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INVESTIGATIONS OF ANOMALOUS FLOW WITH SPECIAL REFERENCE TO THIXOTROPY

An account of the work carried out by

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ABSTRACT

Absolute viscosity measurements under equilibrium flow conditions have been obtained for thixotropic suspensions of titanium dioxide pigments in linseed stand oils. These cover a range of shear rates and the effects of changes in concentration and temperature have been noted. It is shown that over the complete range there are two components of the shearing stress, one which is independent of temperature and another proportional to the viscosity of the medium as this changes with temperature. The temperature independent term is in the form of a frictional resistance which rises to a limiting value as the rate of shear increases; the other may be regarded as a hydrodynamic viscosity term which decreases to a limiting value with increasing shear. The theoretical significance of the variation in these components with concentration is briefly considered.

Thixotropic relaxation has been found to occur in a very complicated way but some approximate measurements on time-dependent viscosities have been made. These indicate how the magnitude and speed of

thixotropic change depend upon the equilibrium rate of shear and on concentration.

CONTENTS

CHAPTER 1

INTRODUCTION

CHAPTER 2

THE THEORY OF MEASUREMENT

CHAPTER 3

THE APPARATUS

CHAPTER 4

CHAPTER 5

CHAPTER 6

CHAPTER 7

CHAPTER 8

APPENDICES

ACKNOWLEDGEMENTS

REFERENCES

CHAPTER 1

INTRODUCTION

1.1 Definitions

The resistance to flow of most simple fluids is found to agree with the law suggested by Newton,

$$f = \eta g, \qquad 1$$

where 'f' denotes the shear stress required to maintain a velocity gradient (or rate of shear strain) 'g' and where 'η' is the viscosity coefficient of the fluid. Where this law holds true to within the limits of experimental accuracy a material is said to show "Normal flow" properties and is sometimes called a "Newtonian" material.

Anomalous flow indicates any deviation from this "Newtonian" condition. In many cases it is still found that one given shear stress produces a unique velocity gradient though the two parameters are no longer proportional as they were for a normal fluid. The viscous properties of these anomalous fluids cannot be described by a single viscosity coefficient since this varies with the rate of shear, but it is convenient to represent them by a flow function of the form

$$F (f, g) = 0. \qquad 2$$

The graph of this function is called the consistency curve.

Some liquids (for example a number of colloidal systems and suspensions) show flow properties that depend on their previous flow-history. In pictorial terms, when worked rapidly they are free flowing or thin; if the rate of working is decreased they gradually thicken. Conversely, if such a material is run steadily at a low shear stress it appears relatively thick; if the shear stress is then increased to a new value, which is maintained constant, the velocity gradient increases towards an equilibrium value as the material thins. Liquids of this type are termed thixotropic and it is clear that instantaneously thixotropic systems, where the relaxation processes are too rapid to be observed, correspond to the class of anomalous fluids described in the last paragraph. The equilibrium flow properties of an ordinarily thixotropic material can be completely described by a consistency curve, but any adequate representation of the time-dependent phenomena requires a family of relaxation curves each of which will depend upon the initial state of the system and the change imposed upon it.

A glossary is given of terms in this thesis which might otherwise be ambiguous but one more deserves special mention here. "False-body" has various shades of meaning in the literature but it is here taken to indicate solid (i.e. "bodied") properties at low imposed shear stresses.

If a gradually increasing shear stress is imposed upon a false-bodied material it will first deform as a solid and then, when the shear stress passes a value defined as the "Yield point", start to flow as a liquid.

Three types of fluid have now been introduced. Thixotropic systems show flow properties that vary with time; instantaneously thixotropic systems form the particular case where changes in viscous resistance are instantaneous; and normal fluids are those for which there is the further condition that the ratio of shear stress to velocity gradient is a constant.

1.2 Aim of research

A study of the flow properties of thixotropic materials required measurements of equilibrium values for a consistency curve and the determination of instantaneous viscous properties during relaxation. The work of Thornton (1953) and Thornton and Rae (1953) had suggested a method by which this might be done and the primary object of this research was to test the use of this method on any suitable material. It was hoped that this might give some experimental data to stimulate a physical theory of thixotropy and it was thought possible that accurate measurements on thixotropy might give some information about the forces between small particles in suspension. There was clear scope for the technical application of a better understanding of thixotropy since this property is shown by materials ranging from paints to protoplasm.

The task of setting up suitable apparatus for this work was eased by taking over that previously used by Thornton and Rae (1953) for the study of instantaneously thixotropic materials and adapting it to the present purpose. But the difficulty of finding or preparing suitable thixotropic specimens was acute since many conditions had to be fulfilled. The material had to have a viscosity range which was suited to the viscometer, it had to have relaxation effects of easily measurable magnitude and duration and there had to be no irreversible change in the flow properties during the experiment due to such factors as evaporation, sedimentation or chemical effects within the material.

Before describing the extent to which these difficulties were overcome a brief survey of some earlier work on anomalous viscosity is given so that the present research may be seen in an appropriate context.

1.3 Historical note

The development in an understanding of anomalous flow properties can be conveniently divided into four periods, though in practice these overlap considerably. In the first period anomalous flow was encountered daily in the work of craftsmen in diverse industries; paints and slurries, dairy products and sauces had to be prepared in the right "consistency" for their intended use. But their preparation depended on the skill of the individual without requiring the measurement of viscosity so that although it was recognized that their behaviour was complicated the nature of their anomalous flow was not appreciated.

The second phase was initiated by experimental observation, for techniques of measurement appropriate to ordinary simple fluids gave inconsistent results with these more complex materials. The viscosity coefficient attributed to a specimen was found to depend on the type and size of viscometer used and in the 1920's a number of papers appeared dealing with observed anomalies in flow. Some of the best scientific work centred on the visual observation of the flow process such as the observation of "plug-flow" along a tube by Bingham (1922) which suggested that the specimen behaved as a solid or very viscous liquid in the central region of the tube where the shear stress was low. Freundlich (1926) showed that for some materials the flow properties depended on the previous flow history by measuring the "setting time" of specimens after shaking them violently in a test-tube. The time necessary for the setting to occur depended on the concentration of the constituents (as well as on the diameter of the tube and many other factors) and gave a measure of "thixotropy". A ninety page index of rheological papers published before 1931 is given by Bingham (1931) and many of these show clearly the initial gropings and bewilderment of the new science of rheology.

Phase three could be described as that in which flow anomalies were not only observed and compared qualitatively with Newtonian behaviour but also measured with reasonable accuracy. To achieve this it has been necessary to define parameters and design experiments for their measurement which shall give results dependent only on the material tested and not on the type of apparatus used. Progress was delayed by repeated attempts to interpret results from conventional viscometers, where the readings were averaged over a wide and often unknown range of shear stresses and velocity gradients, in terms of an assumed equation of flow. In effect the form of the flow function was assumed and the values of the coefficients then calculated, the method being open to the objection that the flow function was not known with any certainty. Scott-Blair (1954) contrasts this approach, which he terms Analytical, with an Integrative approach to the problem. In this the aim was to determine the shape of the flow function directly from experimental results, necessitating a more refined type of experimentation than the analytical approach required.

In fact this more careful experimentation still gives little information about the suitability of a substance for industrial use. It is of value to the physicist who searches for "causes" by isolating specific properties and measuring them, but the usefulness of a given material in a manufacturing process depends upon how all these individual properties are combined. The requirements of industry are best considered as a "Gestalten" of all the physical properties concerned.

It seems that at present industrial rheology and a rigorous scientific inquiry may best part company; the first will be concerned with the use of a substance for a particular purpose, the second with the measurement of viscous and elastic properties independently of the apparatus used. This is the approach followed by Rabinowitsch (1929) and Mooney (1931) and developed in different ways by Schofield and Scott Blair (1930), Clark and Deutsch (1950), Kreiger and Maron (1952) and others. It was used with proved success when Thornton and Rae (1953) showed that the same consistency curves for instantaneously thixotropic materials could be obtained by applying a suitable mathematical and experimental method to two totally different types of viscometer. In this thesis the extension of that work to the more complex and more general case of ordinary time-dependent thixotropic materials is given.

The fourth period in the growth of this branch of science has hardly started but its characteristic is a progress from the description and measurement of thixotropic properties to their explanation in terms of the constituents of a thixotropic system. This theoretical work is difficult, partly because our understanding of viscosity in ordinary liquids (e.g. Andrade, 1934) does not approach in clarity our understanding of the viscosity of gases on the Kinetic theory. Goodeve (1939) has suggested a theory to account for the difference between thixotropic suspensions and pure liquids in terms of attractions between particles and a general account of the recent position in experiment and theory is given by Roscoe (1953).

This short history of rheology is obviously not complete and inevitably fails to give due credit to several workers in the field. But the study of their papers has helped in the progress of this present research, providing warning to heed and example to follow, and it is right that mention should be made of them for pioneering the way. Because of their investigations we started with some qualitative idea of thixotropy and this suggested experiments suited to its closer examination. In this thesis a theoretical section introducing these experiments precedes the record of observations made.

CHAPTER 2.

THE THEORY OF MEASUREMENT.

2.1 The quantities to be measured

We define thixotropy as a reversible change of viscosity due to shear, involving relaxation times of build-up and breakdown. Because of this relaxation the state of a thixotropic fluid at any instant depends on its previous treatment or "pre-history". To define the conditions of flow this prehistory must be determined.

It is convenient to consider an element of fluid across which a constant shear stress is maintained. Thixotropy will show in a relaxation of the velocity gradient until, after a sufficiently long time, the element approximates closely to equilibrium. This equilibrium state might depend on whether the fluid has thickened or thinned during the relaxation but in the materials tested the same velocity gradient was reached at equilibrium for a given shear stress whatever the prehistory had been. At equilibrium all effects of prehistory have been removed and the state of the fluid is defined by the shear stress acting or by the equilibrium velocity gradient. These equilibrium values can be measured and plotted as an "equilibrium consistency curve" in the same way as a consistency curve for an instantaneously thixotropic fluid.

To study the relaxation process the system is run to equilibrium at a shear stress 'f_1' so that this value 'f_1' defines the prehistory of the specimen. The shear stress is then changed to a new constant value 'f_2' and the velocity gradient 'g' is found to change instantaneously and then to continue changing with time until an equilibrium value is again reached. If time is denoted by 't' the flow function for the element may be written as

$$F\ (\ f_1\ ,\ f_2,\ g,\ t\ ) = 0, \qquad 3$$

which may be compared with equation 2. For given values of 'f_1' and 'f_2' the relaxation curve (g, t) indicates the thixotropic properties of the material.

The thixotropic properties of an element of fluid might also be defined and measured in terms of a relaxation of shear stress at constant velocity gradient. It can be shown that this can best be done in a parallel disc viscometer and that in a concentric cylinder viscometer, where the shear stress but not the velocity gradient can be calculated at each point, the analysis of the results gives the relaxation of velocity gradient at constant shear stress. These two definitions of thixotropic relaxation may be compared to the two specific heats of a gas and, as with a gas, there are an infinite number of intermediate conditions.

2.2 Theory

In any viscometer the fluid is subjected to a range of values of shear stress and the velocity gradient consequently varies from one part of the sample to another. If the fluid is Newtonian, or more generally if the functional relationship between the shear stress and velocity gradient is known, it is possible to calculate the viscosity or consistency curve directly from experimental results. But measurements made on the system as a whole do not yield directly the flow properties of an anomalous fluid for which the flow function is not known.

Thornton (1953), following Rabinowitsch (1929) and Mooney (1931), gave a theory for the measurement of anomalous viscosity. Thornton and Rae (1953) applied this theory to derive the consistency curves for instantaneously thixotropic fluids in both concentric cylinder and Poiseuille tube viscometers, the close agreement between the results confirming that this method of measurement gives values independent of the apparatus used.

In order to extend this theory of measurement to the full range of thixotropic fluids it is useful to derive the theory diagrammatically. This presentation has the further advantage that it shows directly the physical significance of the mathematics involved. The theory is given first for an instantaneously thixotropic fluid in a concentric cylinder viscometer.

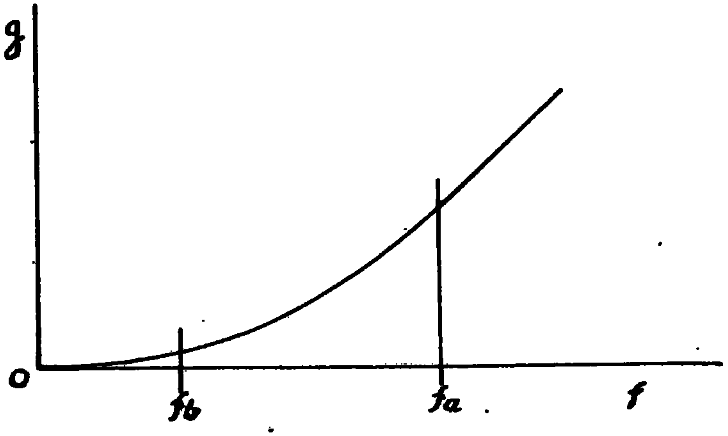
Let the couple acting be 'C', the angular velocity of the outer cylinder 'W', the radii of the inner and outer cylinders 'a' and 'b' and the depth of immersion of the inner cylinder 'h'. 'f' and 'g' denote the shear stress and velocity gradient in an element of the fluid.

The shear stress acting over a cylinder of fluid at a radius 'r' must give the couple 'C', hence, ignoring end effects,

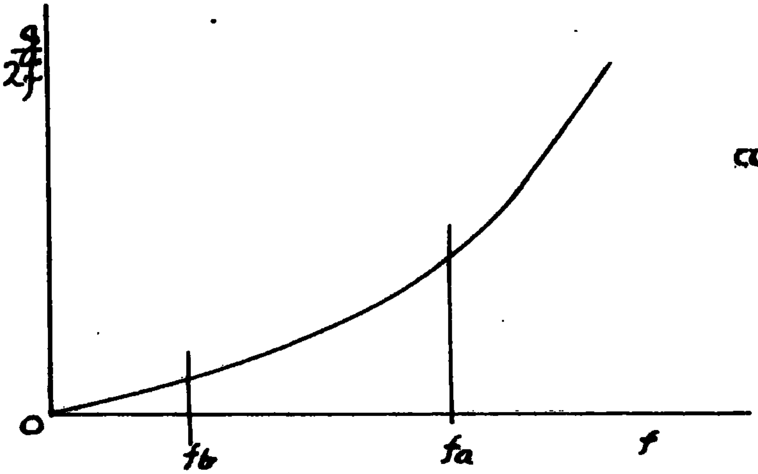
$$f = \frac{C}{2\pi h . r^2} . \qquad 4$$

The difference in angular velocity across the element of fluid between radius 'r' and 'r+dr' is given by

FIGURES 1-3

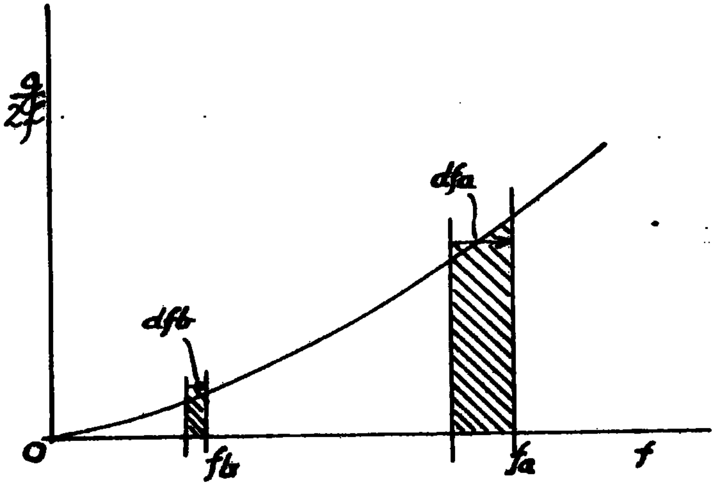


1.



2.

COUPLE C



3.

COUPLE C+dC

$$dw = g.\frac{dr}{r} \qquad 5$$

and the resulting cylinder speed must be

$$W = \int_{0}^{W} dw = \int_{r=a}^{r=b} g.\frac{dr}{r} . \qquad 6$$

With equation 4 this gives

$$W = \int_{g_b/2f_b}^{g_a/2f_a} (g/2f).df . \qquad 7$$

The relationship between 'f' and 'g' is not known but suppose it is of the form sketched in Figure 1. From this a curve of (g/2f) against 'f' can be drawn, as in Figure 2. The area under this curve between the limits of 'f_a' and 'f_b' gives 'W' from equation 7.

If the instrument is run at a changed couple 'C+dC' instead of 'C' the change in the cylinder speed, dW, is given by the change in area under the curve in Figure 2. The shape of this curve is determined only by the properties of the sample and is independent of the apparatus so that the change in area under the curve is due only to an alteration in position of the limits, valued and continuous.

It is quite simple to extend this approach to a thixotropic fluid. It was shown in Section 2.1 (Equation 3) that the relaxation of velocity gradient with time depends on the initial equilibrium shear stress 'f_1' and the shear at which relaxation occurs 'f_2'. This corresponds to running the system as a whole to equilibrium at a couple 'C_1', changing this to 'C_2' and observing the relation of cylinder speed with the time 't'.

In order to calculate 'g' at different times we consider the curve in figures 2 and 3 as $(g/2f\ ,\ f\ )_t$. If in a second experiment the initial couple is C_1' instead of C_1, and the final couple is C_2' instead of C_2, the change in area under the curve will give the instantaneous values of 'g' provided the shape of the curve is unchanged. This condition is fulfilled if the element of fluid which starts from equilibrium at 'F_1' in <u>either</u> the first or second experiment also relaxes at the same value, 'F_2', in <u>both</u> of them. That is, the history of each element must be the same in the two experiments.

Then in the first experiment:

$$F_1 = \frac{C_1}{2\pi h.r^2}\ , \qquad F_2 = \frac{C_2}{2\pi h.r^2}\ . \qquad (4)$$

In the second experiment the element initially at 'F_1' will be at a different radius in the viscometer cup, let this be 'r''. Then:

$$F_1 = \frac{C_1'}{2\pi h.(r')^2} , \qquad F_2 = \frac{C_2'}{2\pi h.(r')^2} . \qquad (4)$$

It follows that the condition for the instantaneous $(g/2f , f)_t$ curve to be the same in the two experiments is that:

$$\frac{C_2'}{C_1'} = \frac{C_2}{C_1} = \frac{F_2}{F_1} = K. \qquad 12$$

If this condition is satisfied the observed cylinder speed after relaxing for a time 't' in several experiments can be plotted as a $(C, W)_t$ curve and the instantaneous values of 'g' calculated from equation 10.

2.3 Operating routine

To combine measurement of the equilibrium consistency curve with an estimate of the relaxation of velocity gradient with time at constant shear stress several experiments are performed. In each the system is first brought to equilibrium under one couple and then is allowed to relax under another couple which bears a constant ratio to the first.

Experiment:

The system is run to equilibrium at an initial couple C_1.

This is changed to C_2 and the speed of the outer cylinder, W, measured as it relaxes.

The experiment is repeated for several values of C_1 and C_2, the ratio of C_2/C_1 being kept constant.

Calculation:

For equilibrium and for chosen intervals of time after changing from C_1 to C_2 curves of W are plotted against C_2, that is $(C, W)_{t,K}$.

The tangents to these give $(dW/dC)_{K,t}$ and hence $(g_a - g_b, t)_{f,K}$.

These are corrected to give $(g_a, t)_{f,K}$.

Results:

The equilibrium values of g at different values of f give the equilibrium consistency curve and the family of (g, t) curves for different values of f and K indicate the relaxation properties.

Assumptions:

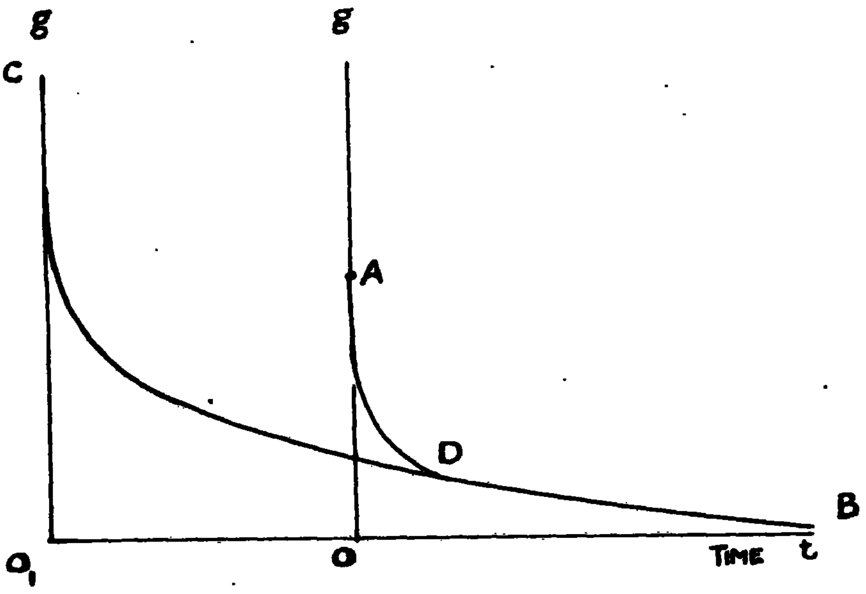
That the $(f, g)_{t,K}$ curves are single valued and continous; that 'f' and 'g' represent the flow properties of the system studied and are not a slip effect depending on the roughening of the surface of the inner cylinder and that appropriate corrections can be made for the "end effect" and the presence of a velocity gradient 'g_b' at the outer cylinder.

2.4 Presentation of results

The operating routine just outlined gives values for the equilibrium consistency curve and for a series of relaxation curves at different values of shear stress 'f' and one value of the ratio 'K'. This ratio is an arbitrarily chosen constant and for the purpose of comparison it may be given different values in different experiments.

During relaxation the velocity gradient at any moment is determined by the shear stress acting and by the viscous state of the fluid. This viscous state will depend on the shear stress 'f', the initial shear stress 'f/K' and the time 't' since changing from one to the other. Consider a second experiment in which relaxation occurs at the same shear stress 'f' but where 'K' is smaller and the initial stress accordingly greater. After some time the velocity gradient must reach some value that it had in the first experiment and since the shear stress is the same the viscous state of the fluid must also be the same. The

FIGURE 4



A-B Relaxation curve when shear changes from F to f
C-B Relaxation curve when shear changes from F to f
D-B Curves expected to coincide

two pre-histories differ but, since they lead to the same value of 'f' and 'g' at a given instant they might be thought to be equivalent to each other. The subsequent relaxation of the velocity gradient depends only on its viscous state at an instant and on the shear stress acting, hence the succeeding points on each relaxation curve should be identical.

This is sketched diagrammatically in figure 4. At first it was thought that the presence of a sudden initial change in 'g' when the shear stress was changed invalidated this argument, but it would seem that since 'g' would have to change instantaneously even if the viscosity coefficient remained momentarily constant a similar change should be expected however "viscous state" is defined. It has not proved possible to conduct an experiment which conclusively proves or disproves this reasoning but it is included as an attempt to show that an experiment conducted with one value of 'K' gives results which are typical for other values of 'K'. One qualification must be made to this statement; it is necessary to determine separate relaxation curves for "build-up" (K<1) and for breakdown (K>1).

CHAPTER 3

THE APPARATUS

3.1 The basic viscometer

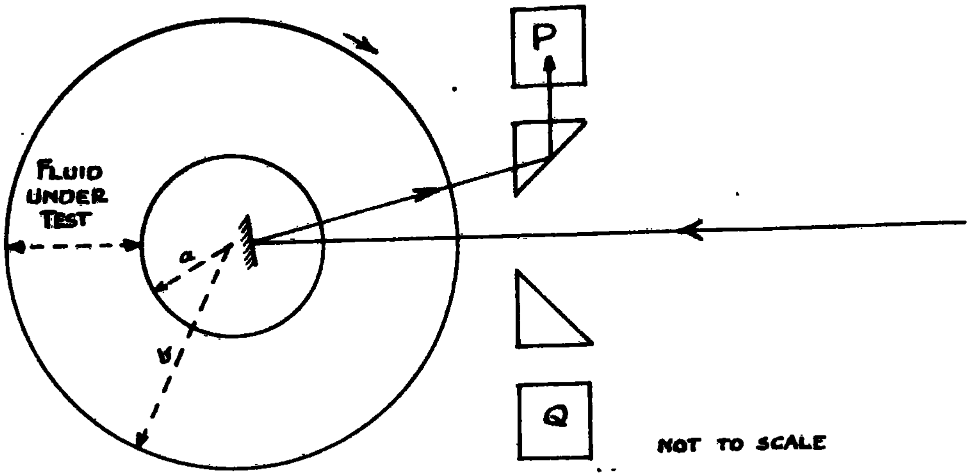
The viscometer used was that designed and built by Thornton and Rae and described fully in the Ph.D. thesis by Rae (1952) and in outline by Thornton and Rae (1953). It was a concentric cylinder viscometer in which the outer cylinder was driven by a variable speed motor and the inner cylinder suspended on a long torsion wire. The driving motor was a B.T.-H "Emotrol" type in which the speed is closely proportional to the armature voltage for a wide range of loads. The armature voltage is automatically matched against a reference voltage in a potentiometer so that the speed can be controlled at any value, in the range 150 to 3,000 revolutions per minute, by rotating the setting on the potentiometer.

In this viscometer the observed deflections of the inner cylinder and speeds of the driving motor gave the values of the couple 'C' and the angular velocity of the outer cylinder 'W' for instantaneously thixotropic materials and the consistency curve of shear stress against velocity gradient could be calculated. It was possible to get a qualitative indication of ordinary time-dependent thixotropy by running the apparatus at one cylinder speed until the deflection was constant, changing the cylinder speed to a new constant value and observing the deflection of the inner cylinder. If this cylinder turned immediately to a new steady deflection (except for a few seconds delay due to inertia effects in the system) the sample was instantaneously thixotropic, if it relaxed gradually to an equilibrium value then the sample was thixotropic in the normal sense.

3.2 Measuring thixotropy

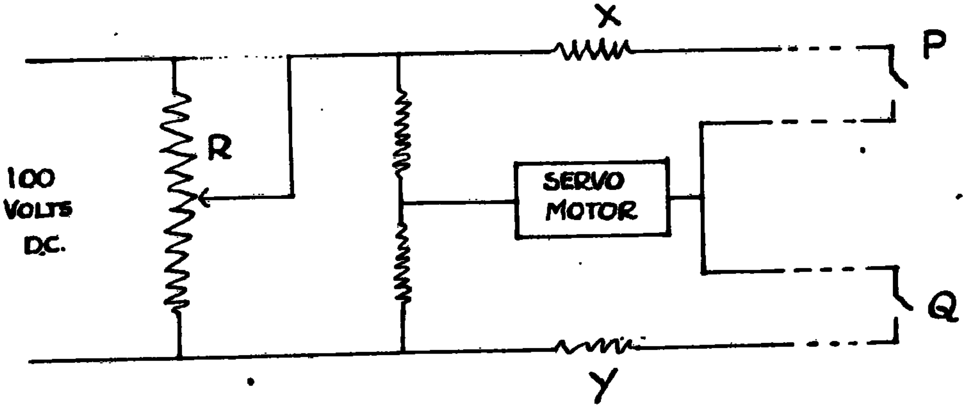
Theory shows that in order to measure the transient values of velocity gradient at a given shear stress in a concentric cylinder viscometer the torque must be maintained constant and the angular velocity of the outer cylinder varied so as to maintain this condition. This was achieved by reflecting a narrow beam of light at a mirror attached to the inner cylinder and using it to operate a servo-motor controlling the speed of the main driving motor. Figures 5 and 6 illustrate the optical and electrical arrangement that was used. The required deflection was selected by adjusting the position of the mirror in relation to the inner cylinder. If the deflection fell below this chosen

FIGURE 5.



NOT TO SCALE

FIGURE 6.



value light was reflected through a prism into the photocell 'P' closing the relay 'P' in the electrical circuit. This energized the field coils of the servometer which rotated the potentiometer setting for the main driving motor so that the outer cylinder was accelerated and the torque increased. If the deflection of the inner cylinder became too large the field coils of the servomotor were energized in the opposite direction and since the armature of this servomotor was independently connected the operation of this motor was reversed and the speed of the outer cylinder reduced. The rheostat R enabled the acceleration and deceleration given to the driving motor to be adjusted, the speed of the servomotor having to be sufficient to maintain a steady torque during the relaxation process without giving rise to excessive oscillation in the cylinder speed. In practice it was found difficult to prevent this 'hunting' at very low speeds but the speed control was satisfactory over a range of cylinder speeds from about 0.05 to 2.50 radians per second, a ratio of fifty to one. A voltmeter in parallel with the servomotor helped in setting the rheostat 'R' and the resistances 'X' and 'Y' were added to guard against a short circuit should both the relays switch 'on' at the same time (for example when the settings of the prisms and photocells were being adjusted).

To record the variation of motor speed with time at constant torque an Honeywell-Brown "Electronik" recorder was used. This could have been connected to a tachometer generator coupled to the motor but it was found more convenient to connect the recorder to the potentiometer reference voltage of the main driving motor. The recorder reading was calibrated against the speed of the driving motor (determined stroboscopically) and frequent checks were made, using a mechanical tachometer, as described in the section on the calibration of the apparatus.

CHAPTER 4

EXPERIMENTAL PROCEDURE

4.1 Calibration of the apparatus

The formulae used in calculation 'f_a' and 'g_a' are:

$$f_a = \frac{C}{2\pi h.a^2} \qquad (4)$$

and

$$g_a - g_b = 2C.\frac{dW}{dC} . \qquad (10)$$

These indicate the measurements which are required in working out the results. The couple acting is proportional to the deflection of the inner cylinder 'θ' and the constant of proportionality - the torsion constant of the suspension wire - was found by timing the period of oscillation of the inner cylinder when it was suspended freely on the torsion wire. If $C = c\theta$

$$\text{then} \quad c = 4\pi^2 I/T^2$$

where 'I' is the moment of inertia of the suspended cylinder and 'T' its time of swing. The cylinder suspended from the wire was the inner cylinder of the viscometer, being a simple brass cylinder of radius 'a' and a small plastic scale. The mass of the scale was so much less than the mass of the cylinder that the moment of inertia was taken as

$(ma^2/2)$, where 'm' is the mass, with an error of a fraction of one per cent. Hence:

$$c = 2\pi^2 ma^2/T^2$$

and therefore $$f = \frac{m}{180\,h}\left(\frac{\pi}{T}\right)^2\theta \text{ dyne cm}^{-2}, \qquad 13$$

where θ is measured in degrees.

It was found that $m = 1145$ gm, to within 1 gm

and for the wire used $T = 1.57$ sec, to within 0.01 sec.

Hence:-

$$f = (25.44)\,\frac{\theta}{h} \text{ dyne cm}^{-2}. \qquad 14$$

The motor was connected by belt and pulleys to the main driving shaft which drove the outer cylinder through reduction gearing. By counting the total number of revolutions of the appropriate parts during a run, using a revolution counter of standard pattern, and by an approximate check from the relative diameters of the pulleys concerned it was found that the ratio

Ang vel driving shaft / ang vel motor spindle = 1/1.225,

where "Ang vel" stands for angular velocity. The gear ratios were calculated from the number of teeth involved and checked by a revolution counter method as above, giving

Ang vel outer cylinder / ang vel driving shaft = 1/106.8

hence

Ang vel outer cylinder / ang vel motor spindle = 1/(1.225 x 106.8).

Then if 'W' is the angular velocity of the outer cylinder in radians per second and 'R' is the motor speed in revolutions per minute,

$$W = R.(8.02 \times 10^{-4}). \qquad 15$$

In order to correct for 'g_b' the ratio of the radii 'a' and 'b' was required. Averaging a number of measurements gave

$a = 1.27$ cm

$b = 4.02$ cm

hence $b^2/a^2 = 10$ and $f_a/f_b = 10$.

The quantities m, T, (W/R), a and b are constants of the apparatus. Any inaccuracy in their determination will lead to the same error in calculating results so that comparison of properties measured on this viscometer ~~measured~~ with those on another viscometer would be impaired. However these errors will not affect the form, but only the scale, of the consistency curves and relaxation curves obtained with this instrument.

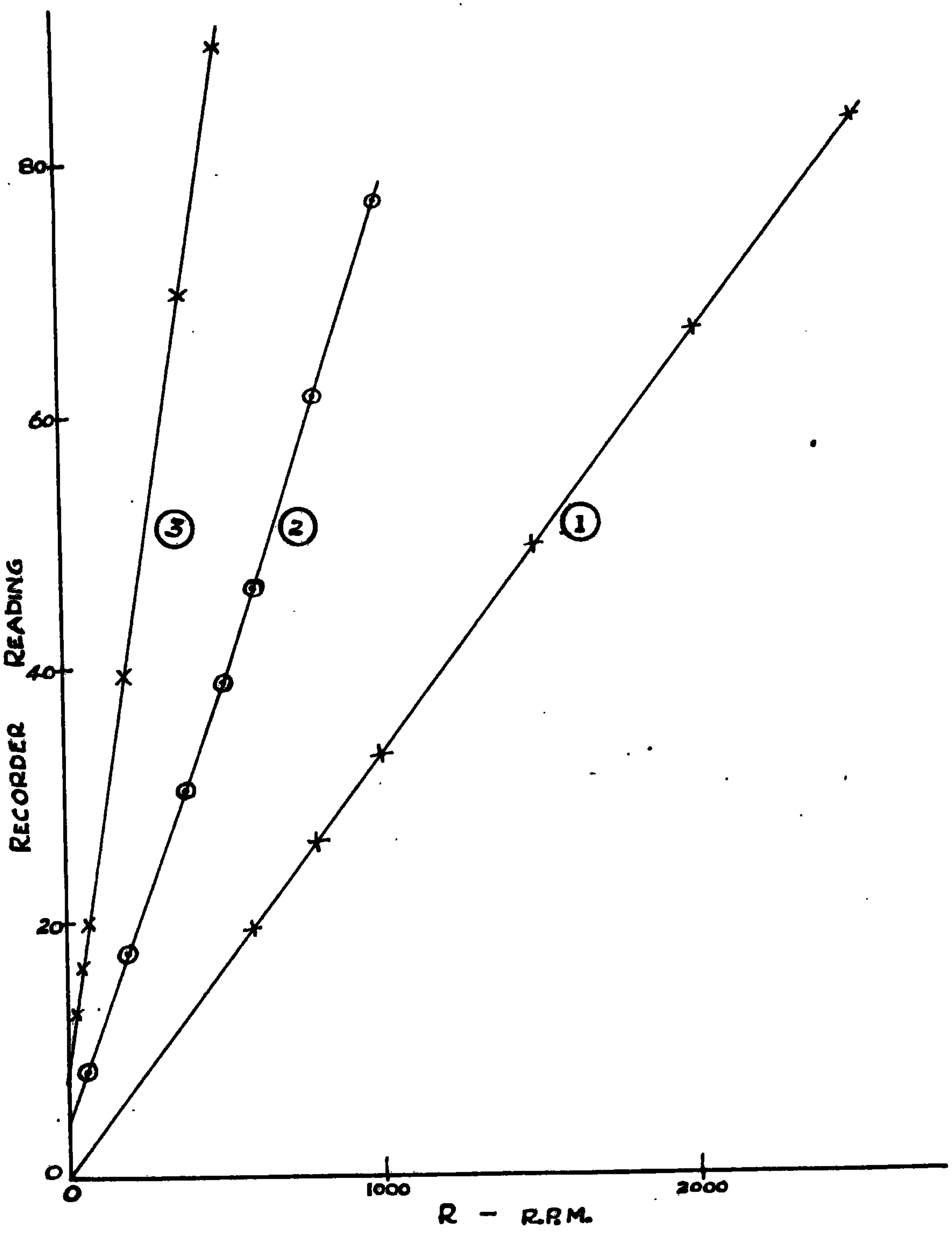
4.2 Experimental observations

4.21 - - Depth of immersion

The value of 'h', the depth of immersion of the inner cylinder in the fluid, was measured by marking the inner cylinder at the surface of the fluid, removing it and measuring the distance between this mark and its lower end. A more rapid and less cumbersome method was developed in which a brass plate rested firmly on the surface of the outer cylinder, or "cup", and a thin needle through the plate dipped into the specimen. On removing the plate the depth of immersion of the needle was measured and the immersion of the inner cylinder calculated after a calibration had been made relating the two. It was found that 'h' was of the order of 10 cm and that it could be measured to within 0.1 cm, an error of less than one per cent.

A correction was necessary for the end effect of this inner cylinder. It is shown in chapter 6 that this correction can be made by adding 1.0 cm to the measured value of 'h'. This end correction is difficult to determine and the error may be as large as 0.1 cm suggesting that the total probable error in the immersion due to the error in measuring 'h' and the error in estimating the end

FIGURE 7. SEE TABLE III



correction is about one per cent. This error is constant for any one specimen in the viscometer, it affects the comparison of properties between one specimen and another or between results obtained for the same specimen in different viscometers but it does not change the shape of the equilibrium consistency curve or of the relaxation curves for the material.

4.22 - - Measuring deflection, speed and time

The deflection of the inner cylinder was maintained during an experiment at a series of predetermined values. A scale attached to the cylinder was viewed through a telescope and aligned with a pointer in the telescope, the measurement of the deflection being subject to an error of about one degree. This error seemed unavoidable, it was due mainly to oscillations of the cylinder about a mean position, these oscillations being attributed to a slight discrepancy in the alignment of the axes of the inner and outer cylinders.

The motor speed 'R' was measured by means of the pen-recorder. Figure 7 shows the calibration for the motor speed, determined stroboscopically and checked with a Smith's tachometer generator, against recorder reading.

The table of results from which the graph was plotted are given in Appendix 1. The three scales were obtained by switching from one resistor to another on a potential divider from which the input to the recorder was taken. To obtain the relaxation curves the motor speed was required at different times after changing from the initial to the final torque and this was estimated directly from the graphs from the recorder. It took about ten seconds to change from one torque-controlled position to another.

The errors in measuring 'θ', 'R' and 't' affect each individual result differently thus altering the form of the consistency and relaxation curves obtained for any sample. A method of estimating these errors and calculating the effect they are likely to have on the results is given in more detail in section 4.4.

4.3 Calculation of results

From the experimental results a curve of 'R' against 'θ' was plotted, being equivalent except for multiplying constants to a graph of cylinder speed 'W' against couple 'C'. The slope of the (θ, R) curve was measured at different points giving $d\theta/dR$ and by substitution in equations 10 and 15 the values of $(g_a - g_b)$ were calculated. If equilibrium values of 'R' were used in drawing the (θ, R) curve this led to the equilibrium consistency curve, if the values of 'R' were all taken at some selected time 't' the instantaneous values of 'g' at that time were obtained. The value of 'f_a' was obtained from equation 14 where 'h' was corrected for the end effect.

For the equilibrium values a curve of 'f_a' against $(g_a - g_b)$ was drawn. Now 'g_b' is the value of 'g_a' if 'f_a' is reduced to one tenth of its value, since 'g_b' is the velocity gradient at the outer boundary where the shear stress is $(a^2/b^2)f_a$ and $a^2/b^2 = 1/10$ If 'b' is considerably greater than 'a' a first approximation for 'g_b' is given by the value of $(g_a - g_b)$ at 'f_b'. For a Newtonian fluid in our viscometer 'g_b' would be one tenth of 'g_a' and the error in approximating as above is about one per cent. The shape of the consistency curves for all the materials studied shows that the error in making this approximation is less than for a Newtonian fluid, that is less than one per cent.

For the time-dependent properties instantaneous values of 'W' led to instantaneous values of 'f_a' and 'g_b'

at different times and it was found convenient to present the results in the form of relaxation curves (g, t) at constant shear stress. The apparent viscosity coefficient (f/g) was calculated in a number of cases but as it is of doubtful physical significance the experimental results given in this thesis are left in terms of shear stress and velocity gradient.

4.4 Accuracy of results

The accuracy of the values obtained for 'f' and 'g' was determined by calculating the combined effect of the estimated errors in measuring each quantity in equations 4 and 10. Each set of results was checked in this way and the probable error calculated from it is shown on the relaxation curves and the equilibrium consistency curves by the magnitude of the co-ordinates plotted.

To calculate 'g' a curve of 'θ' against 'R' had to be drawn for each set of experimental results and its tangent measured at several points. Small errors in the location of consecutive readings of 'θ' and 'R' through which the curve had to be drawn were clearly liable to give large errors in the gradient of the curve between those points so that inaccuracies in measuring 'θ' and 'R' are the most significant source of error in the whole experiment.

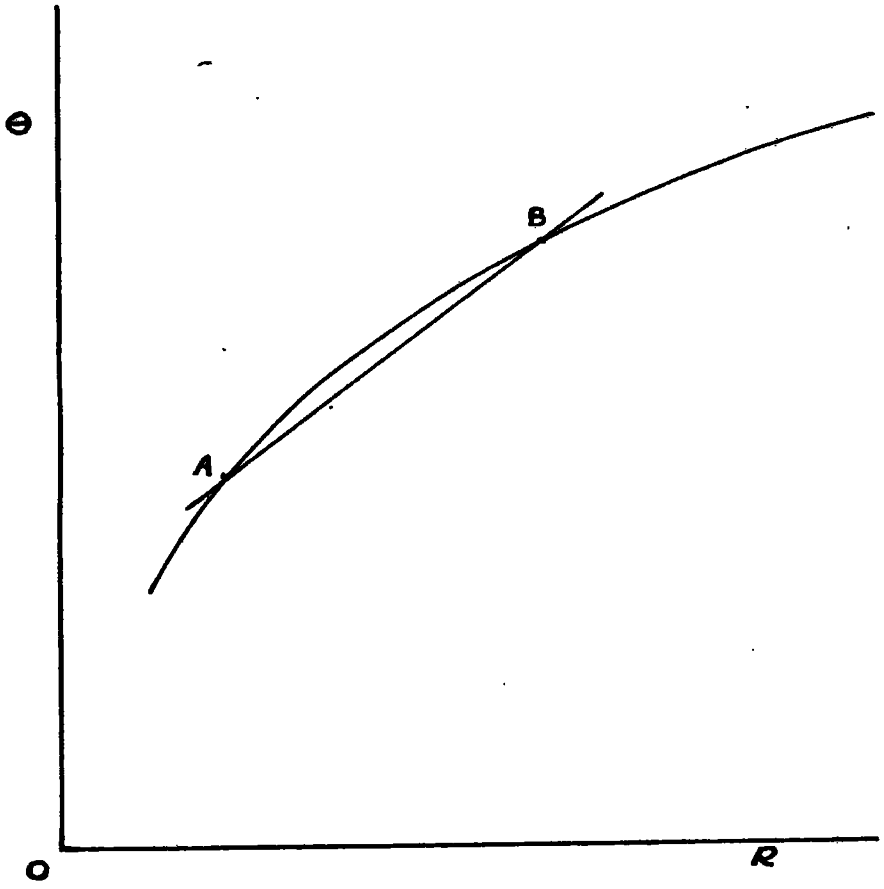
The deflection 'θ' could be read to within one degree, the limit being imposed by a tendency for the cylinder to oscillate about a mean position with an amplitude of one or two degrees. This oscillation was attributed to three possible factors; a lack of alignment between the axes of the inner and outer cylinders, the effect of random vibrations on the flow properties of the material under test and the presence of a small null space in the optical system for maintaining a constant deflection. In one experiment results were compared for the best possible alignment of the axes of the two cylinders with results for a deliberately skew arrangement of the axes and it was found that the main effect was a slow oscillation of the middle cylinder. For any given setting of the torque-control mirror neither the mean deflection nor the equilibrium outer-cylinder speed were greatly changed by altering the accuracy of alignment. It was thought that the small motors driving the fan in the air enclosure and the oil-bath paddle were responsible for most of the "stray" vibration that might affect the sample. These were stopped for a time and the temperature checked to ensure that it was steady, but no appreciable change was observed in the cylinder speed at a constant torque so it was concluded that the effect of vibration due to these subsidiary motors could be ignored. It was concluded that the angle 'θ' was measured to within one degree of its true value after allowing for the oscillation of the cylinder and the null region in the control system.

The motor speed 'R' was measured by a deflection on the pen-recorder, which had an accuracy of about 0.5 per cent at half-scale deflection. The recorder was calibrated against mains frequency using a neon lamp and a stroboscopic disc attached to the motor-spindle. This calibration was frequently checked against a Smith's mechanical tachometer, which could be pressed against the motor spindle when required. These checks showed that the calibration held true whether the load being driven by the motor was small or large, when the motor was cold (on starting) or warm (after running for several hours) and that there was no gradual drift in the relation between motor-speed and recorder deflection during the whole period in which experiments were conducted. By altering the resistance in a potential divider supplying the D.C. reference voltage of the "Emotrol" to the recorder three different scales were obtained and an examination of the graphs from the recorder suggests that, in general, the probable error in reading the speed 'R' can be taken as less than one per cent. There is an exception to this in that the accuracy falls off at the lowest speeds due to difficulty in maintaining a normal control of the torque, but that region is not of great importance in the results given in this thesis.

The viscometer was kept at a constant temperature (usually 25 degrees Centigrade) by mounting the cup in an oil bath and covering the top with an enclosure. Both the oil and the air were kept in motion and the heat supplied to them was thermostatically controlled. The temperature fluctuated up to 0.2 degrees Centigrade, and from the results of an experiment on the temperature variation of flow properties it is known that this represents a fluctuation of 'R' of rather less than one per cent. The probable error in a given value of 'R' must therefore be taken as between one and one and a half per cent.

Having established the inaccuracies in the measured values of 'θ' and 'R' it is necessary to know how these will affect the accuracy with which a curve through several different points (θ, R) may be drawn, for the drawing of this curve is an essential step in the

FIGURE 8



calculation of the velocity gradient 'g'.

When the experimental programme was being planned this problem was considered and an estimate of the accuracy derived which set an upper limit to the errors involved. It was hoped to improve upon the method for assessing the error at a later date but in fact this has proved too difficult. Hence the following calculations only indicate the maximum error that might be involved and not an estimated error, the actual results may be far better than these "errors" suggest, they certainly are not worse.

The basic supposition is that the accuracy in the gradient of a smooth curve drawn through several points (θ, R) will not be worse than the accuracy in the slope of the chord joining two consecutive points. This supposition is valid when the change in slope of the curve is small. Expressed differently, with the aid of figure 8, it is that the error in the gradient of the curve AB between A and B is not greater than the error in the slope of the chord AB, the errors arising from the uncertainty in the precise values for the co-ordinates of A and B.

The probable error of the chord can be calculated since the 'R' values of its end co-ordinates have a probable error of (say) one per cent and the 'θ' values may be considered correct to within one degree. It is convenient to start by calculating the probable errors in an apparent viscosity of the material.

Then apparent viscosity, f/g, = (Constant)($d\theta/dR$).

Error in apparent viscosity = Error in slope of (θ, R) curve

$\leqslant$ Error in slope of chord to (θ, R).

Let ends of chord AB be (θ_1, R_1) and (θ_2, R_2),

then slope of chord $= \dfrac{\theta_1 - \theta_2}{R_1 - R_2}$.

Probable error of ($\theta_1 - \theta_2$) :

If the limiting error for either value of 'θ' is taken as one degree, then ($\theta_1 - \theta_2$) is correct to within one degree with about a 50 per cent probability. (If each value of 'θ' were supposed to lie between '$\theta \pm 1$' degrees with a rectangular distribution then '$\theta_1 - \theta_2$' would lie within 2 degrees of its mean value with a triangular distribution and hence a more than 50 per cent probability of lying within one degree of the mean).

Probable error of ($R_1 - R_2$):

Each value of 'R' has an estimated probable error of one per cent, so that the probable error of the difference can be found in the usual way for statistical errors and is

$$\frac{1}{100}.(R_1^2 + R_2^2)^{\frac{1}{2}}.$$

Total error:

The probable errors may be expressed as increments 'Δ' so that the usual variance formula gives

$$\frac{[\Delta\eta]^2}{\eta^2} = \frac{[\Delta(\theta_1-\theta_2)]^2}{(\theta_1-\theta_2)^2} + \frac{[\Delta(R_1-R_2)]^2}{(R_1-R_2)^2}$$

$$\frac{[\Delta\eta]^2}{\eta^2} = \frac{1}{(\theta_1-\theta_2)^2} + \frac{R_1^2+R_2^2}{100^2(R_1-R_2)^2} \qquad 16$$

The probable errors in 'η' calculated from this formula vary from three to ten per cent, being best when differences between 'θ_1' and 'θ_2', and 'R_1' and 'R_2', are large. Since $\theta_2 = K.\theta_1$ this is the condition that 'K' shall not be near unity, but it will be seen later that other factors affect the choice of a suitable value for 'K'. The calculation for the probable error is open to the objection that if the interval between successive readings on the (θ, R) curve is decreased the calculated error is increased, since both ($\theta_1 - \theta_2$) and ($R_1 - R_2$) become smaller. In fact this is a reminder that this assessment gives only an upper limit to the possible error in the apparent viscosity.

It is clear that the basic assumption relating the error in the gradient of the curve to the error in the slope of the chord needs to be examined. It is obviously not true when the interval between successive points 'AB' is very large and the change in slope of the curve correspondingly great between them; and it clearly gives a false suggestion of great inaccuracy when the two ends 'AB' are very close together. Two methods were used to check the suitability of the intervals chosen; one was worked out in detail for one specimen only and is described at the end of this section, the other was applied to every sample for which the results were thought to be significant and is now described.

Instead of drawing tangents to the (θ, R) curve and measuring their slope an estimate of the gradient was obtained by calculating the slope of the chord joining two successive (θ, R) co-ordinates. A value for the apparent viscosity was obtained by supposing this to be the gradient of the curve at a point mid-way between the chosen co-ordinates with deflection $(\theta_1 + \theta_2)/2$. This supposition is valid under the same conditions as the supposition from which errors were estimated, namely that the change in slope of the (θ, R) curve shall not be large between the values chosen. Using the experimental values of 'θ' and 'R' and calculating the slope between consecutive points gave an arithmetical estimate of the apparent viscosity which was in very close agreement with the graphically deduced values. This confirmed the validity of the arithmetical method of calculation and the suitability of the intervals between successive values of 'θ ' and 'R' in making the calculation; and thus justified the use of these intervals in calculating the limits of error in the apparent viscosity.

Thus far we have considered the error in the apparent viscosity due to the error in $dR/d\theta$. The velocity gradient is given by $2\theta.dR/d\theta$ and 'θ' - the multiplying factor - includes another source of error. However in plotting an equilibrium consistency curve the velocity gradient is plotted against the shear stress, and the shear stress is itself proportional to 'θ'. Hence the estimated limits of error for the apparent viscosity correspond to the error in the velocity gradient when it is displayed against the shear stress in a consistency curve.

The correction for 'g_t' still has to be made but this is quite small. 'g_r' is usually between one and five per cent of 'g_a', so that any error in evaluating 'g_r' is small enough to be neglected. The error in measurement of the apparatus constants is small compared with the errors in 'θ' and 'R' in its effect though allowance must be made for the error in measuring the depth of immersion and the end correction for this depth. This affects the f-scale in an equilibrium curve and is not shown on the graphs, the probable error is about one per cent.

Having established the accuracy with which we may expect to draw a curve through a number of (θ, R) points it is still necessary to find how accurately the gradient of this curve can be measured. To simply align the curve with a rule introduces a risk of large errors and it was decided to measure the gradient with an optical device of high accuracy which is described in Appendix 2. It is there shown that the errors in measuring the slope of the curve are small enough to be neglected.

As a final check on accuracy the experimental values of (θ, R) were plotted for one experiment and the extreme errors shown. A number of curves were drawn through

CHAPTER 5

PREPARATION OF SAMPLES

As indicated before this proved one of the greatest experimental problems of the whole research project since very little information was available about thixotropic materials. Preliminary studies, intended to test the suitability of the apparatus and of the measuring technique, required materials that could be easily and quickly prepared, and Bentonite suspensions in water were used for this work. These were unsatisfactory in many ways, though the results obtained agree with those later gained with more stable materials. The Bentonites were awkward to use because their range of viscosity - from infinite viscosity or false body at low values of shear stress to a few centipoise at higher values - was too large for accurate measurements to be made by any apparatus over the whole range. There were added difficulties due to sedimentation (since the samples had to be between five and ten per cent of Bentonite by weight) and to evaporation from the surface. A specimen of some 25 per cent by weight of Bentonite in glycerine proved more satisfactory but this was only used as a guide in the search for better samples.

At this point it will help to consider the criteria by which we determine a good sample. These fall into two groups, reproducibility and anomaly.

It was essential that during the time taken to complete the experiments on any one sample the irreversible change in properties should be small. That is, for the purpose of an initial test, that the equilibrium motor speed at a given torque should not change appreciably over a period of a week or more. In the Bentonite-in-water suspensions it was difficult to get near this condition due to evaporation and sedimentation; using pigment-in-oil dispersions it was found that some gave good reproducibility and others did not. No doubt in some cases sedimentation was the cause of failure but in others it seems that we must postulate some ageing effect due to chemical reactivity between the pigment and the medium. It was found with most of these samples that after they had been allowed to age for, say, six months, the reproducibility over a period of one week in the viscometer would be good, suggesting that some form of chemical equilibrium had been reached between the two components.

The experiments were designed to measure thixotropy and this task would obviously be eased by having the effect as pronounced as possible. It would be easy to get good reproducibility for a simple 'Newtonian' fluid but it was found difficult to combine reproducibility with this second condition of a pronounced anomaly. In changing from one value of shear stress to another two things were required: first that the ratio of shear stress to velocity gradient at equilibrium should be as different as possible, that is there should be a large departure from the Newtonian condition; secondly that this change should occur over an appreciable time so that the form of the thixotropic relaxation could be investigated. Again it seemed as if the two conditions were mutually opposed, thus a number of specimens containing different concentrations of the same pigment-in-oil dispersion showed almost Newtonian properties at low concentrations and false-bodied properties at high concentrations with normal time-dependent thixotropy in between. It was found convenient to use samples where the relaxation process resulted in as large a total change in cylinder speed as possible and where the system came close to equilibrium in between thirty minutes and four hours.

Figure 9.

Electron-Micrograph
of Titanium dioxide pigment,
Rutile CR.

Photo: British Titan Products Ltd.,

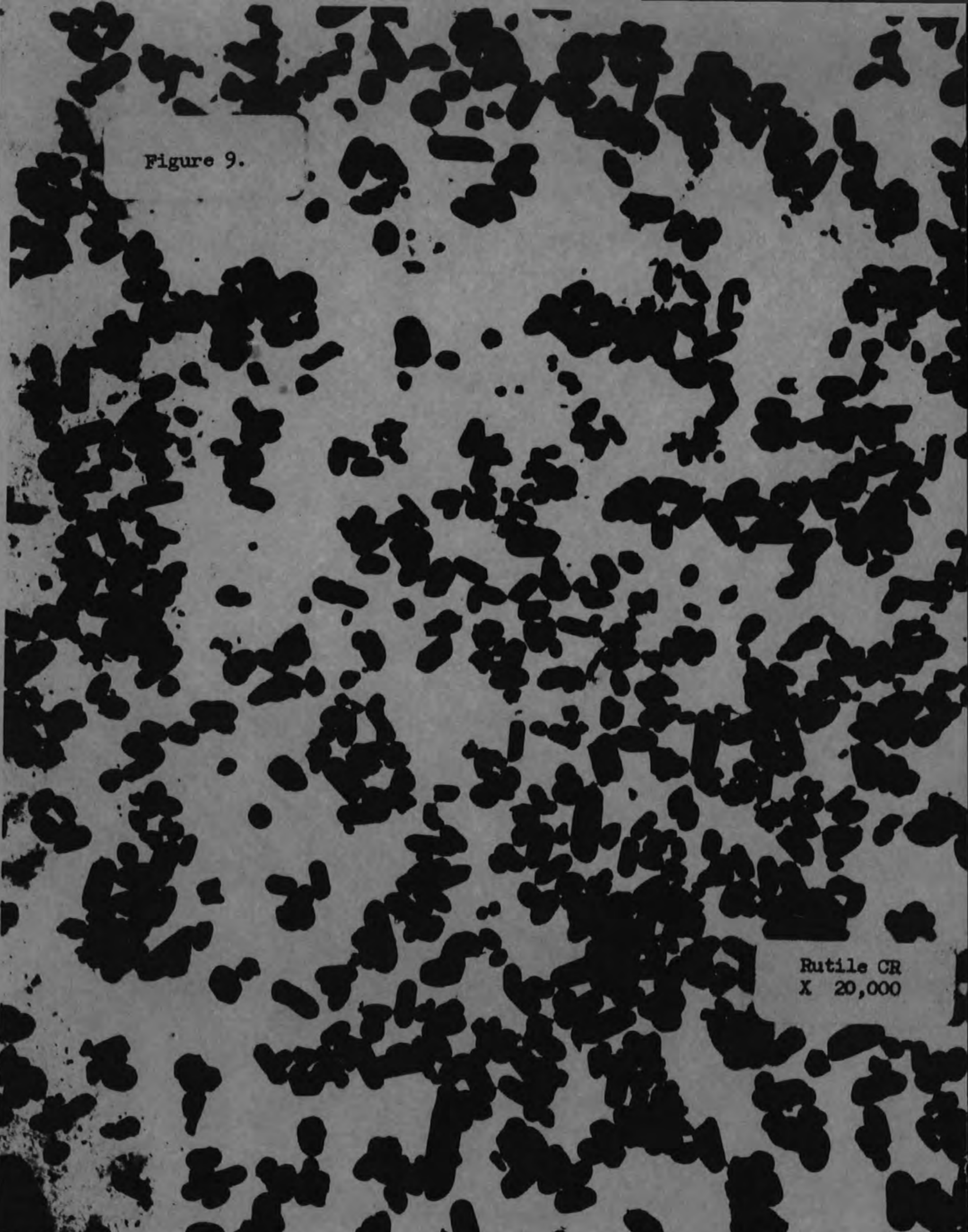


Figure 9.

Rutile CR
X 20,000

Systems with quicker relaxation processes led to inaccuracy in measuring the important changes in the first part of the relaxation; systems taking longer to reach equilibrium made a complete experiment excessively long and reintroduced the problem of ageing and reproducibility.

Preliminary tests suggested that suspensions of Titanium dioxide pigments in oils could have very stable properties and still exhibit thixotropy. These had the added advantage that they followed as a logical sequence the work by Rae (1952) using instantaneously thixotropic systems containing similar pigments. The Research Department of British Titan Products, Ltd., were consulted and on their advice a rutile form of Titanium dioxide was used. An electron micrograph of a typical pigment is shown in figure 9, the mean particle diameter being about 0.25μ. From this micrograph it is evident that the pigment is of almost random shape and the particles tend to have smooth edges.

The oils used differed for different groups of samples being mixtures of alkali refined linseed oils of about one poise (at 25.0 °C) and linseed stand oils prepared under nitrogen of about thirty or sixty poise at 25.0 °C.

Each sample was prepared by milling the pigment and oil in a Ball Mill of the type described by Rae (1952) for about three hours. Longer milling did not change the flow properties so it was assumed that this time was sufficient to ensure a good dispersion. After preparation all samples were stored for six months in a constant temperature enclosure at 25.0 °C. before use. The temperature at which experiments were conducted in the viscometer was also 25.0 °C.

The suitability of some twenty samples was tested by trial runs in the apparatus. At first this was done soon after their preparation without allowing a period for ageing, but it was later discovered that the ageing process included an alteration in the flow properties of the sample. In some cases samples which at first seemed suitable for use in the apparatus were found after ageing to have only slightly anomalous flow with which accurate measurements would have been impossible. Since the search for appropriate specimens had to be guided by information on the properties of those already prepared the problem of ageing delayed this search considerably. In the preliminary tests the relaxation of cylinder speed with time when a constant torque was maintained was used to determine suitable thixotropic properties.

CHAPTER 6

EXPERIMENTAL RESULTS

6.1 Introduction

A full description of the flow properties of any thixotropic material requires the investigation of both equilibrium and instantaneous properties during relaxation. The equilibrium properties can be described by a single consistency curve but the relaxation properties need to be represented by a range of curves having differing initial and final values for the shear stress. If the form of the relaxation curve is the same at any shear stress, so that different initial values for the equilibrium shear stress only displace the time-origin of the relaxation curve, (Figure 4) the problem is simplified.

The task of experiment thus becomes:-

(1) To obtain the equilibrium consistency curve

(2) To check how the relaxation depends upon the initial shear stress

(3) To compare relaxation curves for build-up and breakdown

(4) To find any regularities in the relaxation process.

For convenience in presentation the results under equilibrium conditions and the time-dependent phenomena are grouped separately but these two groups of information on a sample each come from the same experiments. Both equilibrium and relaxation properties are given under three headings. First, a typical sample is selected and the calculation performed in full; then the effect of varying the temperature of a chosen sample is given; finally the variation of properties with concentration is recorded. Many different samples were tested and the results given are typical of the properties discovered.

6.2 Equilibrium properties

The cup of the viscometer was filled and after the temperature of the sample had risen to the 25.0 °C of the apparatus the motor was run so that the inner cylinder was deflected. When this deflection had brought one mirror into the controlling position opposite the prisms and photocells the motor speed was allowed to increase automatically whilst the deflection remained constant. After the motor speed (which was displayed on the chart of the recorder) had been constant for a considerable time it was increased by means of an over-riding manual control until a second torque-control mirror took over. This was repeated for all the mirrors mounted on the inner cylinder, usually five, and the motor speed was then reduced in the same way. With the motor speed increasing the relaxation process was one of breakdown, or thinning; with the motor speed decreasing it was of build-up, or thickening. The ratios of the torques were 'K' and '1/K'.

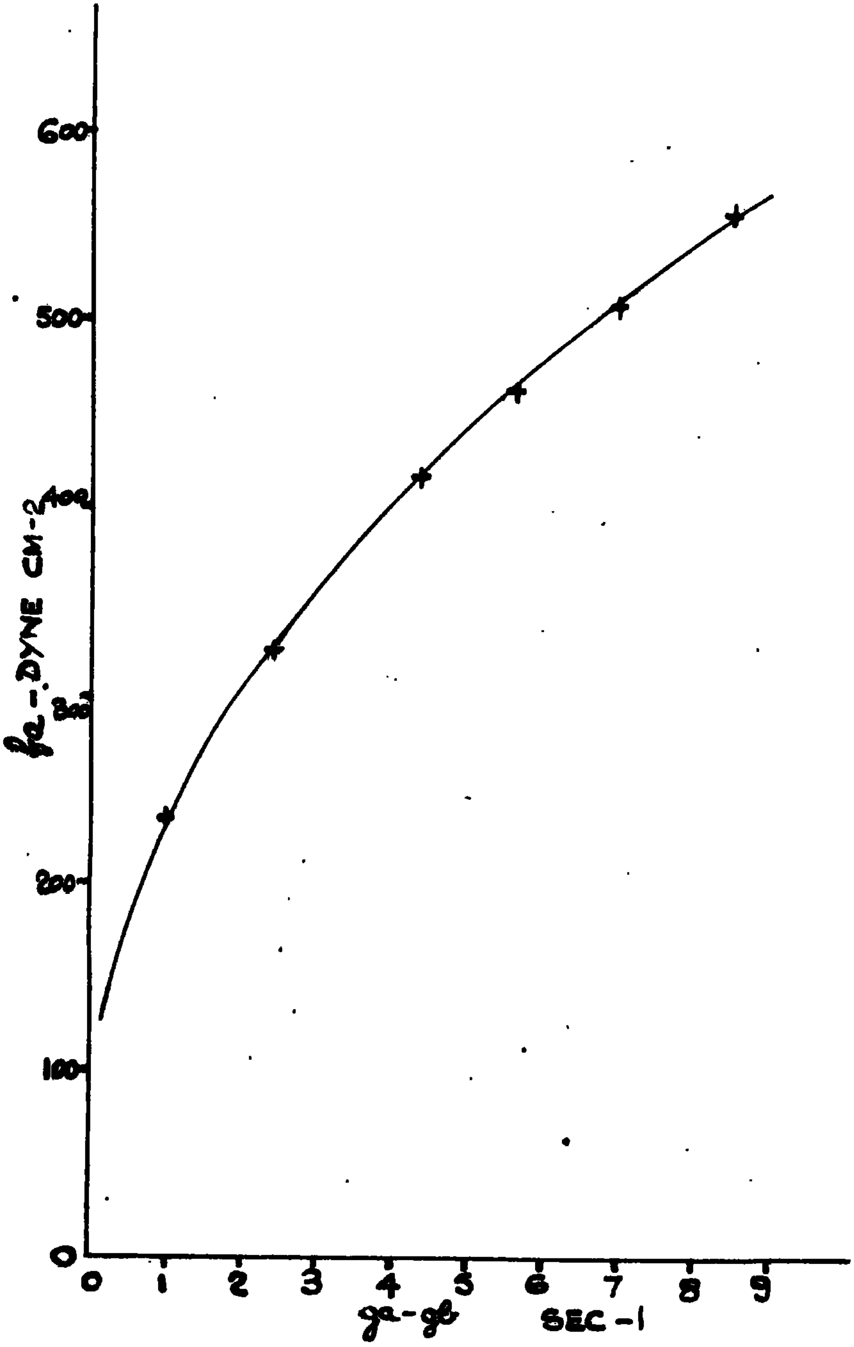
It was found that with the motor speed both increasing and decreasing all the samples studied came to equilibrium at the same values. It follows that the equilibrium rate of strain at a given shear stress must be independent of the prehistory of the material, that is to say the velocity gradient approaches the same equilibrium value after a long time under a given shear stress whether the material was initially in a thicker or thinner state.

6.21 - - Equilibrium properties of a typical material

The properties here described are similar to those found for all the pigment-oil dispersions studied and have been worked out in some detail for eleven different samples. The particular material chosen for this example is T13, prepared by milling together 1840 gm of Rutile Titanium

FIGURE 11

SEE TABLE III



dioxide (in the "Rutiox CR" form) with 500 ml of linseed stand oil (approx 30 poise) and 500 ml alkali refined linseed oil (approx 1 poise). The specific gravity of Rutile is 4.26 so the sample has thus 30 per cent concentration by volume of pigment. It was stored for five months at 25°C before testing in the viscometer.

The equilibrium motor speed for different deflections gives the (θ, R) curve, figure 10. By measuring the slope of this curve ($g_a - g_b$) was obtained. The calculation of 'f_a' depended upon the depth of immersion of the inner cylinder and the nature of the end-effect. The results in figure 10, curve A, were obtained with a depth of immersion 10.0 cm. The inner cylinder and cup were then removed and some of the sample emptied out for a second experiment with a depth of immersion 4.0 cm. This gave the results for curve B in figure 10. It was argued that the difference between the two equilibrium curves must be due to the difference in length of the cylinder immersed, care having been taken to see that the gap between the lower end of the inner cylinder and the base of the cup was the same in this and in all experiments. If it is assumed that any disturbance to the flow pattern near the end of the lower cylinder does not extend as far as 4.0 cm up the cylinder then the difference between the two equilibrium curves must be due to a length of cylinder 6.0 cm (the difference between the two depths of immersion) for which equations 4 and 11 are exactly true.

By proportion the effect of a true 10.0 cm immersion was calculated and compared with the observed (θ, R) curve for that immersion. The difference between them is shown in figure 10 as curve C. It was found that this discrepancy between the results for a true 10.0 cm immersion and a measured 10 cm immersion could be allowed for by adding a simple end correction to the measured length and that this correction was 1.0 ± 0.1 cm.

Having now derived 'f_a' and $(g_a - g_b)$ these values were plotted against each other as in figure 11. To a first approximation 'g_b' is the value of $(g_a - g_b)$ at $f_a/10$. This correction is very small and the consistency curve (f_a, g_a) is similar to figure 11.

6.22 Variation with temperature

The sample used in this experiment was T17, a 30 per cent by volume concentration of Titanium dioxide ("Rutiox" CR) in a 50-50 mixture of 30 poise linseed stand oil and 2 poise alkali refined linseed oil. The

FIGURE 12

SEE TABLE IV

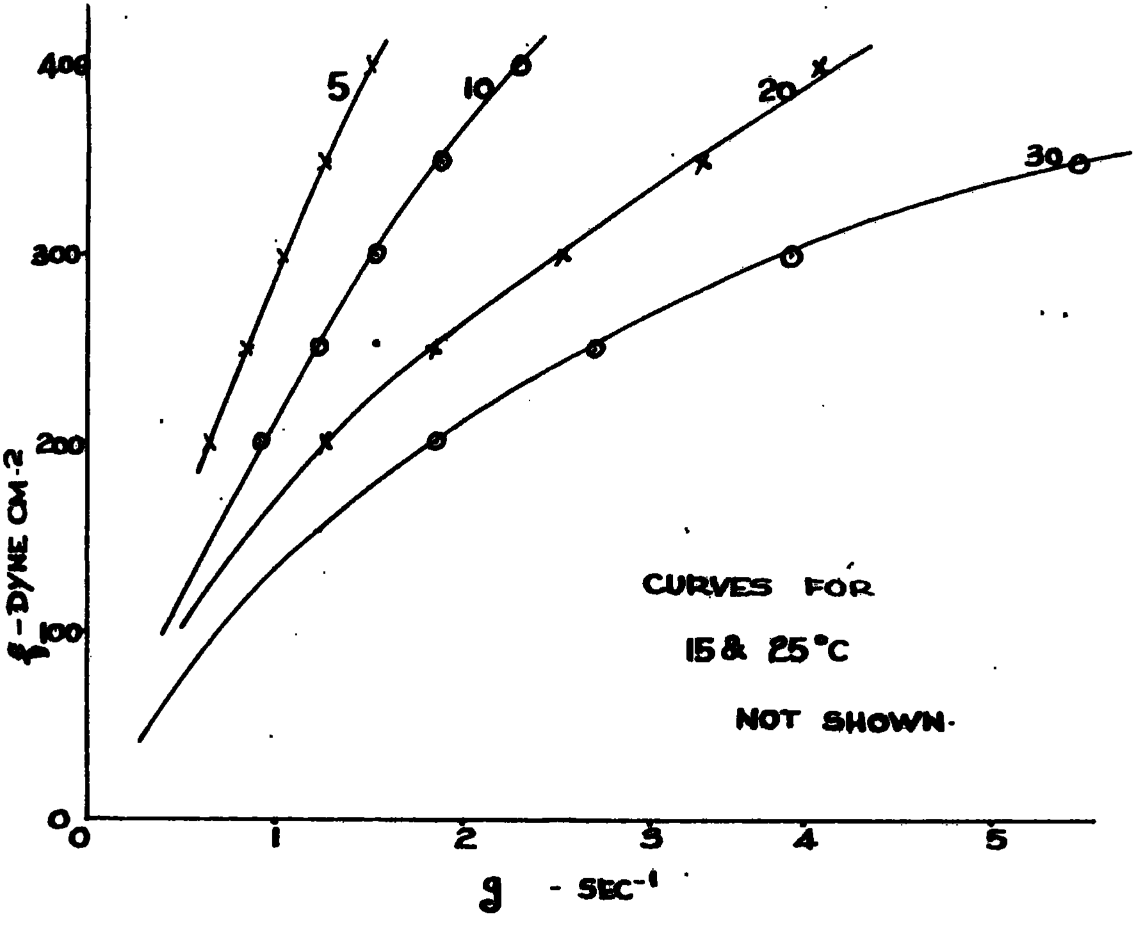
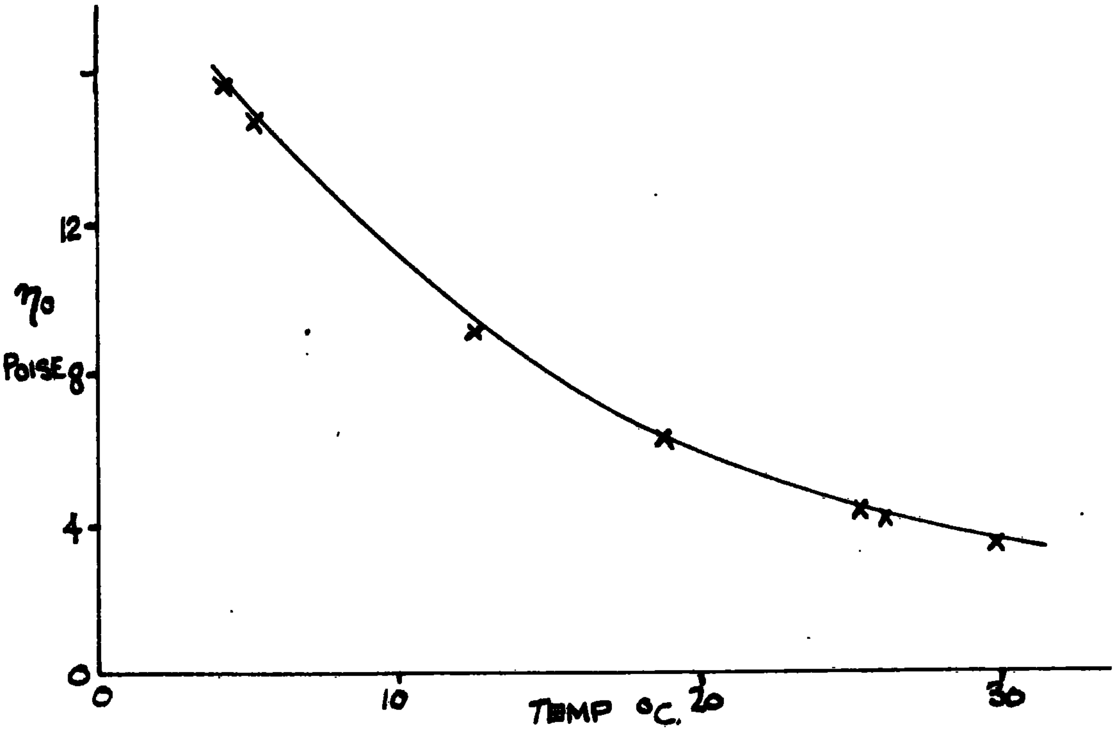
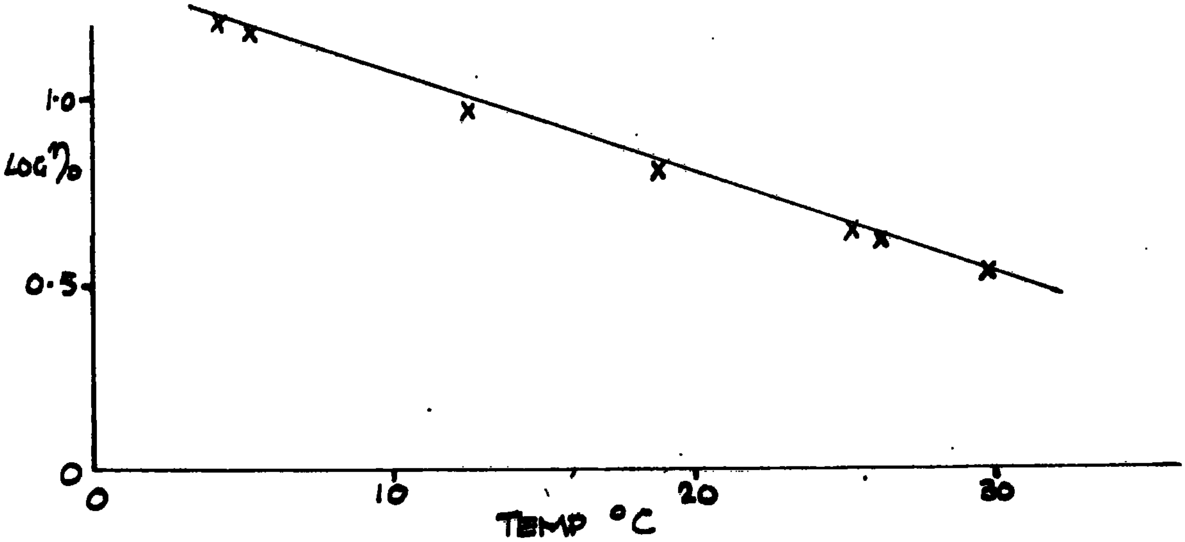


FIGURE 13

SEE TABLE V



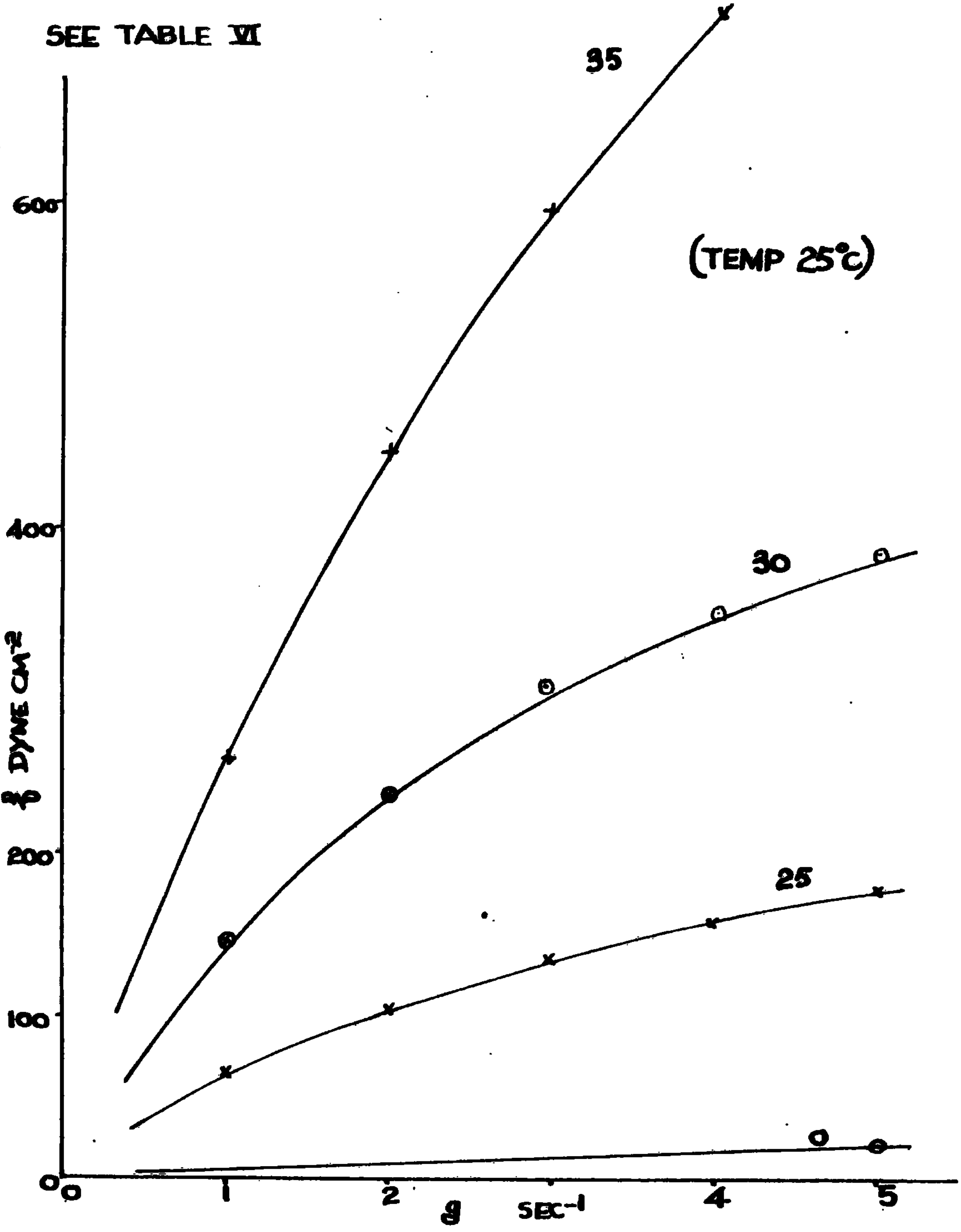


apparatus was maintained at 20, 25 and 30 °C by means of the heaters and thermostats and cooled with ice (together with some solid carbon dioxide to help lower the temperature initially) to give readings at reasonably steady temperatures of 5 and 11 °C.

Curves were plotted of motor speed against temperature for a given deflection and these were used to obtain curves of 'θ' against 'R' at different temperatures and hence the equilibrium consistency curves at different temperatures. These are shown in figure 12; the experiment was repeated three times and these curves are typical. In order to interpret these results (as in chapter 7) the variation of the viscosity of the medium alone with temperature was measured, this is shown in figure 13. The measurement was made in a British Standard Specification Ostwald type viscometer which was compared with a National Physical Laboratory calibrated viscometer of the same type. These viscometers were used in accord with the routine prescribed in the British Standards Institution pamphlet, B.S.S. 188:1937 (revised July 1953) for a number 4 size instrument. A constant temperature was maintained to within 0.1 °C by mounting them in a water bath containing a paddle, heater (or ice) and thermostat. The method

FIGURE 14

SEE TABLE VI



gave the kinematic viscosity and the density of the medium was measured with a Westphal balance and found to be 0.936 gm cm $^{-3}$, the variation with temperature being less than 0.0003 gm cm $^{-3}$ °C $^{-1}$.

6.23 Variation with concentration

For this experiment three similar oil and pigment systems were prepared, of 25, 30 and 35 per cent concentration by volume. The constituents were the same as for 'T17' in section 6.22, but the results for a concentration of 30 per cent at 25°C are not strictly comparable since different "batches" of pigment and oil were used in the manufacture. Although nominally the same these were often found to differ appreciably in many properties. As in all these experiments tests were made for reproducibility. The samples were stored for five or six months at 25°C before use and the observed irreversible changes in the duration of the experiment were well within the limits of experimental error. The equilibrium consistency curves are shown in figure 14.

6.3 Time-dependent properties

The curves on the Recorder chart showing the relaxation of motor speed at constant torque were analysed to derive the curves for the relaxation of the velocity gradient. The experiments were the same ones as those from which the equilibrium consistency curves were calculated by the method already described.

To ensure reasonable accuracy it was thought that 'K', the ratio of final to initial torques, should be large for breakdown and small for build-up. In the first experiments two mirrors were set in position on the inner cylinder, one at double the deflection of the other, so that the values of 'K' were 2.0 and 0.5. Several results were obtained in which it was noticed that though there was pronounced relaxation of the motor speed with time 'g_a' was found, on analysis, to change almost instantaneously to its new value. It was reasoned that since the relaxation in cylinder speed and hence in 'R' was due to the total relaxation of all the sample in the cup with a range of velocity gradients from 'g_b' to 'g_a', and since it was found that 'g_a' hardly relaxed at all, relaxation phenomena must be more pronounced at velocity gradients lower than 'g_a'. This suggestion was supported by several of the relaxation curves for velocity gradient which showed for the breakdown process (occurring at a large shear stress) a very rapid process or very small change in properties and for build-up (at smaller shear stress) a long-period relaxation. It would be rash to assume that the relaxation times associated with breakdown and build-up should be the same but it was thought that this observation lent force to the argument already advanced for supposing the relaxation process to depend upon the particular shear stress (or velocity gradient) at which it was taking place.

It was necessary to investigate this by calculating the relaxation of velocity gradient at different values of equilibrium shear stress and the same value of 'K'. If the deflections in the first experiment described above were 'θ' and '2θ' it was now desirable to make the range of torques 'θ, 2θ, 4θ, 8θ...', but a range of 1:4 or 1:8 in the deflection required such a range in the cylinder speed that the experiment became unwieldly and inaccurate. The alternative was to choose values of 'K' nearer to unity and most experiments were conducted with five pre-set mirrors on the inner cylinder giving torque ratios between adjacent settings of 0.8 for build-up and 1.25 for breakdown. Sometimes only three of these mirrors were used giving 'K' equal to 0.64 and 1.56.

In this work we were measuring a small change in flow properties, of a complex nature, which were super-

FIGURE 15

SEE TABLE VII

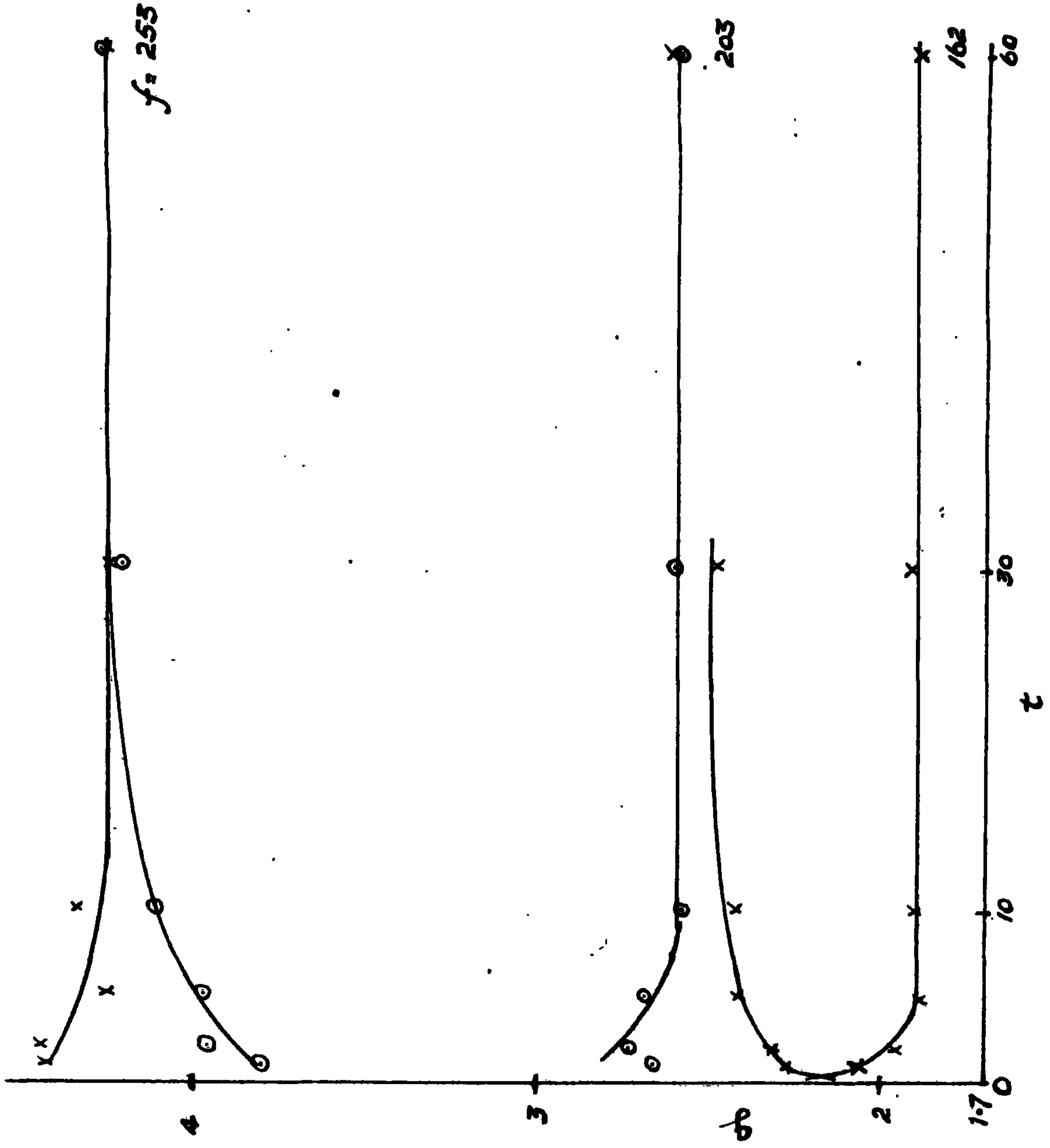
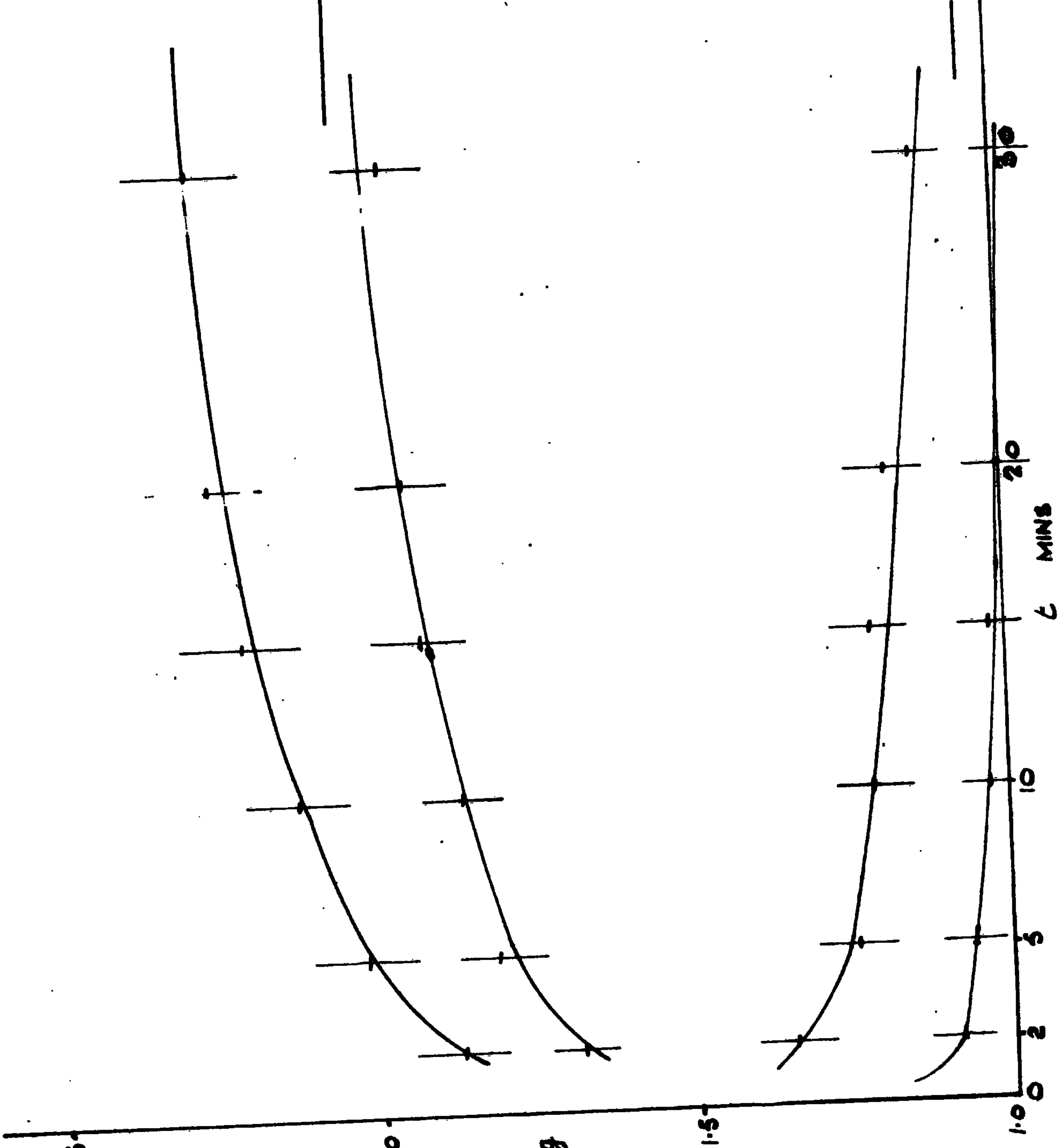


FIGURE 16 SEE TABLE VIII

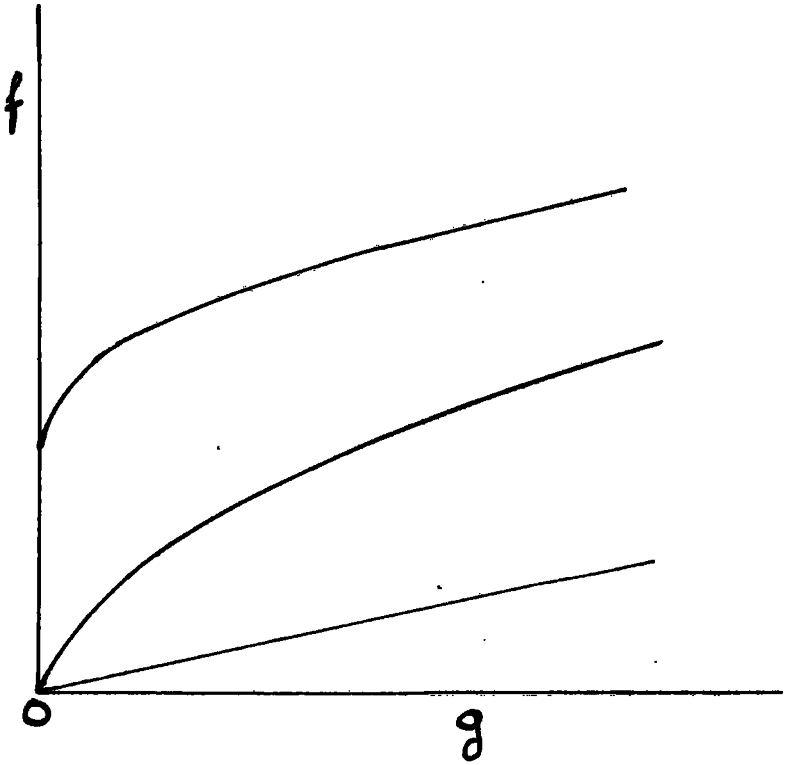


imposed on a system for which the equilibrium properties had already proved difficult to assess. By choosing values of 'K' fairly close to unity the task of obtaining accurate results for the instantaneous values of the velocity gradient became even more difficult. For this reason it is considered that the experimental results here presented are qualitative in nature. Although a comparison of relaxation properties at a given shear stress for which 'K' was taken as 0.64 and 0.8 show similarities similar to those predicted in section 2.4 (and figure 4) they are of insufficient accuracy to provide experimental support for that suggestion.

6.31 - - Time dependent properties of typical materials

Typical relaxation curves for 'K' equal to 0.8 and 1.25 are shown in diagrams 15 and 16. Figure 15 shows curves for sample T14, a 30 per cent by volume concentration of "Rutiox HD" in 50/50 30 poise linseed stand oil and 2 poise alkali refined linseed oil. Figure 16 shows some results on sample T13, it will be noticed that the lower curves, showing build-up, are still not very near equilibrium after 30 minutes.

FIGURE 17.



CHAPTER 7

DISCUSSION

7.1 Introduction

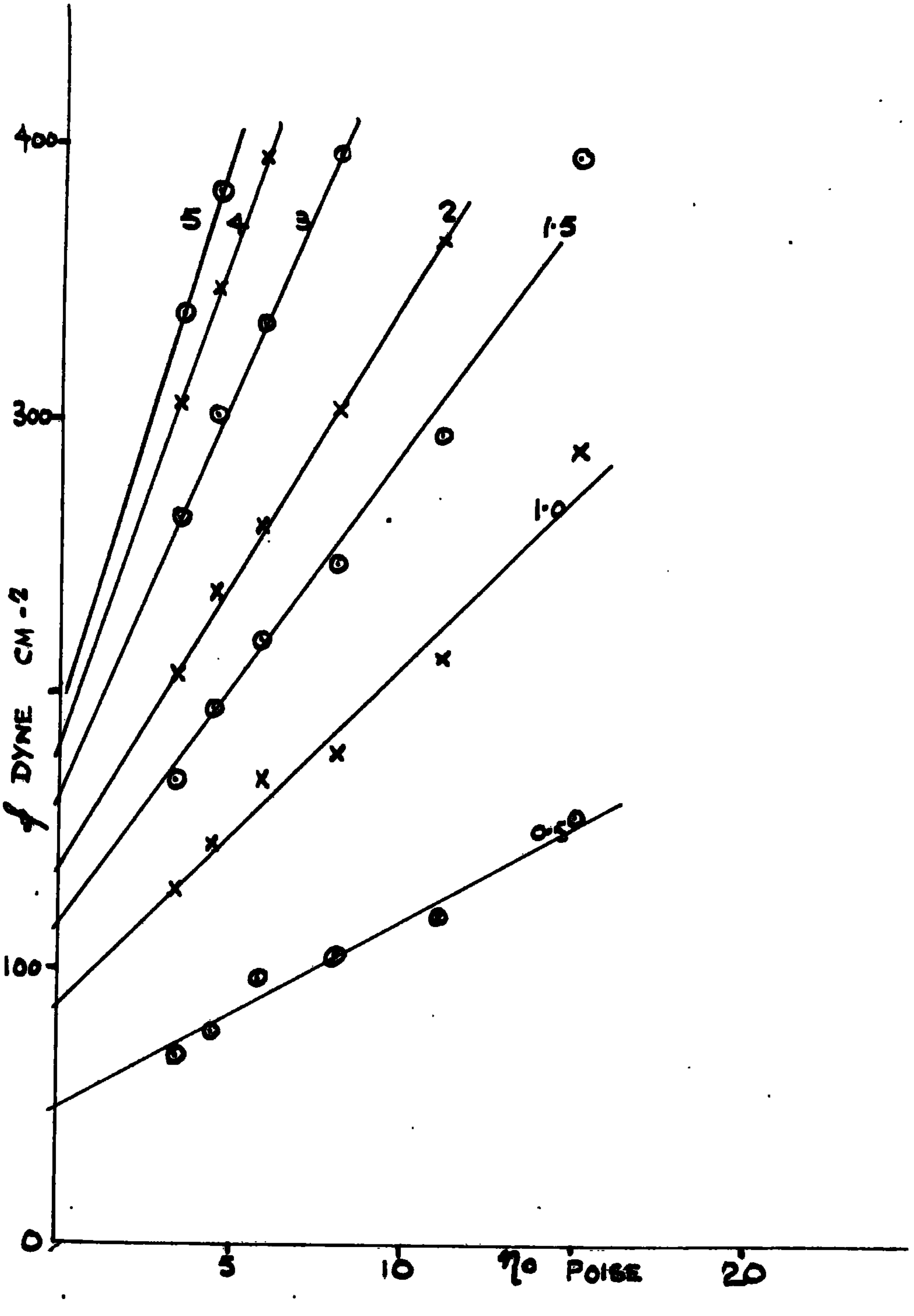
The results presented in the last chapter show that it is possible to measure the equilibrium flow behaviour of thixotropic materials and get some indication about their relaxation properties. These were examined in an attempt to find some pattern underlying them and some possible explanation of their form.

7.2 Equilibrium properties

7.21 - - Equilibrium properties of a typical material

Figure 19 is a sketch of typical equilibrium consistency curves for Newtonian, ordinarily thixotropic and false-bodied materials. It is seen that time-dependent thixotropy is a property of fluids intermediate in behaviour between the Newtonian and false-bodied; alternatively thixotropy may be regarded as a general case for which Newtonian and false-bodied properties are limiting conditions. Thixotropy is less pronounced at high rates of shear, where the consistency curve approaches linearity, suggesting that

FIGURE 18 SEE TABLE IX (SAMPLE T17)



thixotropic properties are in some way connected with the degree of curvature of the equilibrium consistency curve.

7.22 - - Temperature dependence and the flow function

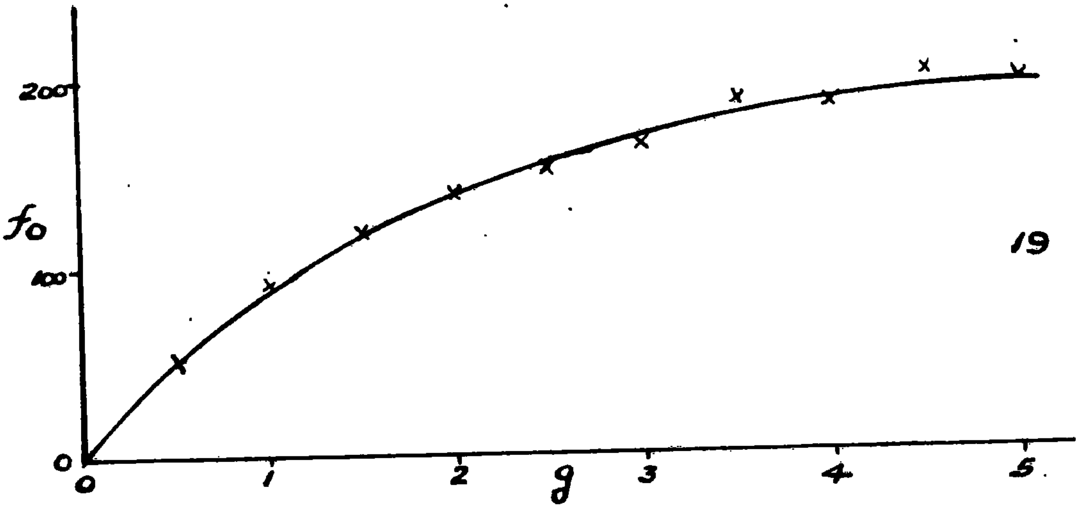
The temperature variation in the equilibrium flow properties must be due in part to changes in the viscosity of the medium. To investigate this relationship the variation in the shear stress with temperature at selected values of the velocity gradient was first deduced from figure 12. Using the known variation in the viscosity of the medium with temperature (figure 13) a graph was plotted showing the shear stress required to maintain a given velocity gradient in the sample against the viscosity of the medium. This is shown in figure 18, the numbers by each curve indicating the value of the velocity gradient. To a high degree of accuracy these curves are straight lines and the equation for any one of them may be written as

$$f = f_o + m\eta_o g, \qquad 17$$

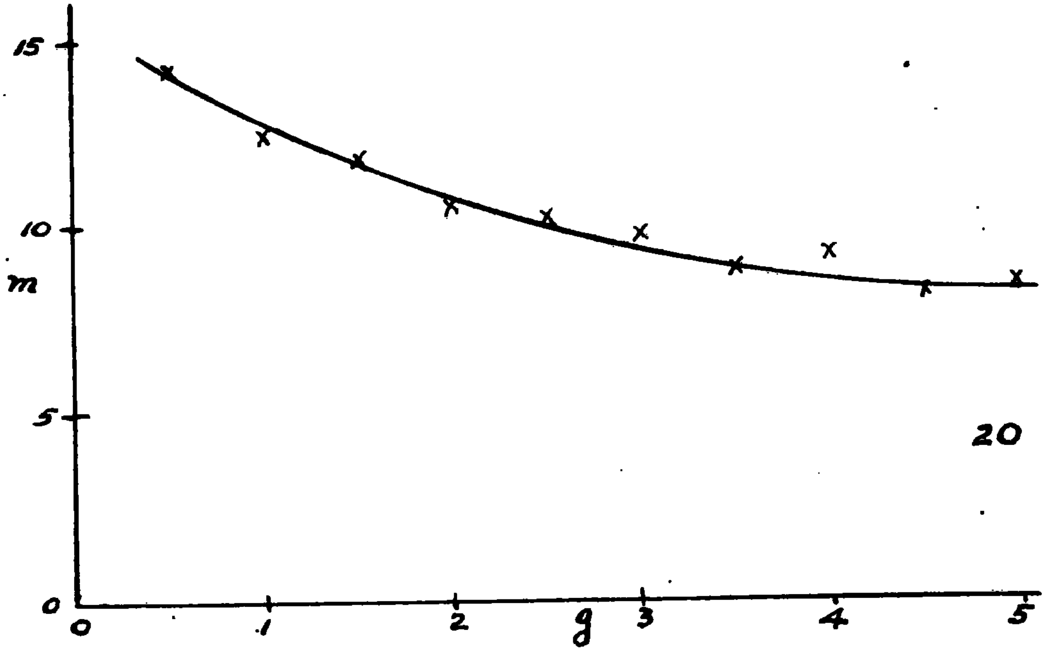
where 'f_o' is the intercept and 'mg' the slope.

This equation signifies that over the temperature range from 5 to 30 °C (a range in the viscosity of the medium of 3.4 to 15 poise) the shear stress required to

FIGURE 19 & 20 SEE TABLE X



19



20

maintain a given velocity gradient in the sample is given by the sum of a constant term and a term proportional to the viscosity of the medium. The values of both the intercept and the slope vary with the velocity gradient and figures 19 and 20 show this change of 'f_0' and 'm' with 'g'. It is clear that at large velocity gradients 'f_0' and 'm' both tend towards constant values - this was the reason for choosing the slope as 'mg' and not just 'm'. Thus at high rates of shear equation 17, with 'f_0' and 'm' as constants, describes the equilibrium flow properties of the material.

This flow function for high rates of shear corresponds to the equations of flow suggested by Bingham (1922), Buckingham (1921) and Reiner (1926). The deduction of the equation from experimental results given here confirms that the first term is independent of temperature and the second proportional to the viscosity of the medium. Its importance lies in the extension of this function to low rates of shear - that is to the curved part of the equilibrium consistency curve. Although in this region 'f_0' and 'm' are no longer constants but parameters depending on the rate of shear, it is evident that the dependence on temperature takes the same form.

Goodeve and Whitfield (1938) take 'f_0' as a coefficient of thixotropy and Goodeve (1939) derives it theoretically from a supposition of inter-action between the particles and suggests that it is independent of temperature. Rae (1952) also suggests that the effect of inter-particle forces does not vary with temperature and it is reasonable to suppose that the 'f_0' term gives the resistance to flow due to inter-particle forces. The '$m\eta_0 g$' term has the usual form for the hydrodynamic viscosity of a system of non-interacting particles. The variation of 'm' and 'f_0' with velocity gradient may be explained qualitatively in terms of a disruption of structure at high rates of shear.

It was thought possible that the change in pigment concentration as the liquid expanded with a rise in temperature might affect the results. The change in concentration was calculated and its contribution to the shear stress at a constant velocity gradient estimated by comparison with the experimental curves for the variation of equilibrium properties with concentration. The effect was found to be very small and no correction was made for it.

FIGURE 21 SEE TABLE X

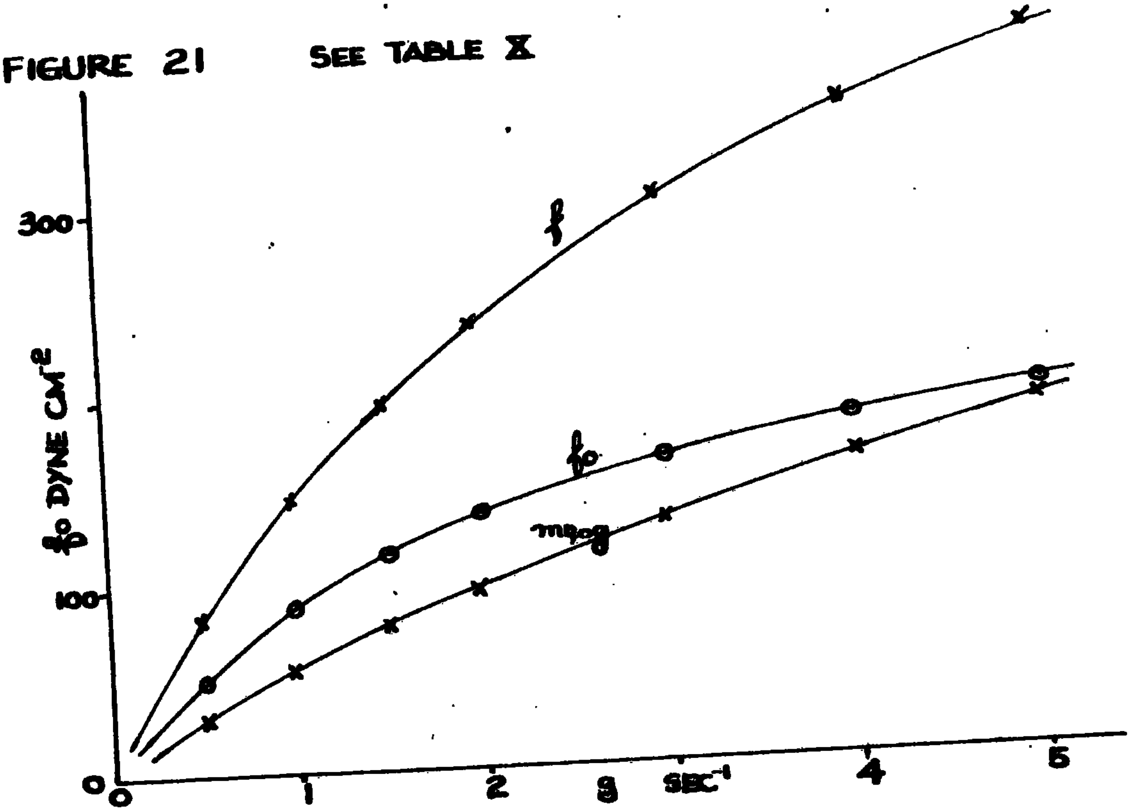


FIGURE 22 SEE TABLE XI

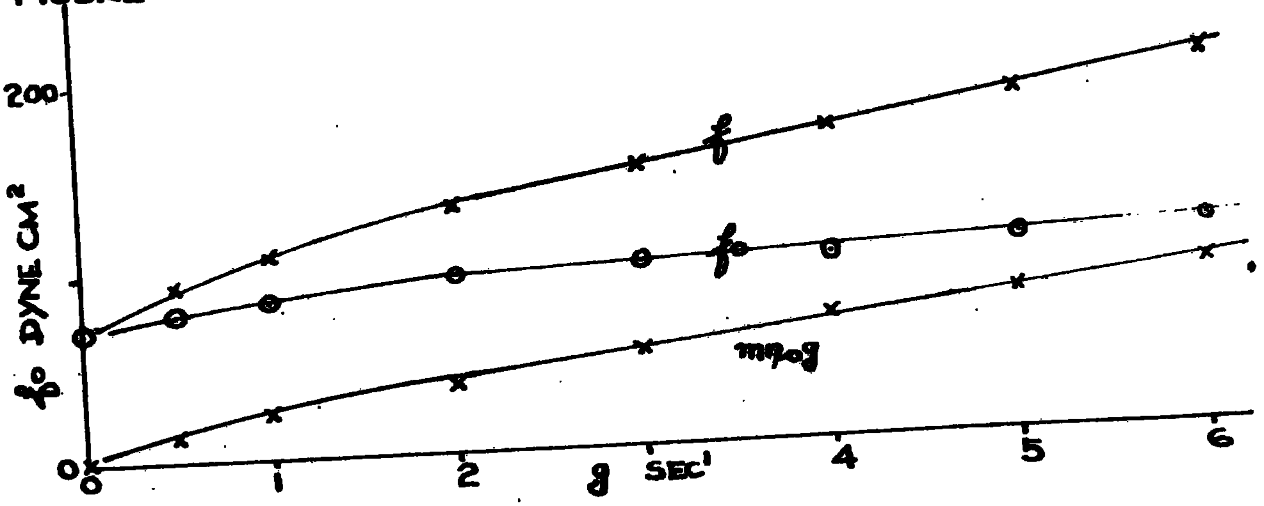
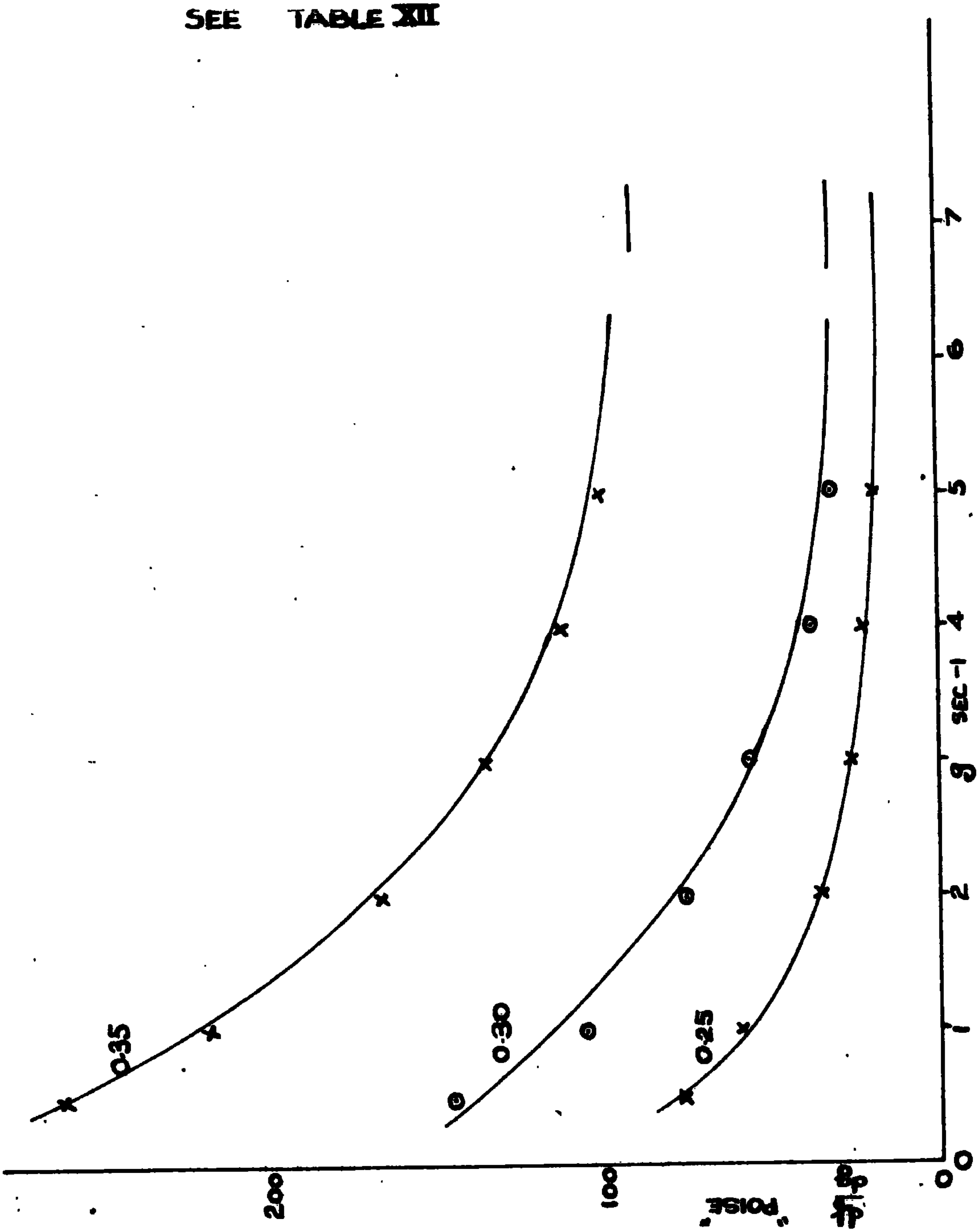


Figure 21 summarizes the properties described by the flow function. It shows the separate contributions from the temperature dependent and temperature independent terms to the value of the shear stress in the consistency curve for a specimen at 25 °C. A similar analysis has now been applied to some results given by Rae (1952) for the temperature dependence of an instantaneously thixotropic but false-bodied material (10 per cent anatase Titanium dioxide in oil of approx 2 poise). The suggested flow function was found valid for this material; 'f_o' and 'm' varied with the rate of shear much as in figures 19 and 20, except that 'f_o' started at the yield value when the rate of shear was zero. Figure 22 shows the separate contributions to the shear stress for this material.

It was concluded that the flow function given as equation 17 is valid for a wide range of anomalous fluids. It was derived for normally thixotropic materials - the general case - and found true for an instantaneously thixotropic sample exhibiting the complication of "false-body"; it clearly covers Newtonian systems as the special case when 'f_o' is zero and 'm' constant for all rates of shear. It would be valuable to check this equation by

FIGURE 23

SEE TABLE XII



preparing and testing samples in media of differing viscosity but it is doubtful if the results would be conclusive. The flow properties of thixotropic systems seem remarkably dependent on chemical reactivity between the pigment and the medium and any change in this reactivity, using media of different viscosities, would mask the viscous effect. Whilst the reactivity may also vary with temperature the properties of the samples tested did not suffer any permanent change when the temperature was altered for a time and the method given above would seem the one best suited to the derivation of a flow function from experiment.

7.23 - - Concentration effects and inter particle forces

In order to study the variation in equilibrium flow properties with concentration it is easiest to start by considering the limiting form of the flow function at high rates of shear. Then the parameters 'f_o' and 'm' are constants and the equilibrium consistency curve is a straight line of slope '$m\eta_o$' which, when produced, makes an intercept on the 'stress' axis of 'f_o'. Figure 23 shows the slope 'df/dg' of the equilibrium curves for three different concentrations (shown in figure 14) plotted against the velocity gradient 'g'. It is clear that these curves do not all reach the limiting condition within the range of

FIGURE 24

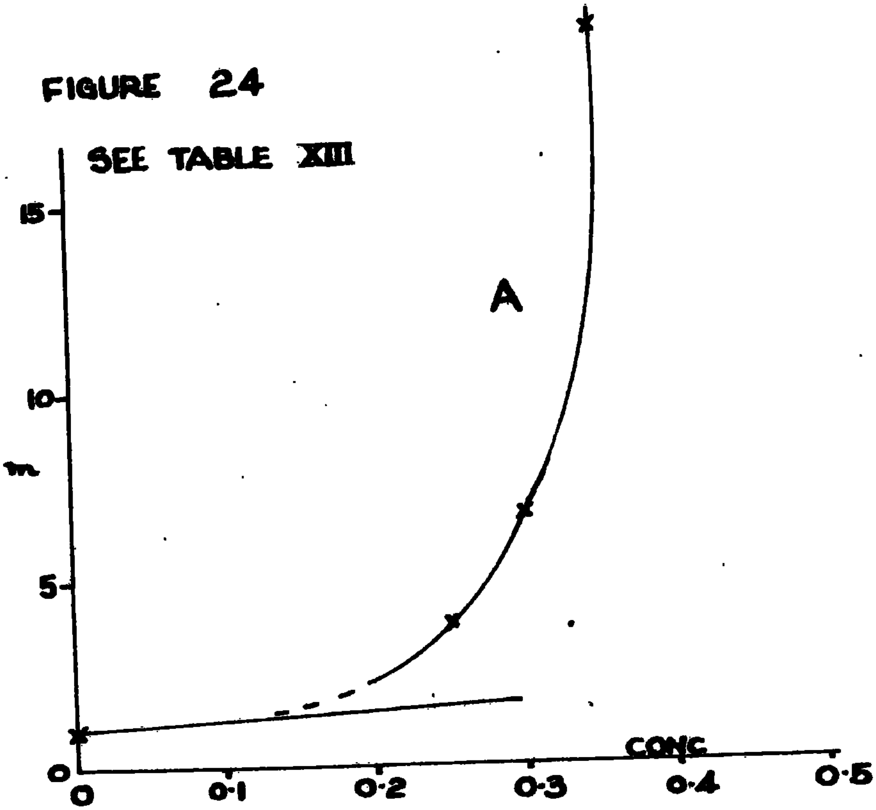
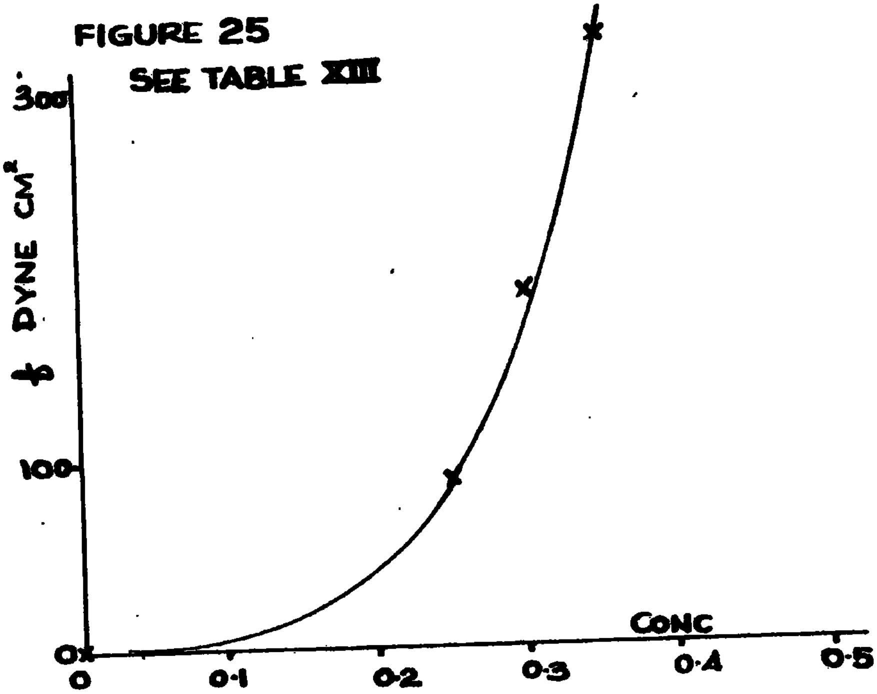

SEE TABLE XIII

FIGURE 25


SEE TABLE XIII

values obtained for 'g' and the estimated limit of '$m\eta_o$' is necessarily approximate. The three values obtained for 'm' by this method are plotted against concentration in figure 24. These results, shown as curve A, are compared with the theoretical line suggested by Einstein (1906, 1911) for spherical particles at infinite dilution for which the equation is "$m = 1 + 2.5c$", where 'c' is concentration. From the limiting values of 'm' the limiting values of 'f_o' were calculated. Their variation with concentration is shown in figure 25.

We are now able to consider a qualitative picture of thixotropic flow. This is based on the model advanced by Goodeve (1939) in which particles brought close to each other link together. When flow occurs in a suspension, particles in adjacent layers move over one another; links are formed between them and then broken as the flow continues. The breaking of each link is said to impart an impulse to each particle. Multiplying the magnitude of this impulse by the number affecting a unit area in unit time gives the rate of change in momentum and hence the shear stress required. The magnitude of the impulses is found to be inversely proportional to the velocity gradient and the frequency with which they occur proportional to it.

They thus give a contribution to the shear stress which is independent of the velocity gradient, accounting for the constant value of 'f_o' in equation 17 at high rates of shear.

Vand (1948) suggests that at high concentrations fairly permanent links formed between particles make them behave as "clots" or "flocculates" and that at the highest concentrations the structure must be continuous throughout the suspension. The disruption of this structure and the subsequent reduction in mean size of the flocculates with an increasing rate of shear could account for the variation in value of 'f_o' and 'm' with rate of shear. At low rates of shear large flocculates would necessarily have large distances between them and any contribution to shear due to their interaction would be small. They would also immobilise a proportion of the liquid thus increasing the hydrodynamic viscosity. At high rates of shear when 'f_o' and 'm' are constant the particles would be individually dispersed in the medium.

In the materials used to obtain the results for this thesis the concentration of particles was usually about 0.3 (by volume). This suggests that their separation is small compared with their size and it might be expected that they would form a closely linked structure. Despite this an attempt was made to develop the Goodeve theory to give a quantitative interpretation of the results and this is now described in outline.

Suppose that instead of forming links there is an inverse nth power law of attraction between every particle in the system. Then the effect of this would be greatest when one particle passes over another in an adjacent layer. As the particles approach one another the force between them supports the existing velocity gradient, as they separate it acts against it. A conceptual difficulty arises here, for it must be supposed that inter-particle forces contribute to the shear stress only when acting against the velocity gradient; (this corresponds to the supposition by Goodeve that an impulse is given when particles are separated but not when a 'link' is formed). It can be argued that when inter-particle forces act in support of the velocity gradient they do useful 'work' in maintaining it, but that when they act against it energy is dissipated. It was found possible to derive the same equation for the shear stress either by considering the transfer of momentum per unit area or the dissipation of energy per unit volume.

For this model the shear stress required to overcome the inter-particle forces is inversely proportional to the (n + 2) th power of their mean separation. A comparison between this prediction (for an ideal model of discrete spherical particles) and the variation in 'f_o' with concentration obtained experimentally would suggest that the value of 'n' was about twelve. On modifying the theory to allow for an inverse power law of force between particle surfaces instead of particle centres the value of 'n' became about 1.8.

It is not suggested that this comparison between the modified Goodeve model and experiment has any significance at present. But it suggests a possible extension of the work in this field. Experimentally it is necessary to work at high rates of shear, preferably with suspensions of chemically inactive spherical particles of uniform size. Small glass or polystyrene spheres suspended in an oil of suitable density might satisfy this condition. An investigation of the variation in flow properties with temperature would confirm or disprove the validity of equation 17 and, if valid, the change in 'f_o' with differing concentrations could then be found. On the theoretical side it would be necessary to justify the suppositions in calculating the shear stress and select a suitable parameter (e.g. distance between centres, least separation of surfaces) to describe the mean separation between the particles.

7.3 Time dependent properties.

7.31 - - Typical materials

Figures 15 and 16 are typical of a great number of curves obtained experimentally for the relaxation of velocity gradient at constant shear stress. All of them show a characteristic form - an instantaneous change in velocity gradient when the shear stress is changed (time = zero on graphs), followed by a slow relaxation towards the equilibrium value.

The instantaneous change had been expected, for even if the system retained momentarily its original viscosity or "structure" the velocity gradient would change suddenly with a sudden change in the shear stress. An examination of this change shows that neither the apparent viscosity nor the value of the parameters 'f_o' and 'm' remains momentarily constant. Assuming the validity of the flow equation it follows that a change from one value of shear stress to another is accompanied by a sudden change in both 'f_o' and 'm' and then a gradual relaxation in these quantities. This must be interpreted as a sudden change in "structure" followed by a gradual one.

The relaxation process is thus seen to be very complicated. To describe it at all we need two concepts; a magnitude of thixotropic change - which can be considered as the change in 'f_o' and 'm' for a given change in shear stress; and a relaxation time - which for curves combining an instantaneous change with a slow relaxation is difficult to define with any accuracy. Since 'f_o' and 'm' both must be determined by the "structure" of the system they are not independent constants and the change in either of them can be taken to indicate the magnitude of the thixotropic change involved. Possibly df_o/df or df_o/dg would be a preferable "coefficient of thixotropy" to the 'f_o' suggested by Goodeve.

The results obtained do not give genuinely quantitative information about relaxation properties, but they give a clear indication of the variation of thixotropic effects with rate of shear (or shear stress) and with concentration.

FIGURE 26

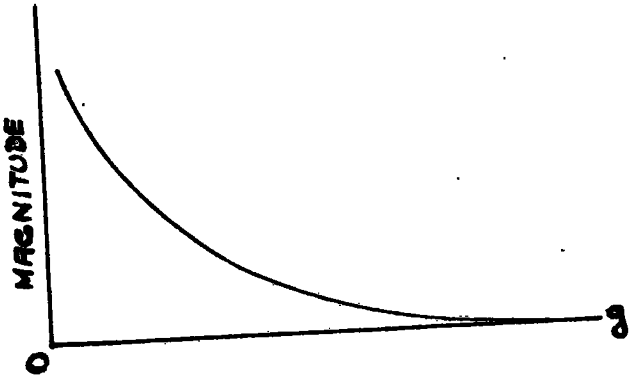
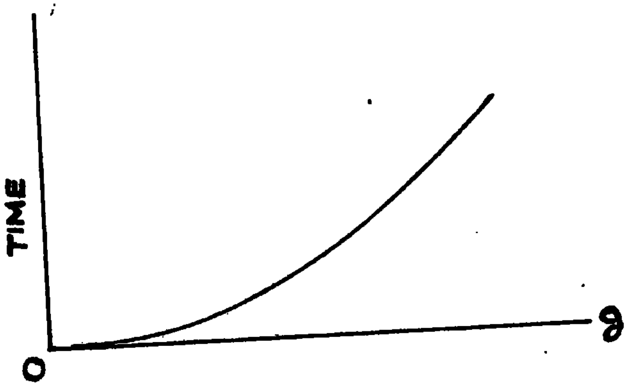


FIGURE 27



It was found that at high rates of shear thixotropic relaxation could not be detected and this is attributed to the very small changes in magnitude of 'f_0' and 'm' in this range. As described in section 6.31 thixotropic relaxation was often more pronounced at velocity gradients less than that at the inner cylinder, this being the only way to explain pronounced relaxation of the cylinder speed with negligible relaxation of 'g_a' observed in some experiments. Figure 26 is a sketch showing the suggested relation between magnitude of thixotropic change and velocity gradient. If the relaxation time is defined as the time taken to reach within a given percentage of the equilibrium position then figure 27 shows the behaviour found in a number of experiments. Then Newtonian flow is seen to be a particular case of thixotropic flow when the magnitude of change in the flow properties is zero and the relaxation time infinite; instantaneously thixotropic false-bodied materials show large but very rapid changes in their properties.

In order to compare thixotropic properties between one material and another it is necessary to specify the velocity gradients at which the comparison is to be made. This led to difficulties in assessing the variation of time-dependent properties with temperature and concentration and

FIGURE 28

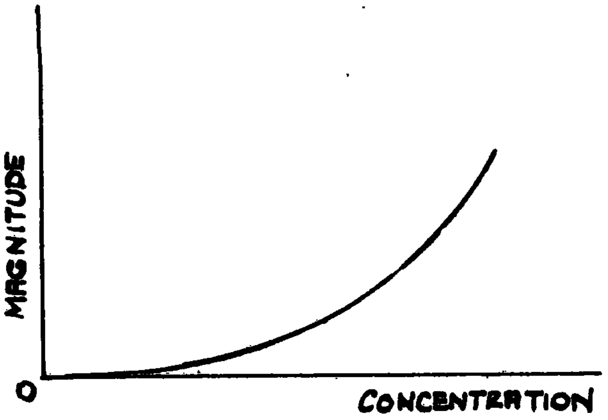
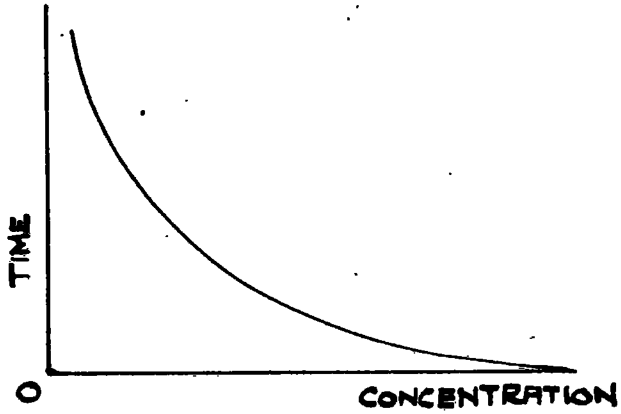


FIGURE 29



no experimental results are given for this. However it was observed that increases in concentration increased the deviation from normal flow towards false-bodied properties and figures 28 and 29 show qualitatively the variation in magnitude and "relaxation time" with concentration.

These diagrams show the factors which determine the suitability of a material for a quantitative study of thixotropy. Both the concentration of the specimen and the range of velocity gradients over which it is studied must be such that the magnitude and time-variation of changes in the flow properties are susceptible to accurate measurement.

CHAPTER 8

CONCLUSION

It has been shown that the equilibrium properties of a thixotropic suspension can be measured with reasonable accuracy and that they are completely represented by a single consistency curve. From the observed variation in these properties with temperature it was deduced that, at any given velocity gradient, the shear stress is given by the equation

$$f = f_o + m\eta_o g, \qquad 17$$

where 'f_o' and 'm' are constant in the temperature range 5 to 30 °C and 'η_o' is the viscosity of the medium. The temperature dependent component of the shear stress, '$m\eta_o g$', is comparable to the viscous effect of a system of non-interacting particles; 'f_o' is attributed to the effect of inter-particle forces.

Both 'f_o' and 'm' vary with the velocity gradient 'g', approaching limiting values when this is large. At high velocity gradients, when 'f_o' and 'm' may be considered constant, equation 17 reduces to the familiar "Bingham" form. Its deviation from this form at low velocity gradients may be explained qualitatively in terms of a flocculation of the particles. The extent of this flocculation, or in more general terms the "structure" of the system, is seen to depend on the velocity gradient, since equation 17 describes the variation in shear stress with temperature at constant velocity gradient (and not the variation in velocity gradient with temperature at constant shear stress). This is in agreement with a suggestion made on theoretical grounds by Goodeve (1939) that when flow occurs in a system of particles the number of interactions between them in unit time is proportional to the velocity gradient. In its general form, with 'f_o' and 'm' as parameters whose value depends on the velocity gradient, equation 17 represents the flow properties of the thixotropic and instantaneously thixotropic false-bodied materials considered over the whole range of velocity gradients; it is also valid for Newtonian fluids. It shows that the shear stress has two components, one proportional to the viscosity of the medium and the other independent of temperature. An experiment has been suggested which would use these conclusions to gain information on the nature of inter-particle forces from the measurement of consistency curves at large velocity gradients.

Experimental results indicate that the relaxation process is very complicated and that it depends upon the range of velocity gradients (or shear stresses) considered. Curves are given showing the approximate relationship between time-dependent properties and velocity gradient, and also their variation with concentration. These indicate some of the considerations involved in designing experiments and seeking materials for further work in this field.

These results were all obtained with suspensions of Titanium dioxide pigment in oils and their application to the behaviour of thixotropic materials in general might be questioned. The suitability of the flow function, and of the curves describing thixotropic relaxation, in considering the properties of other materials must be the subject of further experiment: The approximate results obtained earlier for Bentonite suspensions are very similar to those for the pigment-in-oil suspensions; including consistency curves of the same form and a similar variation in thixotropic relaxation time with velocity gradient and with concentration. The Bentonite in water suspensions were of six to eight per cent concentration of Bentonite by mass; they were normally thixotropic but showed false bodied behaviour as well. The Bentonite suspensions in glycerine were of twenty and thirty per cent by mass and had normal thixotropic properties without false-body. Hence Bentonite particles, with a plate-like structure differing greatly from Titanium dioxide pigments, give similar thixotropic properties when suspended in various liquids. It is therefore legitimate to expect that the results here given in some detail for Titanium dioxide suspensions will be found typical of thixotropic behaviour.

APPENDICES

APPENDIX 1

TABLES OF RESULTS

Experimental results are presented graphically in the body of the thesis and the numerical values from which these graphs were drawn are now given.

In these tables of results the quantities below have the dimensions noted:

f	shear stress	dyne cm^{-2}
g	velocity gradient	sec^{-1}
θ	deflection	angular degrees
R	motor speed	revolutions per minute
t	time	minutes

INDEX TO TABLES.

For figure	7	see table	I
	10		II
	11		III
	12		IV
	13		V
	14		VI
	15		VII
	16		VIII
	18		IX
	19 - 21		X
	22		XI
	23		XII
	24 & 25		XIII

TABLE I Calibration curve for pen-recorder.

(Figure 7)

Motor speed (R)	Reading on scale of recorder		
	Scale 1	Scale 2	Scale 3
25			13.0
50		8.3	16.0
75			20.0
188		17.7	39.5
375		30.5	69.5
500		39.0	89.5
600	19.7	46.5	
800	26.3	61.5	
1000	33.0	77.0	
1500	49.6		
2000	66.5		
2500	83.5		

TABLE II Flow curves for sample T13

(Figure 10)

(i) $h = 10.0$ cm

θ	R
110	255
120	320
130.5	430
219	1750
241	2200
260.5	2630

(ii) $h = 4.0$ cm

θ	R
37	55
48	214
52	300
57.5	420
80	1000
98.5	1730
107.5	2190
119	2650

(iii) The difference between these curves gives the curve for a true immersion of 6.0 cm and that for 10.0 cm was calculated. The discrepancy between this and the curve already given for a measured 10.0 cm immersion is '$\Delta\theta$' and is shown to be proportional to 'θ'_{10}'.

(Cont.)

R	θ_{10}	θ_4	θ'_{10}	'$\Delta\theta$'	$\Delta\theta/\theta'_{10}$ X 10
200	100	46	92	9	1.0
600	146	66	133	13	0.98
1000	176	80	160	16	1.00
1400	201	91	183	18	0.98
1800	222	101	202	20	0.99
2200	241	110	218	23	1.05

The last column gives the end correction, which was taken as 1.0 ± 0.1 cm.

TABLE III Equilibrium consistency curve for sample T13

(Figure 11)

θ	f_a	$dR/d\theta$	$2\theta dR/d\theta$	$g_a - g_b$	g_b
100	231	6.2	1240	0.99	0.027
140	324	10.7	3000	2.40	
180	417	15.0	5400	4.32	
200	463	17.8	7120	5.70	0.04
220	510	19.5	8580	7.07	
240	556	21.4	10272	8.22	0.10

For this calculation 'h' was taken as the corrected value of 11.0 cm, hence $f_a = 25.44\ (\theta/h)$. The correction for g_b was very small and was neglected. The errors in $(g_a - g_b)$ decrease as 'θ' increase, being 5% for $\theta = 100$, 4% for $\theta = 140$, then 3%.

TABLE IV Variation in equilibrium properties with temperature

(Figure 12)

Values of velocity gradient shown against shear stress and temperature.

		Temperature in °C.						
		5	10	15	20	25	30	Error in 'g'
Shear	200	0.66	0.92	-	1.28	1.55	1.86	5%
stress	250	0.85	1.22	-	1.85	2.19	2.69	4%
f	300	1.04	1.53	1.93	2.52	2.96	3.93	4%
	350	1.27	1.88	2.47	3.26	4.03	5.45	3%
	400	1.51	2.29	3.02	4.09	5.59		3%

TABLE V Variation in viscosity of medium with temperature

(Figure 13)

Temp. °C	η_0 poise	log η_0
4.2	15.8	1.20
5.2	14.8	1.17
12.5	9.20	0.964
18.7	6.32	0.801
25.2	4.39	0.642
26.1	4.17	0.620
29.8	3.43	0.535
29.9	3.41	0.533

TABLE VI Variation in equilibrium properties with concentration.

(Figure 14)

Values of shear stress shown against velocity gradient and concentration

Concentration (proportion by volume) of pigment.

		0.25	0.30	0.35
Vel	1	65	146	260
grad	2	104	237	448
'g'	3	135	302	595
	4	158	347	718
	5	178	384	824

The shear stress of the medium alone (concentration thus zero) rises linearly to 22.25 dyne cm^{-2} at $g = 5$.

TABLE VII Relaxation curves for sample T14

(Figure 15)

Values of velocity gradient shown against shear stress and time

	Shear stress, f			
Time	162	203	253	316
1	2.06	2.66	4.42	
2	1.96	2.73	4.44	
5	1.88	2.68	4.24	
10	1.90	2.57	4.33	
30	1.91	2.60	4.24	
60	1.89	2.59	4.26	
Equilibrium	1.88	2.60	4.28	
1		2.27	3.80	6.02
2		2.31	3.96	6.19
5		2.41	3.97	6.22
10		2.42	4.11	6.17
30		2.48	4.21	6.19
60		2.62	4.28	-
Equilibrium		2.57	4.27	6.14
Probable errors in 'g'	7	6	5	4 per cent

TABLE VIII Relaxation curves for sample T14

(Figure 16)

Values of velocity gradient shown against shear stress and time

Time	Shear stress, f			
	306	327	246	262
2	1.68	1.87	1.08	1.34
5	1.81	2.02	1.06	1.24
10	1.86	2.12	1.03	1.21
15	1.92	2.20	1.02	1.21
20	1.94	2.25	1.00	1.18
30	1.96	2.27	0.98	1.12
Equilibrium	2.04	2.28	0.86	1.04
Errors	3½	4	5	5

per cent

<u>TABLE IX</u> (Figure 18) Variation in shear stress at constant velocity gradient as medium viscosity changes with temperature.

Values of shear stress shown against velocity gradient and medium viscosity.

		η_0					
		15.0	11.0	8.0	5.8	4.45	3.40
Values	0.5	156	120	106	97	83	72
of	1	290	214	180	170	146	130
g	.5	397	295	248	220	195	172
	2	-	366	305	262	237	207
	.5	-	-	355	300	272	238
	3	-	-	397	335	302	264
	.5	-	-	-	366	326	290
	4	-	-	-	396	348	306
	.5	-	-	-	424	366	323
	5	-	-	-	-	384	339

TABLE X Variation of 'f_o', 'm' and 'f' and '$m\eta_o g$' with 'g'.

(Figures 19 - 21)

'f', 'f_o' and '$m\eta_o g$' are in dyne cm^{-2} and 'm' is a pure number.

g	f_o	m	$m\eta_o g$	f
0.5	50	14.2	31.6	83
1.0	90	12.4	55	146
.5	117	11.8	79	195
2.0	137	10.5	93	237
.5	150	10.2	114	272
3.0	164	9.7	130	302
.5	185	8.8	137	326
4.0	183	9.2	164	348
.5	200	8.1	161	366
5.0	195	8.4	187	384

TABLE XI Analysis of Rae's results, as Table X.

(Figure 22)

g	f_0	m	$m \eta_0 g$	f
0.0	70	-	0	70
0.5	78	15.6	14	92
1.0	83	13.6	24	107
2	95	10.7	37	132
3	100	9.9	52	152
4	101	9.8	67	168
5	107	9.0	78	185
6	112	8.5	89	201

TABLE XII (Figure 23) Change in slope of equilibrium curves with velocity gradient at different concentrations.

Values of 'df/dg' shown against velocity gradient and concentration.

		Concentration		
Vel		0.25	0.30	0.35
grad	0.5	77	146	262
g	1	59	106	218
	2	35	76	167
	3	26	56	135
	4	22	38	112
	5	19?	32	100

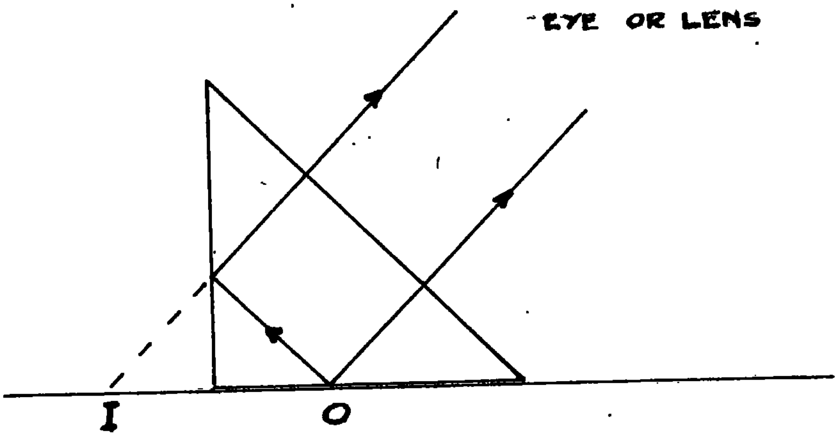
TABLE XIII The dependence of 'f_o' and 'm' on concentration

(Figures 24 & 25)

Conc	m	f_o
0.25	3.8	90
0.30	6.7	190
0.35	19.6	326
0.00	1.0	0

FIGURE 30

SECTION IN VERTICAL PLANE



APPENDIX 2

MEASURING THE GRADIENT OF A CURVE

As described in Section 4.4 it was necessary to measure accurately the gradient at different points on a curve drawn through several values of 'θ' and 'R'. The alignment of a straight edge tangentially to the curve was found on inspection to give a large random error and a more accurate method was sought.

The method eventually chosen employed a right-angled prism. This rested on the curve (figure 29) with the face opposite the right-angled edge uppermost, so that the vertical face acted as a mirror. Viewed from above the portion of the curve on which the prism rested was seen twice, once directly through the lower face of the prism and once reflected in the vertical face. If the edge of the prism was normal to the curve the two images met at the edge in one smooth line; if the prism was at an angle 'α' to the normal the object and image curves differed by an angle '2α' at the reflecting surface.

In order to measure the gradient at a given point on the curve the prism was placed with the vertical surface above the point and its edge approximately normal to the curve. It was rotated slowly until the direct and reflected images of the curve appeared to join in one smooth line, the edge of the prism then was normal to the curve at the selected point. The slope of the normal was measured and the gradient calculated.

The accuracy of measurement with this device was tested by using it to determine the slope of a line drawn at about 45 degrees to the two axes. The result for thirty readings was 0.987 ± 0.002 for the value of the tangent, the root mean square deviation of individual readings being 0.01. Hence in any one reading the value of the tangent was obtained with a probable error of one per cent, a better accuracy than that with which the (θ, R) curves could be drawn.

Two modifications were tested for accuracy in the way described above. In one a lens was mounted above the prism and the curve and its reflected image viewed through this. The lens gave a linear but not an angular magnification and, as would be expected, the statistical accuracy was the same as for ordinary vision. However eyestrain was decreased and this adaptation was used in practice. In the other modification, a long-focus microscope was used in place of the lens; with this the field of view was greatly restricted and it was found that the accuracy was decreased.

APPENDIX 3

GLOSSARY

Much confusion has arisen in rheology due to inadequate definition of the terms used. The definitions taken as a basis in this thesis are in accord with most current European usage.

Anomalous flow:

Any deviation from Normal flow - except that turbulence at high rates of shear is sometimes regarded as a "Normal" property.

Apparent viscosity:

The ratio of shear stress to rate of shear strain in an element of fluid.

Breakdown:

Thixotropic breakdown is said to occur when the apparent viscosity decreases, that is the material "thins". If the viscosity changes are attributed to "structure" in the system "thinning" would involve the breakdown of this structure.

Build-up:

The opposite process to breakdown; in this the material "thickens".

False-body:

The absence of flow at small shear stresses; hence behaviour like a solid body in this region.

Instantaneous thixotropy:

A special case of thixotropy in which there are instantaneous reversible changes in viscosity with changing shear stress.

Normal flow:

Flow in which the velocity gradient is proportional to the imposed shear stress.

Rheology:

The science of the deformation and flow of matter.

Thixotropy:

An isothermal reversible decrease of viscosity with increase of rate of shear involving relaxation time of breakdown (hence also an increase of viscosity with decrease of rate of shear involving a relaxation time of build-up). (Following Goodeve, 1939).

Viscosity:

This is used in the above definitions in the sense of "Apparent viscosity".

APPENDIX 4

LIST OF SYMBOLS USED

Symbols of frequent occurrence in the thesis are listed here for convenience.

General usage:

c	concentration
f	shear stress
g	velocity gradient
t	time
	viscosity or apparent viscosity
f_o	(equation 17) a temperature independent contribution to shear stress
m	(equation 17) a parameter determining the temperature dependent contribution to shear stress
η_o	(equation 17) the viscosity of the medium alone

Rotating cylinder viscometer:

a	radius of inner cylinder
b	radius of outer cylinder
c	torsion constant of wire
h	depth of immersion of the inner cylinder
r	radius of an "element" of liquid in the cup
C	couple acting
R	speed of the driving motor
θ	angular deflection of the inner cylinder
W	angular velocity of the outer cylinder
dw	angular velocity across an element of liquid 'dr'
dW	difference in 'W' in two experiments with couples differing by 'dC'

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