB5315	TA Instruments (basic mode)	TA Instruments (Simplex)	Fig P	TA Instruments (basic mode)	TA Instruments (Simplex)	Fig P
Temperature	K Casson viscosity coefficient	K Casson viscosity coefficient	K Casson viscosity coefficient	σ_y Yield stress	σ_y Yield stress	σ_y Yield stress
°C	Pa.s	Pa.s	Pa.s	Pa.	Pa.	Pa.
5	2387	1996	1971	404	515	508
15	585	496	496	386	484	484
25	174	142	142	320	440	440

TA Instruments currently supply the CSL rheometer with a data analysis software package for use with Microsoft Windows V3.1. The software has the option to operate using a Simplex linear programming analysis procedure. A full description of the mathematical method is given in Numerical Recipes in Fortran: The art of Scientific Computing by Press et al ⁽²⁾.

The use of this mode of operation gave results which are in close agreement with those calculated by a commercial graphics and data analysis package, Biosoft Fig P. This can be seen from the data presented in Table 2. The Fig P package uses the Marquardt-Levenberg analytical method which has become the standard for non-linear least squares routines⁽²⁾.

The Casson equation (3) can be rearranged to give:

$$\sigma^{1/2} = \sigma_y^{1/2} + K^{1/2} * \gamma^{1/2} \quad (4)$$

The variables σ and γ were scaled by taking square roots and the data were fitted in Fig P using the linear function:

$$y = mx + c \quad (5)$$

This gave yield and viscosity values which were in agreement with the basic mode of TA analysis. This result indicates that the basic analysis mode of TA software calculates the Casson viscosity coefficient as a reduced linear function, Figure 14. As the absolute values of the data are smaller when the square root is taken, the sum of the squares is also smaller and as the span of the data has been reduced, less weighting is given in the analysis to the larger data values. This exercise has shown that the use of a simple approach to solve the Casson function can lead to discrepancies with solutions obtained using more complex mathematical procedures. Different approaches to data analysis may produce different values for the rheological parameters. It is for the researcher to decide the validity of the mathematical approach used and the relevance of the variation in derived coefficients in relation to the ultimate use of the data. However the method used to determine these rheological coefficients should be stated to allow similar mathematical treatment.

Figure 14 shows the result of solving the Casson equation as a linear function (ie. taking the square root of the data). It can be seen that the Casson equation does not successfully describe the flow behaviour below 0.5s^{-1} . The investigation of functions to describe the flow characteristics more fully was not performed as the information was analysed over a comparable range as previous work⁽¹⁾, $0.1 - 10\text{s}^{-1}$.

Further investigation has also shown that differences between rheological parameters are also encountered when determining the viscosity of Newtonian fluids using different mathematical approaches. A Newtonian liquid, PTB reference oil was measured and the data and analyses are presented in Figure 15.

Differences were found to be due to treatment of the yield parameter from the Bingham viscosity equation, (Equation 8).

$$\sigma = \tau_y + \eta \gamma \quad (6)$$

where:

σ = stress, τ_y = yield stress = 0 for the special case of a Newtonian fluid

η = Newtonian viscosity and γ = shear rate

Line 1 (red) results from a linear regression solving for the viscosity and yield stress. Line 2 (green) shows the effect of adjusting the yield stress to zero but maintaining the same viscosity, (gradient). This is the case actually presented by the instrument. Line 3, (blue) shows the situation where a yield stress of zero is set, ie. Newtonian flow, the dynamic viscosity is calculated to be 12.39Pa.s.

PTB derive viscosities for their reference oils by a primary method based on capillarity. The flow data resulting from such methods after allowing for temperature and other experimental effects enables the calculation of fluid viscosities. PTB make it clear in their literature that use of these reference fluids for calibration of a rotational rheometry system requires that the instrument's rotational torque also to be calibrated. However, the discrepancy in the results presented here can not be solely attributed to experimental errors, a large proportion of the error results from the method of data processing used. An explanation for this approach of solving for a notional yield and assuming the same gradient but with zero yield, is that it compensates for the errors at low shear rates which could be assigned to the resolution of the measurement instrument. This approach can lead to anomalies when comparing data acquired by different manufacturers and/or different operators who expect a yield stress of zero in their calculations of a Newtonian viscosity.

As mathematical software packages are designed to allow the user to tailor the use of the selected functions for their own use, the fact that discrepancies can arise when resolving data for simple functions requires standardisation in methods of data presentation. Discussions will be undertaken with TA as to their methods of analysis. For the present it is advisable to include a brief description of the analytical method used to allow the identification of the mathematical parameters when presenting calculated viscosity data.

The increased modelling of rheological properties and the use of elaborate mathematical software packages to solve proposed equations combined with extant calculated parameters can lead to fundamental errors being combined into new models describing the rheological behaviour of materials. The present work highlights the requirement for standard methods for presenting flow data, this obviously requires the co-operation of instrument manufacturers and rheological software suppliers with investigators in the field.

3.3.2 Capillary Extrusion Rheometry

A Carter Baker Enterprises NPL Racer capillary die rheometer was used to obtain flow data at high shear rates. Due to a restricted range of dies, only a limited range of shear rates was used. These data are presented in Figure 16 and are compared to flow data obtained by constant stress and Contraves techniques. A good correlation can be seen between the higher rate rotational data and the lowest rate capillary data, despite the limited range of capillary die data. The Carter-Baker Enterprises/NPL RACER capillary die extrusion rheometer as developed at NPL has the capability to operate at shear rates as low as 10s^{-1} by use of the appropriate die. Dies with an aperture of 4mm have now been received and a number of experiments will be carried out to extend the range of the data obtained by use of the capillary die technique.

3.3.3 Oscillatory Rheometry

An alternative method of obtaining rheological data is by use of oscillatory rheometry covering a range of frequencies. Data collected by this method can be compared with constant flow data by use of the Cox-Merz relationship⁽³⁾, Figure 17, provided that the material is tested within its linear viscoelastic region. Measurements are difficult for filled systems as these tend to have a very limited linear viscoelastic range, if any at all. A subsequent shear stress sweep established the material's linear viscoelastic region. From this data it could be seen that the data displayed in Figure 16 for low shear rates was collected outside the linear visco-elastic region. Thus the difference between the two curves has been attributed to the strain dependence of the viscosity for the material.

4 CONCLUSIONS

This work has highlighted the importance of checking the calibration procedures for rotational rheometry instruments to ensure the accurate determination of rheological parameters. The method/s used in the mathematical treatment of the raw data in the determination of these rheological parameters should be stated clearly.

The comparison of viscosity measurement techniques indicated good agreement between the rotational methods used. Further work on the use of the capillary die technique is necessary to acquire more data to compare with rotational techniques. The lack of a linear viscoelastic region for the materials investigated severely limits the use of the Cox-Merz relationship for determining steady shear flow data from oscillatory measurements.

A major concern is the interpretation and mathematical implementation of analysis routines for the determination of rheological parameters. The software supplied by TA Instruments (V1.13 for Windows and V5.59 for DOS) calculates the Newtonian viscosity permitting a yield parameter. Previous versions of the TA Instruments DOS software V5.2 and V5.4 have also been configured in a similar way. As seen from Figure 15, a Newtonian fit, (Equation 6), to the experimental data gives a poor correlation with the data.

The method of determining the Casson viscosity can influence the values calculated for rheological constants. Discussions will be held with TA as to the operation of their software.

Comparison of the overall flow behaviour of the adhesives tested with those reported by Li et al⁽¹⁾ indicates that the adhesives tested have similar flow characteristics and, that within the limitations of the software, these can be described by the Casson equation.

In conclusion, there is a requirement for standard methods for presenting flow data, this obviously requires the co-operation of instrument manufacturers and rheological software suppliers with investigators in the field.

5. REFERENCES

1. Li C, Masich K A, Dickie, R A. A survey of rheological properties of one-component epoxy adhesives. J. Adhesion 1990 32.
2. Numerical recipes in Fortran the art of scientific computing
W.H.,Press, S.A. Teukolsky, W.T. Vetterling, B.P., Flannery
2nd edition Cambridge University Press
3. Cox W P, Merz E H J. Polym. Sci 1958 28 pp619-622

6. LIST OF FIGURES

- 1 Photograph of a Rheomet 30 rheometer
- 2 Schematic of TA 500 CSL Rheometer
- 3 The Carter-Baker Enterprises/NPL RACER capillary die extrusion rheometer
- 4 Casson viscosities and yields for PPGY5000 using cone and plate and concentric cylinder geometries
- 5 Flow curves for 3M 7823G adhesive measured using constant stress rheometry
- 6 Casson viscosities and yields for Ciba-Giegy XB5315 using concentric cylinders
- 7 The high temperature system of the TA 500 CSL rheometer
- 8 Schematic of the modified disposable plate system for the TA 500 CSL rheometer
- 9 The variation of apparent viscosity with measurement gap for a reference oil
- 10 Variation from parallel of a 4cm parallel plate around it's periphery
- 11 Ciba XB5315 adhesive shear stress sweep at 5°C
- 12 Ciba XB5315 adhesive shear stress sweep at 15°C
- 13 Ciba XB5315 adhesive shear stress sweep at 25°C
- 14 Linear fit of Casson function for Ciba-Giegy XB5315 adhesive
- 15 PTB reference oil depicting calculated Newtonian analyses.
- 16 Comparison of viscosities obtained by parallel plate (constant flow), capillary die and concentric cylinder techniques.
- 17 Comparison of viscosities obtained by dynamic (oscillatory), capillary die and concentric cylinder techniques.

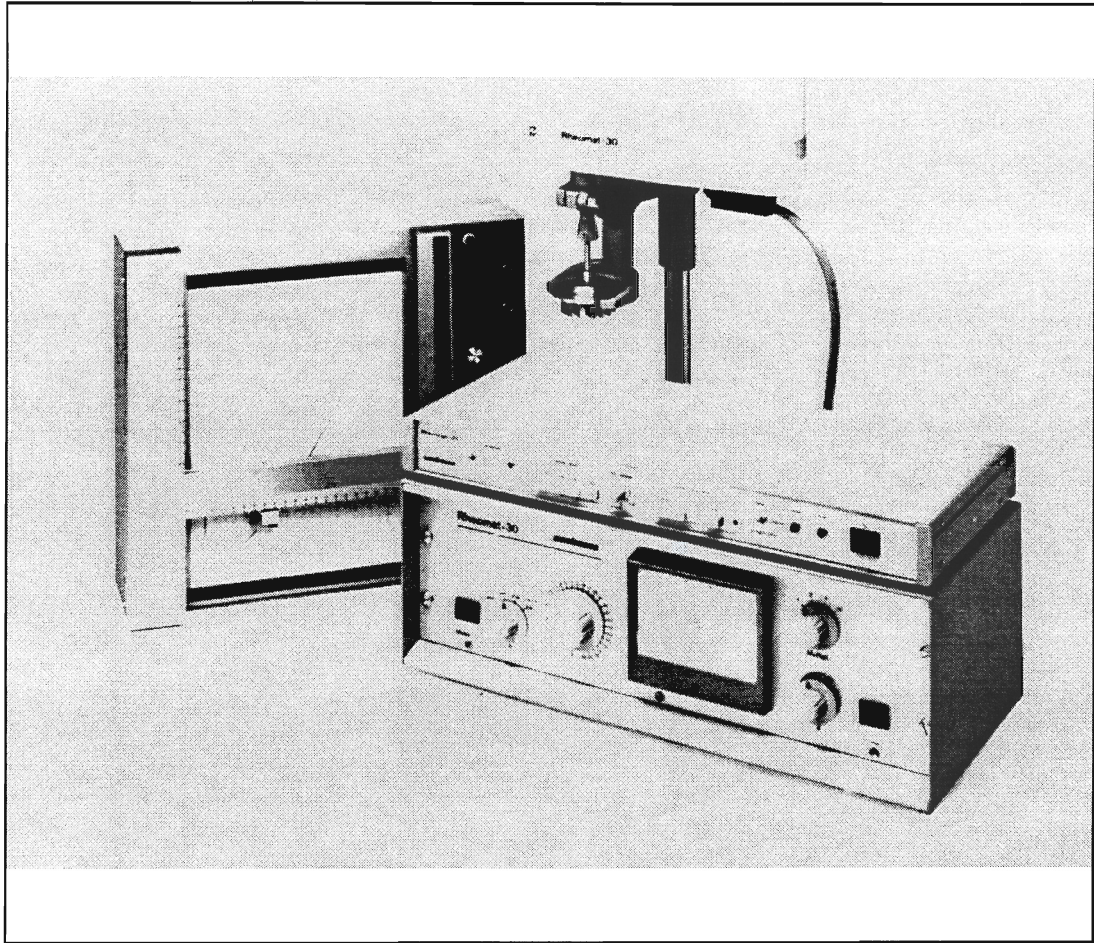


Figure 1: Photograph of a Rheomet 30 rheometer

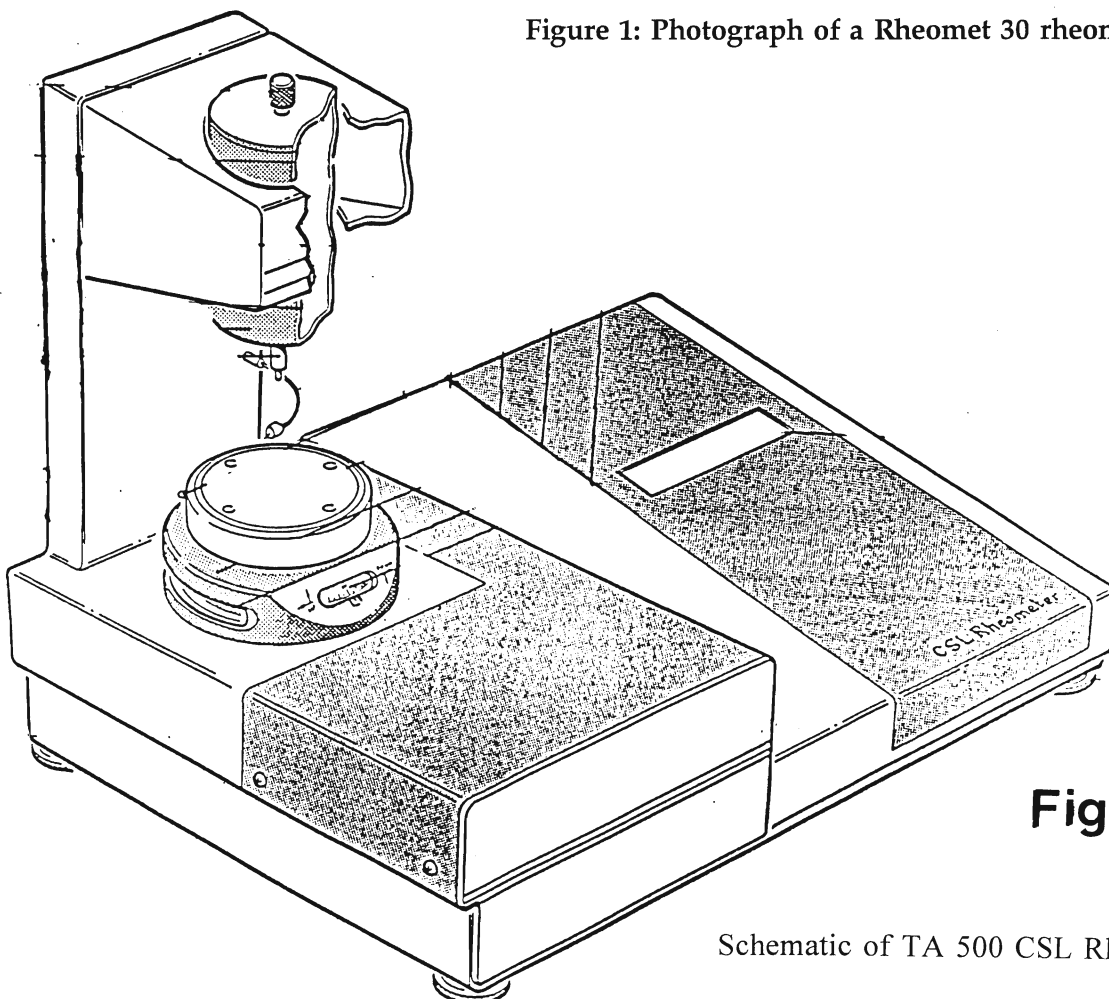
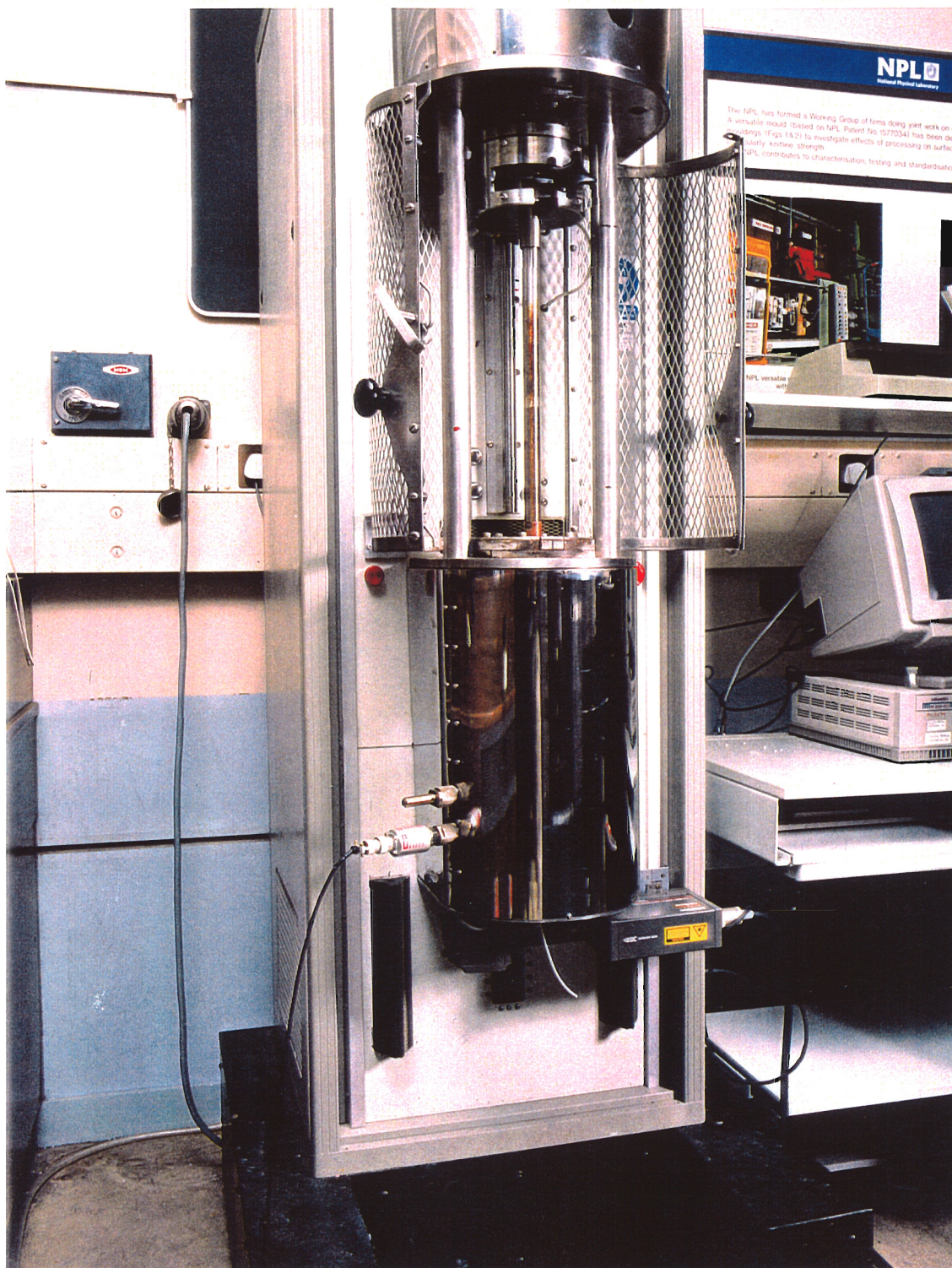


Figure2

Schematic of TA 500 CSL Rheometer



The Carter-Baker Enterprises/NPL RACER capillary die extrusion rheometer

Figure 3

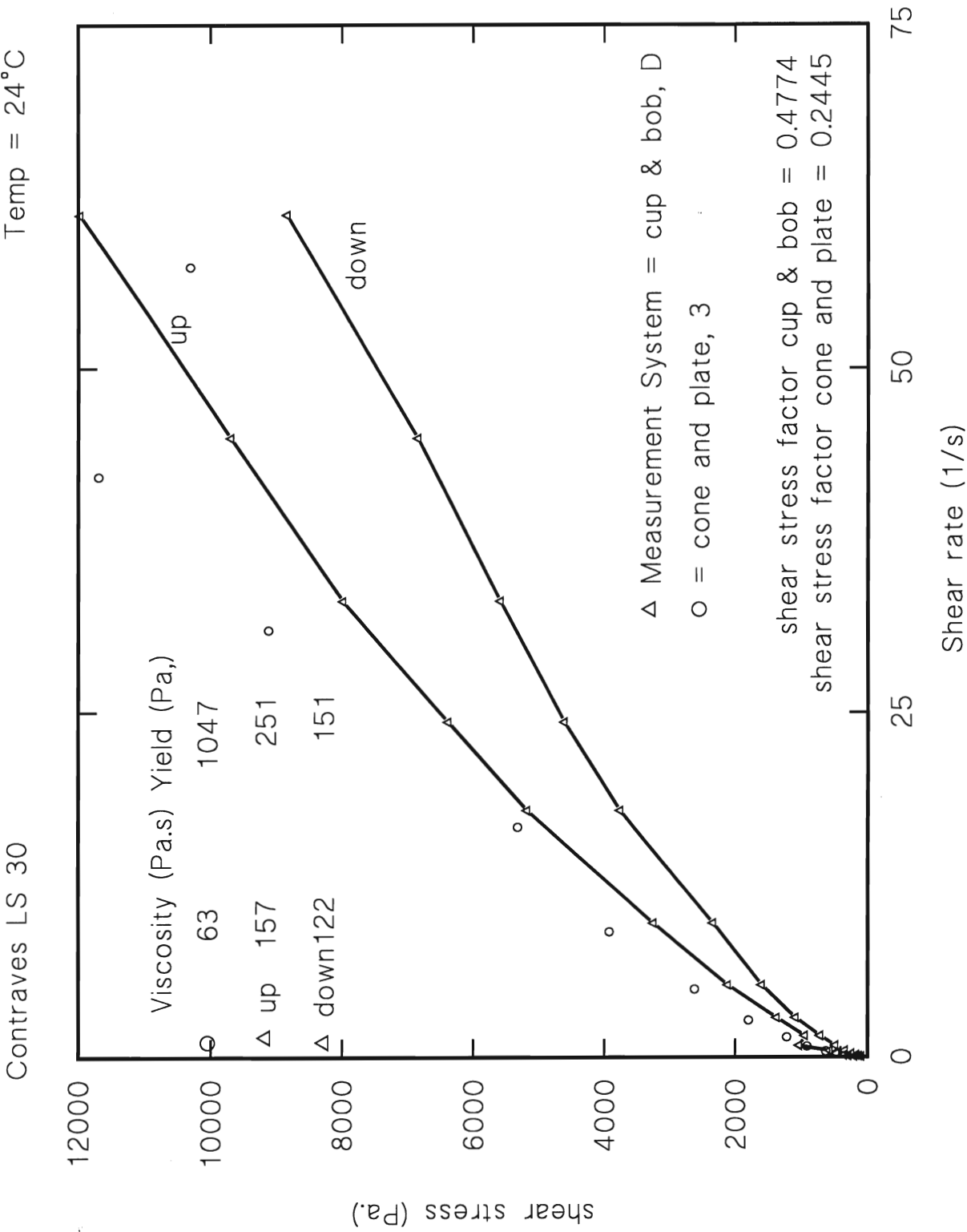
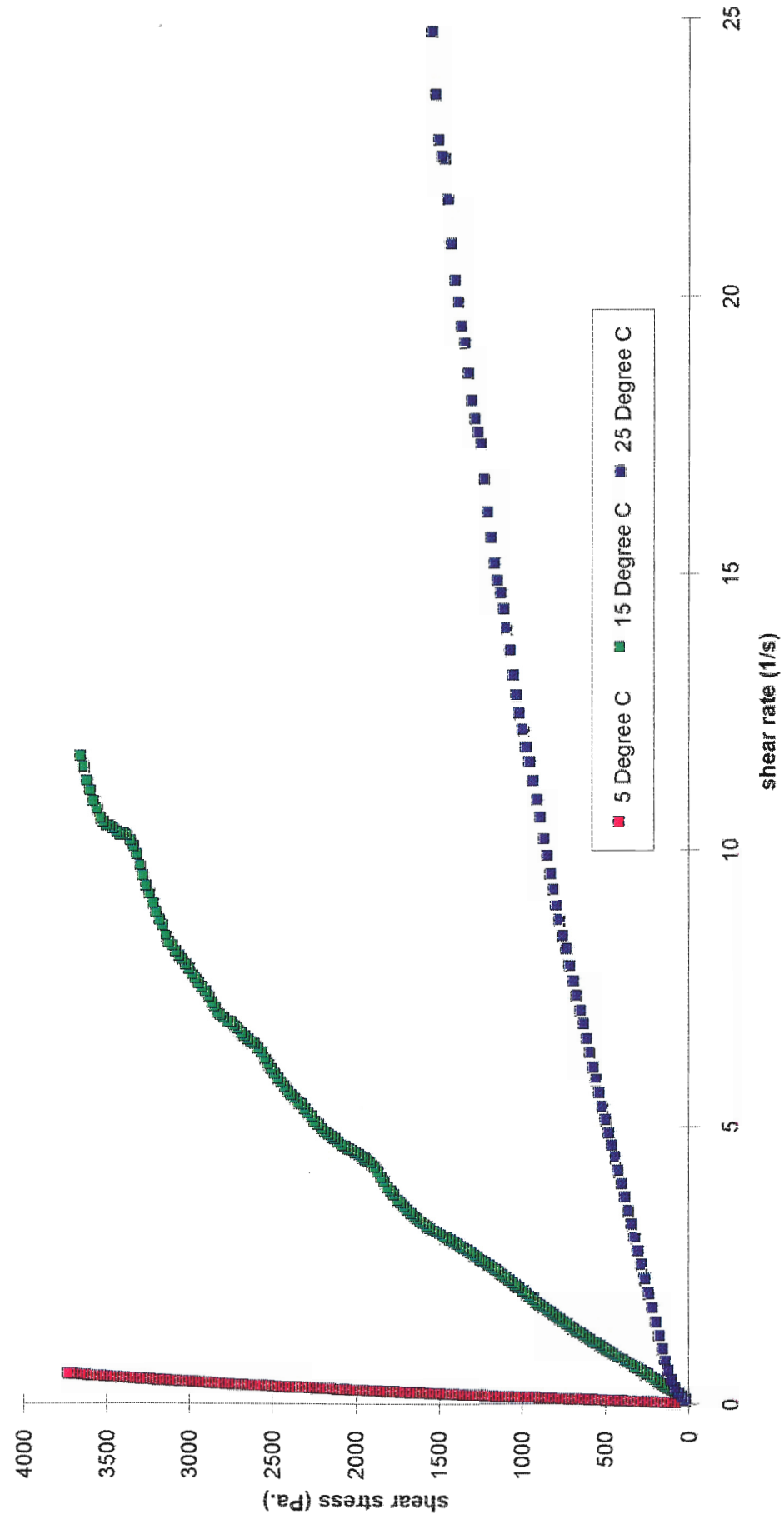


Figure 4 Casson viscosities and yields of PPGY5000

Figure 5: Flow curves for 3M 7823G adhesive measured using constant stress rheometry
Measurement geometry = 4cm parallel plate



Contraves LS30, cup & bob, MS D

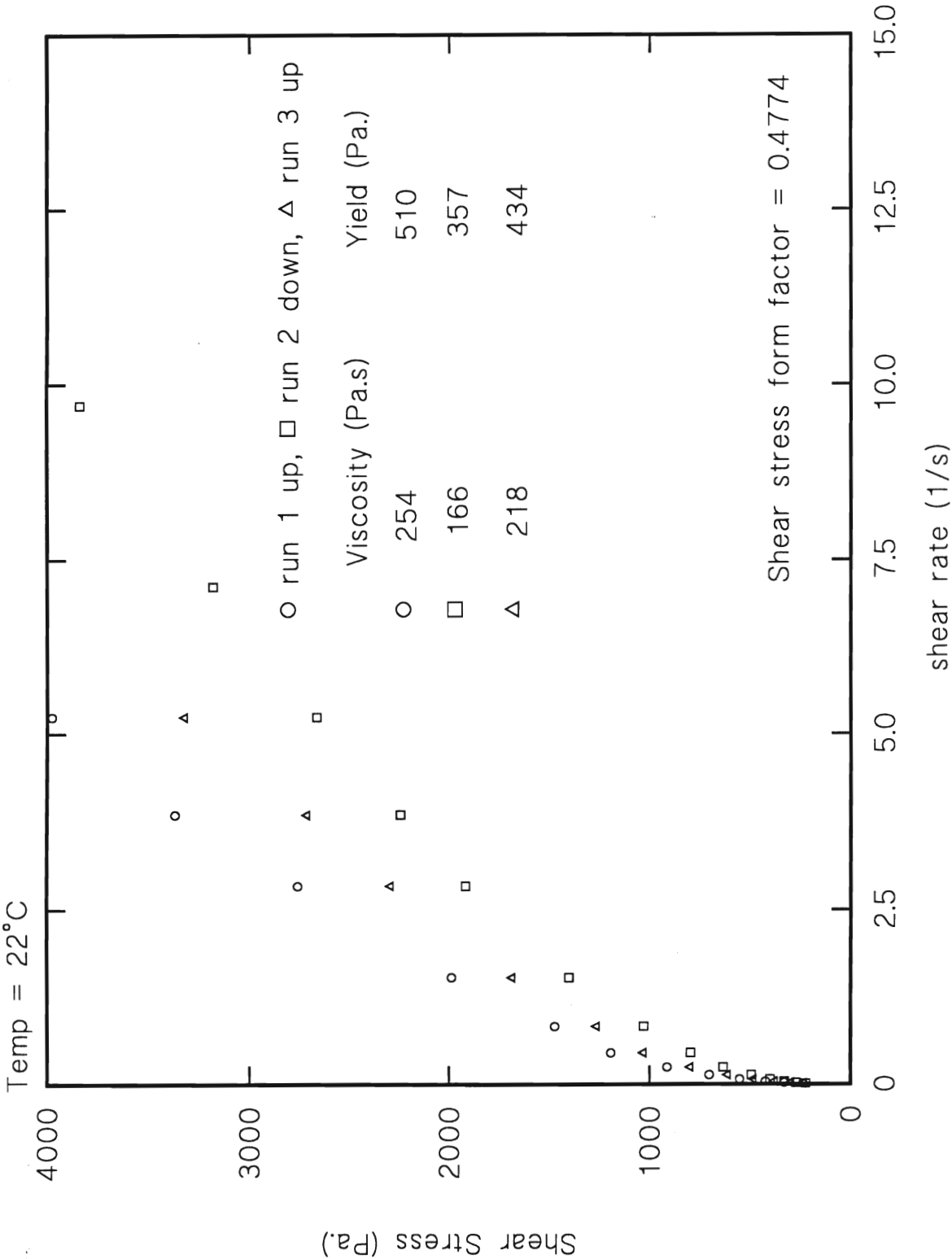
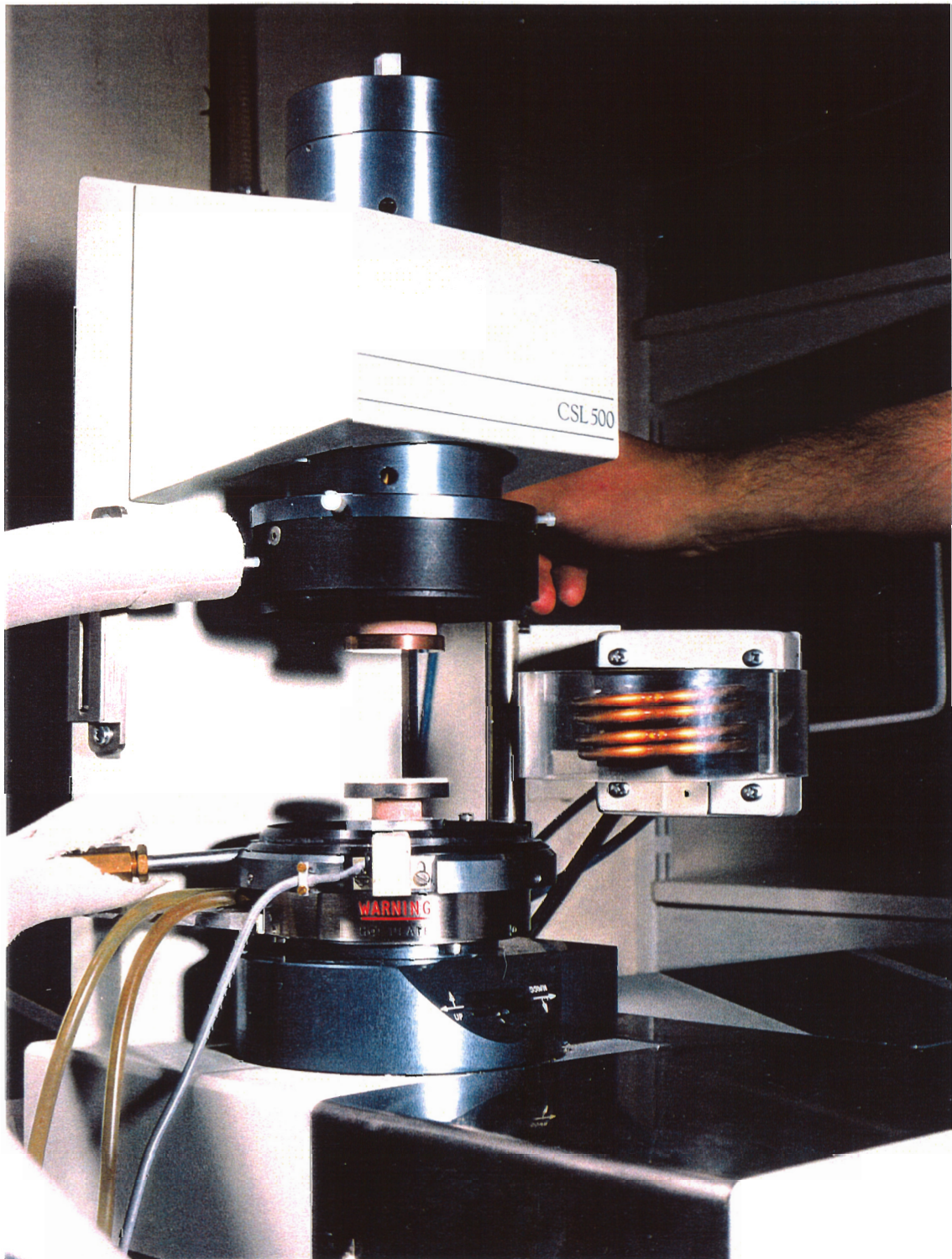


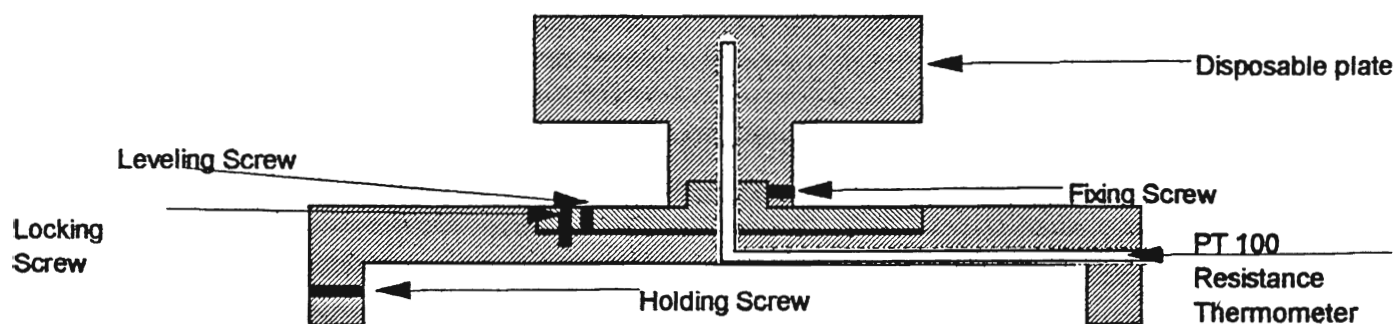
Figure 6 Casson viscosities and yields for XB5315 using cup and bob geometry



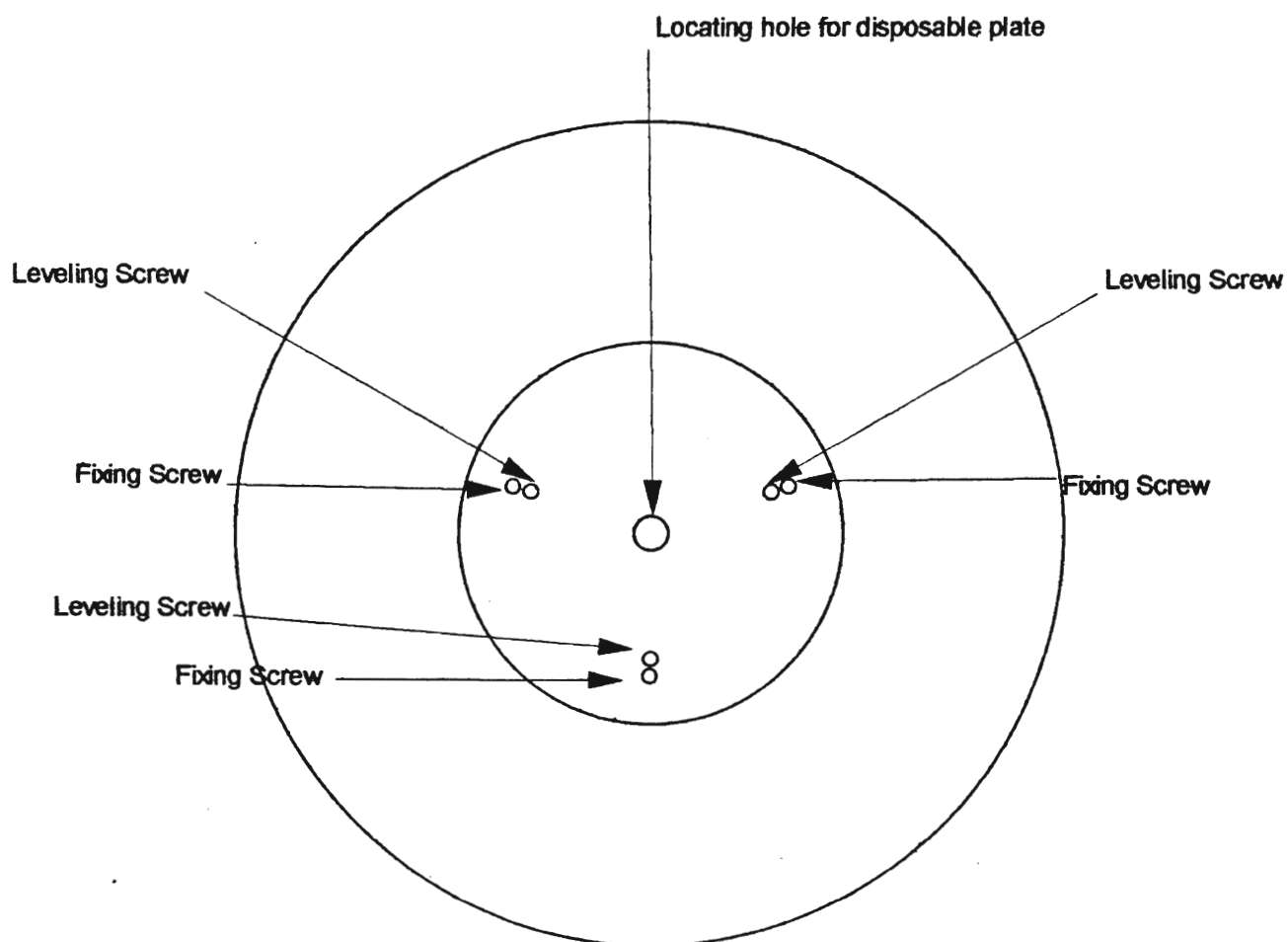
The high temperature system of the TA 500 CSL rheometer

Figure7

Plan View (cutaway)



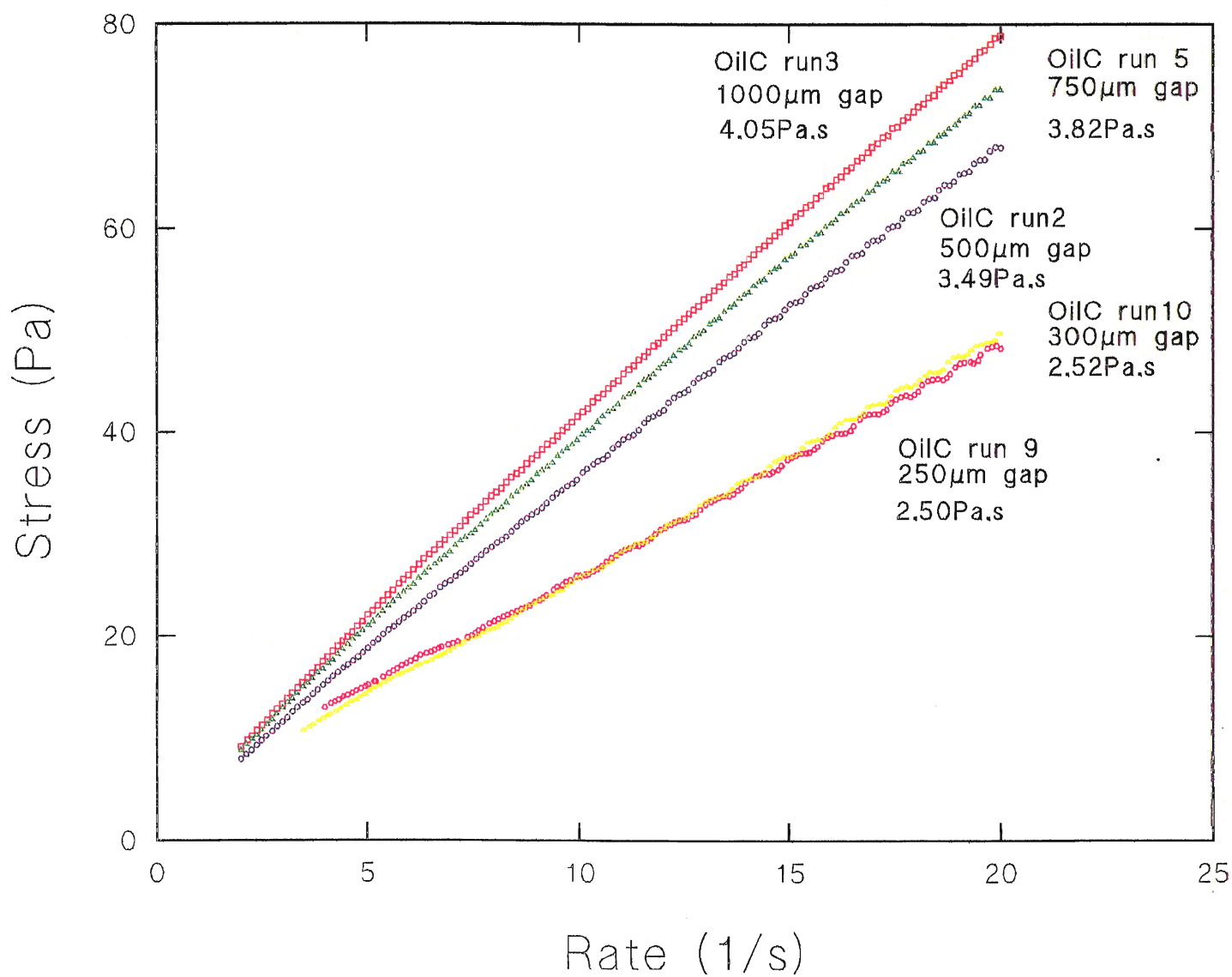
Top View



Schematic of the modified disposable plate system for the TA 500 CSL rheometer

Figure 8

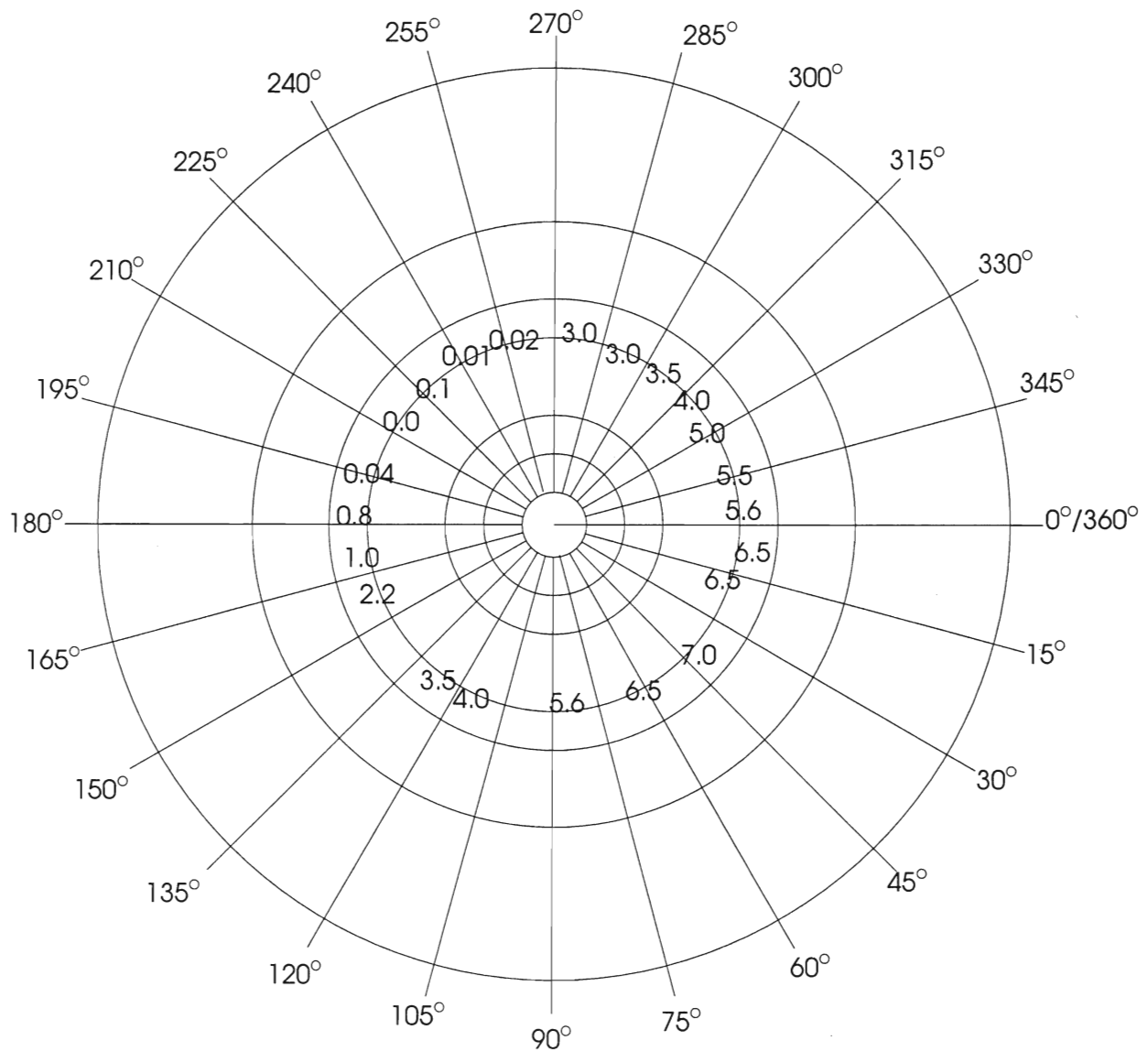
PTB Standard Oil Quoted Viscosity at 25°C = 5.049Pa.s
4cm disposable parallel aluminium plates



The variation of apparent viscosity with gap for a PTB reference oil measured using the TA 500 CSL rheometer

Figure9

Variation from parallel of a 4cm disposable aluminium lower parallel plate around the periphery (deviations in microns)



Top plate variation = 2 microns

Variation from parallel of a 4cm parallel plate around it's periphery

Figure 10

Ciba XB5315 Adhesive Shear Stress Sweep at 5°C (Casson Fit)

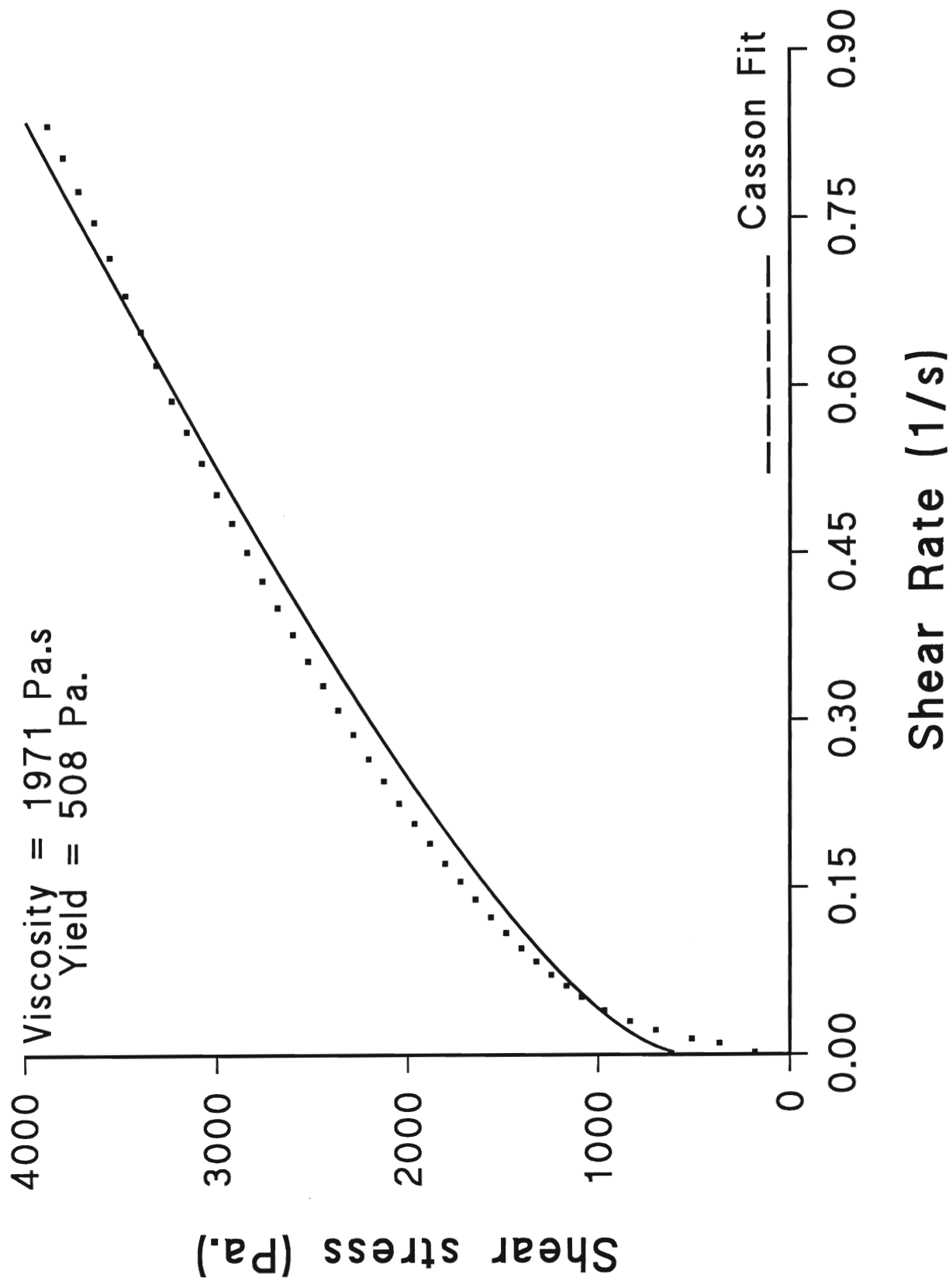


Figure 11

Ciba 5315 Adhesive Shear Stress Sweep at 15°C (Casson Fit)

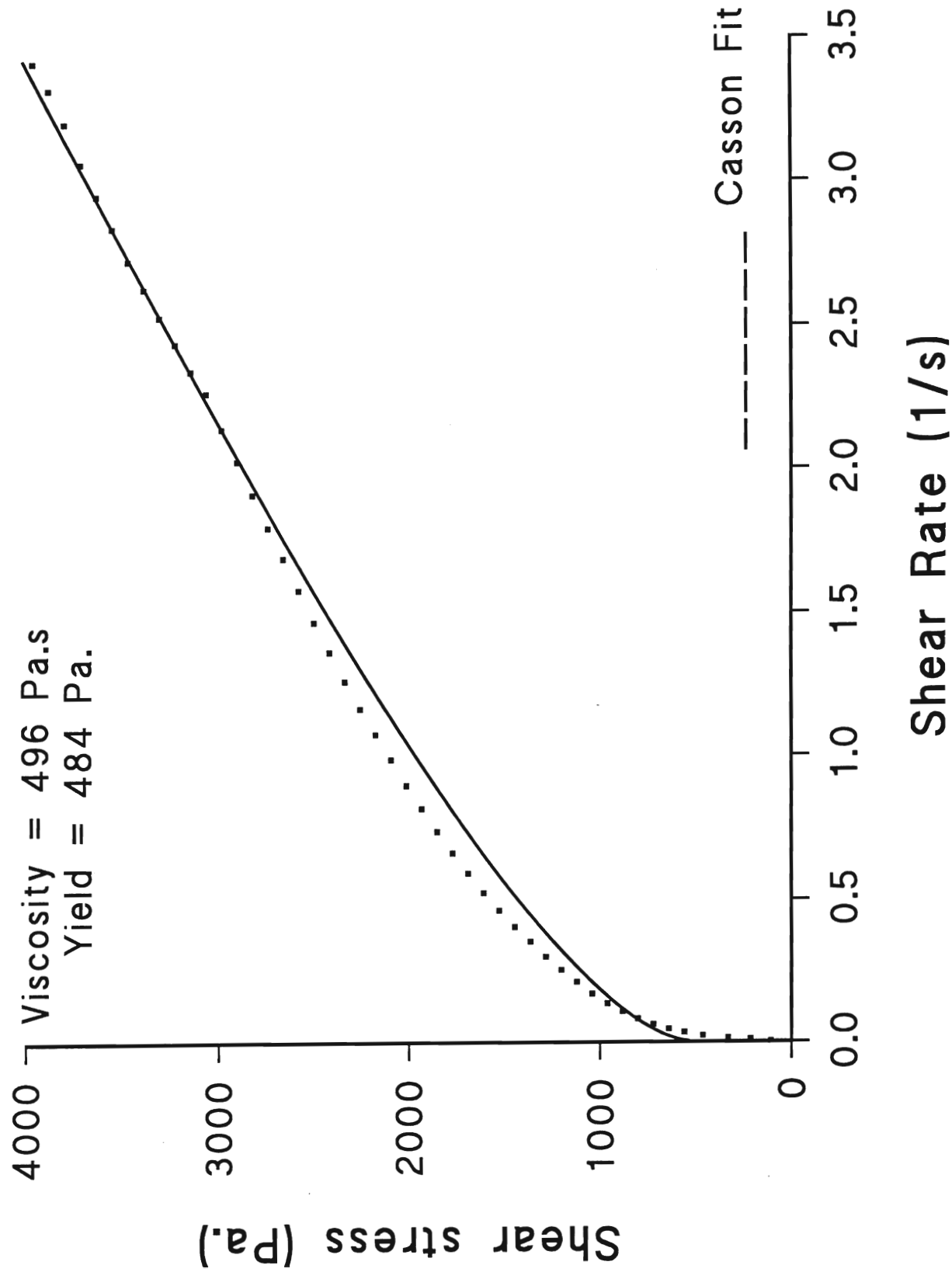


Figure 12

Figure 13: Ciba 5315 Adhesive Shear Stress Sweep at 25°C

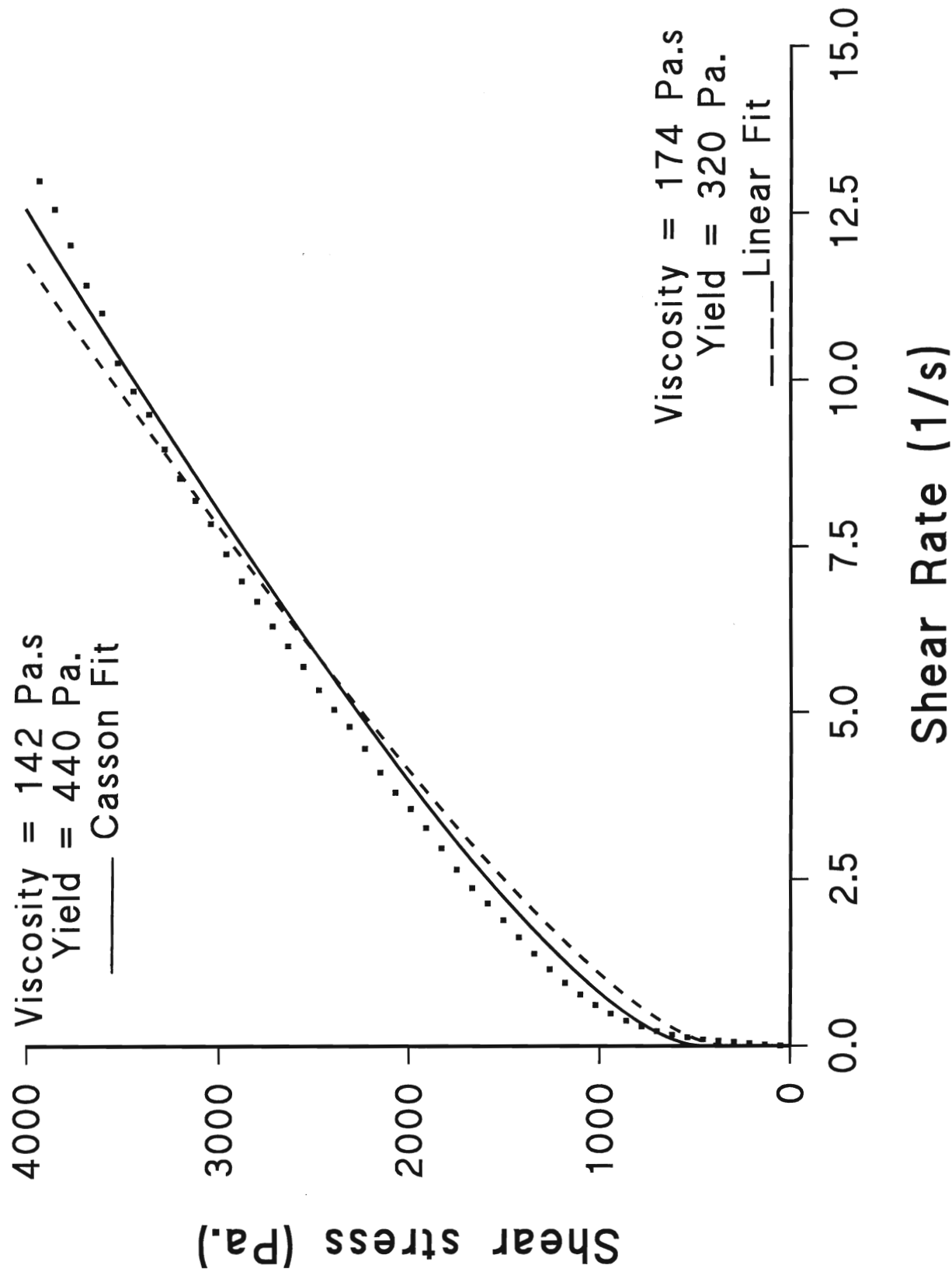


Figure 14: Linear fit of Casson function

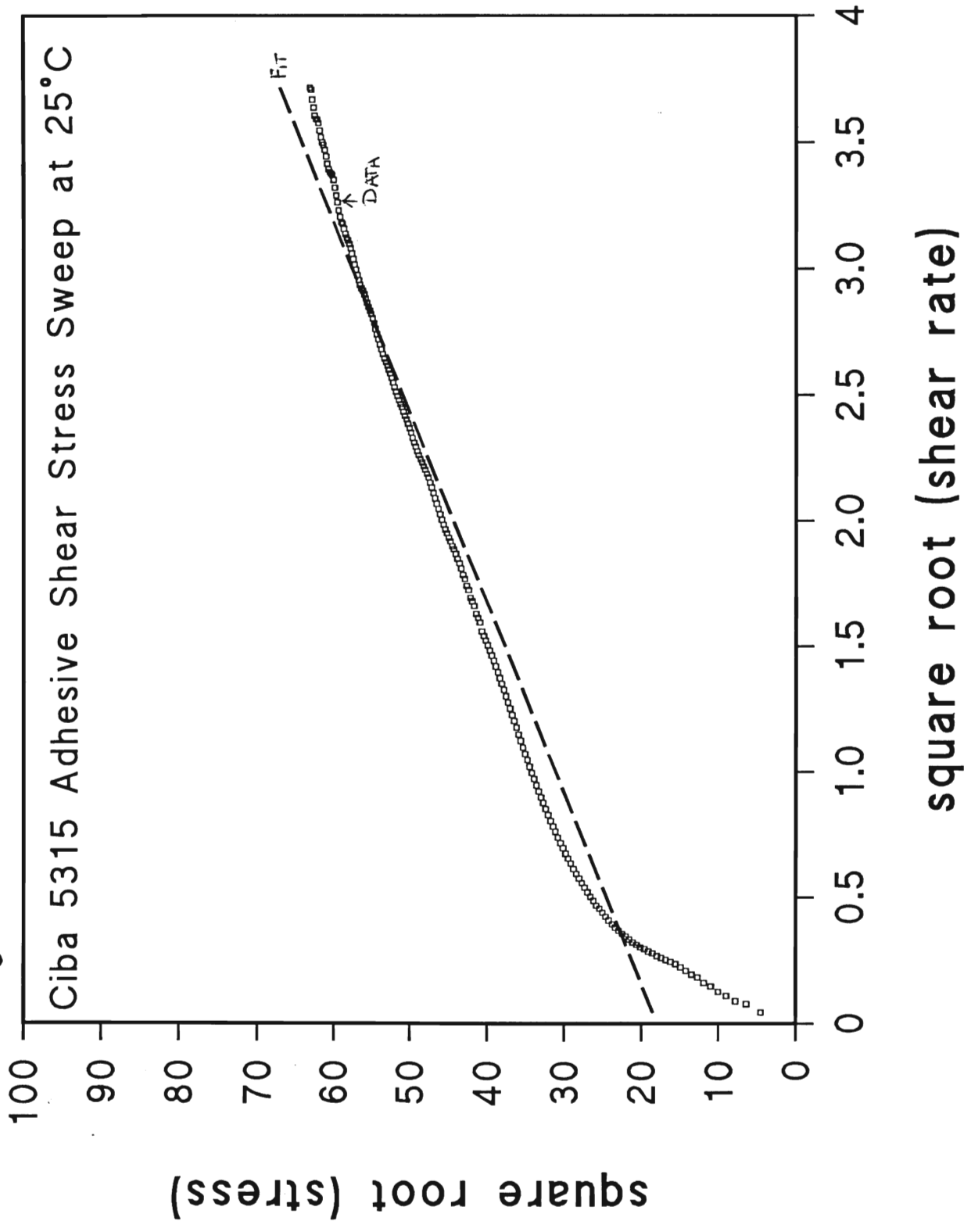
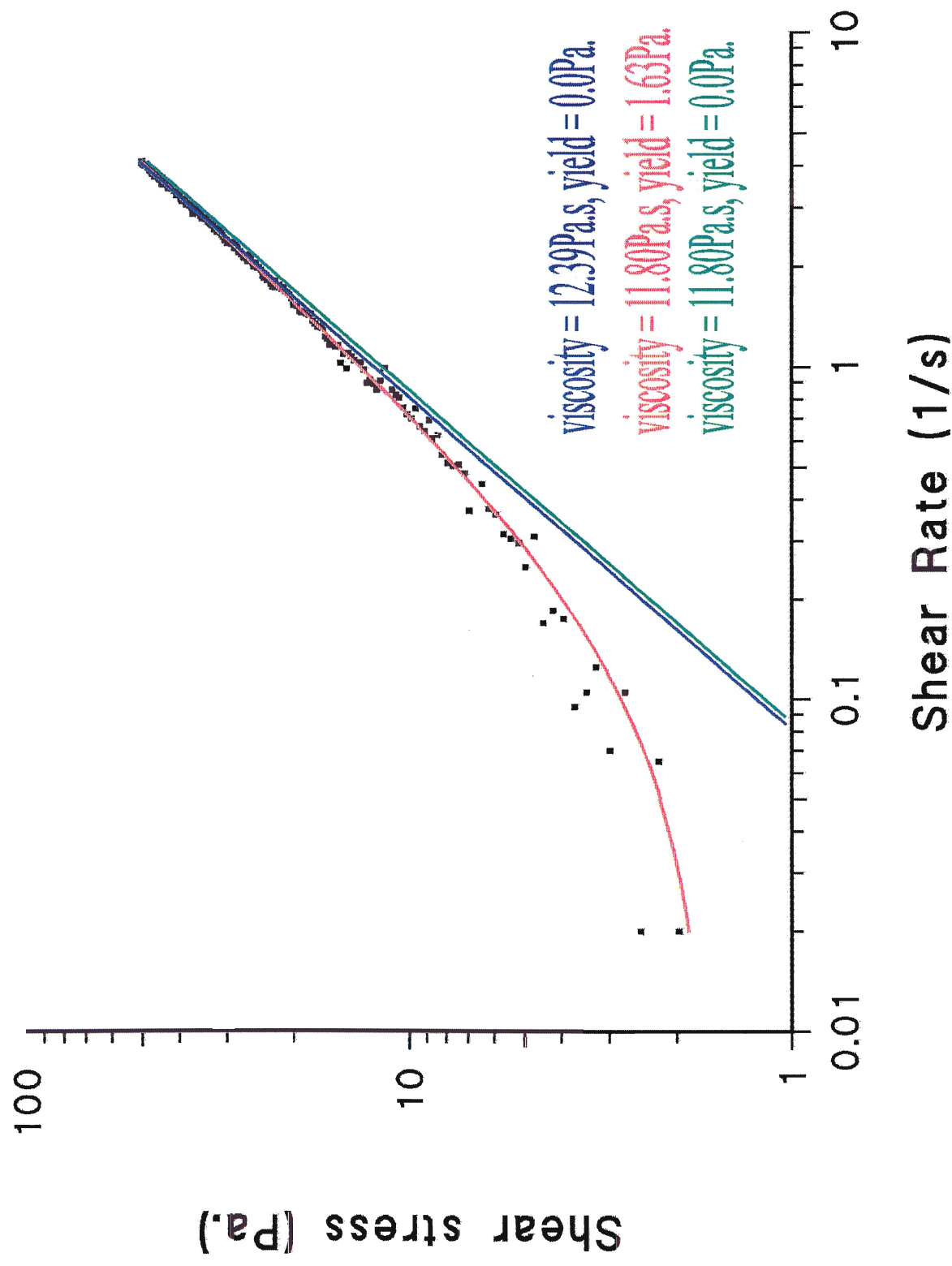


Figure 15: PTB Reference Oil (12.23 Pa.s) calculated Newtonian fits.



Nominal Temp. 25°C
Ciba-Geigy XB5315

Figure 16: Comparison of constant stress, capillary die and Contraves measurements

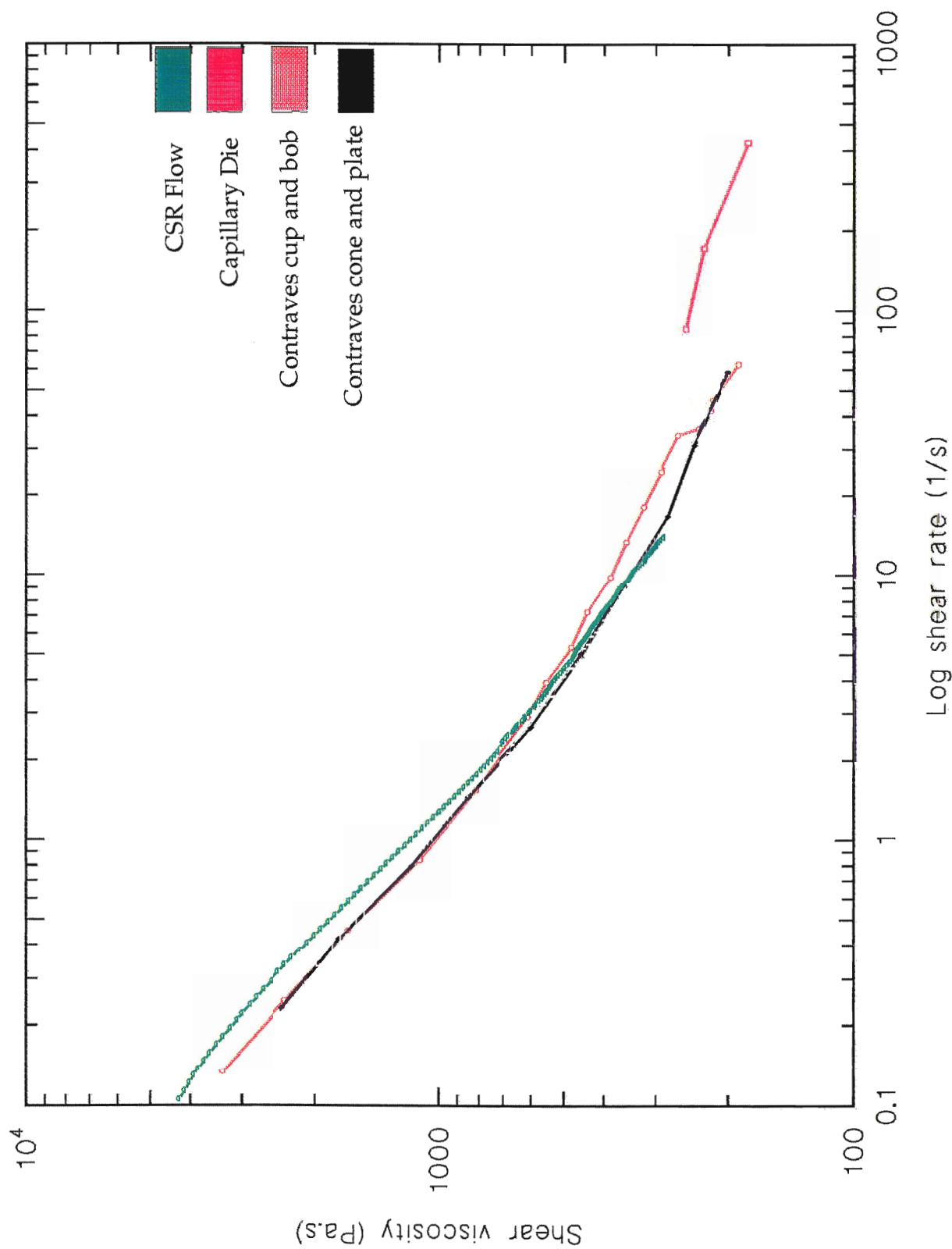


Figure 17: Cox-Merz plot-Dynamic oscillatory, capillary die and contraves measurements

