TIME DEPENDENT RHEOLOGY OF ARTIFICIAL

SLURRIES

by

JOHN PETER BROWN

(Dip.Tech.)Battersea College of Technology, London 1963

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF

THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in the Department

of

CHEMICAL ENGINEERING

We accept this thesis as conforming to the
required standard

Members of the Department of
Chemical Engineering

THE UNIVERSITY OF BRITISH COLUMBIA

May, 1965

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Department of Chemical Engineering

The University of British Columbia,
Vancouver 8, Canada

Date May 27th 1965

ABSTRACT

A method was developed for the preparation of slurries showing time dependent rheological properties, using artificial particles of constant shape and size, such that the effects of the slurry parameters, particle shape, size, concentration, and dispersing medium viscosity could be investigated separately. Two particle shapes were investigated, elliptical plate and rectangular plate. There were five sizes of elliptical plate particles with the surface area varied at nearly constant length to width ratio, and four sizes of rectangular plate particles with a length to width ratio varying from 1.92 to 4.85. Only one particle thickness was considered.

The rheological state exhibited by the time dependent dispersions was found to be dependent on all the parameters investigated. The thixotropic state occurring with the smaller size particles became increasingly time dependent with the increase in particle surface area or length to width ratio. The transition to the false bodied state occurred with the largest size particles and the largest length to width ratios.

Equilibrium apparent viscosity was found to increase linearly with particle surface area for thixotropic slurries with constant particle shape and dispersing medium viscosity. Also, equilibrium apparent viscosity was found to increase linearly with dispersing medium viscosity for thixotropic dispersions with constant particle shape, size, and concentration. The variation of the parameter of length to width ratio was found to have the greatest effect on the time dependency of the slurry.

Ragged decay curves were obtained from the slurries made up from

particles with the larger surface areas and length to width ratios. The ragged decay curves indicated a structural breakdown or that particle interference was taking place.

The rate of decay of apparent viscosity of the slurries was shown to follow a curve which is approximated by the mathematical relationship for a second order-zero order reversible reaction mechanism. This theoretical model was found to fit regardless of slurry parameters or rheological state. The main determinants of the forward rate constant k_1 were found to be particle surface area, length to width ratio, concentration and dispersing medium viscosity.

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ACKNOWLEDGEMENT

I am indebted to Dr. K.L. Pinder, under whose guidance this study was made, for his encouragement and assistance during the course of this project.

The assistance of Mr. R. Muelchen and the Workshop staff is appreciated for their proficiency at building the equipment to the specifications required.

I also wish to thank the National Research Council of Canada for financial assistance received, and the Department of Chemical Engineering at U.B.C. for additional support.

INTRODUCTION

The general approaches to the investigation of thixotropic slurries during the past thirty years have been the classification of materials and known rheological states, explanations for time dependent mechanisms, and attempts to obtain formal relationships to describe thixotropic behaviour.

The early literature is complicated by many authors misusing the term thixotropy to define other non-Newtonian behaviour. To rectify this situation Scott Blair (39) presented a general classification of materials, and Pryce-Jones (35) gave detailed definitions of the presently known rheological states.

Freundlich and Juliusburger (13) first defined thixotropy as 'the reversible isothermal gel/sol/gel transformations induced by shear and subsequent rest.' The present day accepted definition is by Alves, Boucher and Pigford (2), 'Thixotropic fluids possess a structure the breakdown of which is a function of time as well as the rate of shear. This structure can rebuild itself if not prevented from doing so by externally applied forces.'

Reviewers of the literature (7,28,33,35,41,43,47) agree closely on the meaning of non-time dependent behaviour, but in the case of time dependent behaviour wide discrepancies are found. Most confusion has arisen between thixotropic and false body behaviours since both exhibit similar decay curves.

Thixotropic dispersions decay to an equilibrium state which is Newtonian, independent of shear rate.

False body dispersions decay to an equilibrium state which is pseudoplastic, dependent on shear rate.

These difficulties in definitions have probably arisen because of the problems encountered in measuring and distinguishing time dependent rheo-

logical properties.

Measurement of the time dependent properties of dispersions is generally carried out using a rotating concentric cylinder type viscometer (7,15,29,32,34,36,37,42,43,48). Some of the data obtainable from this type of instrument are not easily interpreted due to the differing rates of gel reformation caused by particle shape and size, degree of dispersion and aging effects. It has been suggested that many slurries may be thixotropic but the decay time is so rapid it cannot be recorded.

The rate of gel reformation has been studied by several workers (13,46) by either suspending a ball or a plate in the dispersion and measuring the force required just to start it moving at different time intervals after thorough shearing. Zero flow characteristics of gels were obtainable but no contribution to the calculation of flow properties were made.

Gels have also been shown to exhibit elastoviscous properties which cause the yield point to increase after a period of shear (14). Measurements of this property were made by observing the return of a rotating cylinder after the rotation had been suddenly stopped (34). Abduragimova et al (1) showed elastoviscous recovery to follow Hooke's law and proposed that a ragged viscosity time curve should be obtained because of the periodicity.

Over the last half century there has been an increasing awareness of time dependent flow systems. They confronted industry initially as a problem to be overcome or avoided, but as data have been gathered, increasing use has been made of the property of time dependence. Many clay slurries exhibit this property, and extensive damage has been caused by large tracts of land (24) flowing because of viscosity reduction by vibrations. It also affects the quality of glazes and may be correlated to the porosity of crucibles. The printing industry has encountered problems maintaining the flow characteristics of inks manufactured from fine suspensions of carbon

black. Paint manufacturers (7,11,29) use the property to obtain better blot outs and smooth surfaces, minimizing hard settlements, sagging and the flow of paint after application. Many cosmetic and pharmaceutical products have thixotropic properties imparted to them, so that they can be smoothed onto the skin as a fluid and will then cling as a gel. The trend in the chemical industry has been to the transportation of oils and slurries in pipe-lines. (2,4,27,32). Difficulties have been encountered in pipe-line design for non-Newtonians. Many materials at low temperature have been found to be time dependent, forming gels, which increase pressure drop and cause blockages.

There is a general agreement that the isothermal gel/sol/gel transformation induced by shear and subsequent rest, corresponds to the breaking down and subsequent building up of some form of structure.

Kistler (25) postulated the existence of cybotactic complexes in liquids. A random mesh theory of gel structure was proposed by Broughton and Squires (5) and modified by Goodeve (14). A scaffold structure was proposed by Goodeve (14) and by Peters (31), Hofmann (23) called this random mesh structure a "card house" or "touching rod structure." Heller et al (20) postulated that the network was due to the association of aggregates which are composed of primary particles not in close touch but which assume equilibrium distances corresponding to positions of least energy. M'Ewen and Pratt (26) proposed a three dimensional structure based on a system of cross-linked ribbons, where the particles are aligned edge-to-edge in positions of potential minima.

Many authors (1,7,11,13,24,25,26,31,32,34,39,45,) have reported that particle shape, size, and concentration effect the time dependency of slurries, but difficulties have been encountered whilst trying to correlate these properties due to the small size and irregular shape of particles

in known thixotropic dispersions.

Thixotropic liquids are now depicted as a large network structure of loosely bonded macromolecules, filaments or particles suspended in a Newtonian solvent or solution. It is then assumed that the shear stress generated within the system during flow is largely due to the resistance offered by the network structure and particle interference. The decrease in viscosity with time at constant rates of shear is attributed to the progressive destruction of the weak network linkages (1,26). The gel reformation is the re-orientation of the particles to reform the random network structure.

The nature of the interparticle forces responsible for the network structure is still of some dispute. The decay phenomenon seems to be caused by rupture of weak secondary bonds between molecules or particles (1,2,6,36,40,44). These forces are probably electrical (40,44) in character for most cases. In some cases the forces may be physical, i.e., the wrapping-around action of long chain molecules of the polymeric type. The formation of the random structure is most likely caused from like charged particles repelling each other; at the same time adsorption of the surrounding liquid on the suspended particles can lead to lowered mobility of the liquid. This is reinforced by van der Waal's forces causing attraction at particle edges. The overall results of these effects is to form a random structured gel.

Several theoretical models and many empirical equations have been produced to correlate the parameters involved in thixotropic dispersions. Dodge and Metzner (10) have developed a power law theory to explain all rheological phenomena; although this works well with Newtonian and pseudoplastic solutions, it is not applicable to thixotropic fluids. A more general model is the Ellis Model (44) which has three adjustable parameters, but also fails to take into account all the parameters involved

in thixotropic fluids.

There have been numerous attempts to correlate the parameters which impart time dependency to thixotropic slurries, but to date no general correlation has been produced. Pryce-Jones (34) studied these systems extensively and suggested that viscosity is determined by the following variables:

- 1) Temperature
- 2) particle concentration
- 3) particle size
- 4) particle shape
- 5) solvent viscosity
- 6) dispersion factor
- 7) hysteresis factor

All but the last two properties are well known. The ultimate degree of dispersion is determined by the interfacial relationship of the fluid and the solid surface. Slurries of the same material can exhibit several different rheological states as they become wetted. The curve for the plot of shear force against increasing shear rate for a thixotropic material does not correspond to the one for decreasing shear rate. Green, Weltman and Kuhns (16,17,47,48) have developed a theory around this hysteresis effect, but the correlations developed are limited to the systems studied.

Empirical equations have been developed which correlate viscosity, concentration, and shape factor (usually the ratio of length to width raised to either the 1st or 2nd power) (11,45). All these equations have been limited to the system under study.

Other approaches have been to compare data obtained from the flow of slurries in test sections of pipe lines (2,27) with data obtained from

a variety of viscometers on the same material, from which graphs have been developed for pipe line design.

Other properties of slurries have been shown to be time dependent. A structural theory has been developed using the phenomena of streaming birefringence for the time dependence measurements of dilute dispersions (26). The properties of dielectric constants (30,45) and electrical conductivity (31) of slurries have been found to have similar time dependent effects upon shearing as observed with viscosity. Empirical equations have been developed based on these properties but are limited to the dispersions under study. Properties of streaming birefringence, dielectric constants, and electrical conductivity, of thixotropic dispersions have been found to be dependent on particle orientation, and to a lesser extent particle shape, size, and concentration.

Several workers (6,12,22,27,37,41,46,) have noticed that the apparent viscosity-time curves for thixotropic dispersions approximate the concentration-time curves for a chemical reaction. From this analogy several theories for the thixotropic decay process have been compared to a single stage low order reversible reaction mechanism. Eyring and co-workers (18,22) have developed a first order rate equation around the shear stress-shear rate hysteresis curve. This theory is further complicated by the introduction of intermolecular distances into the equation.

Denny and Brodkey (8) also developed a theory utilizing data from the shear stress-shear rate diagram, assuming a first order reaction mechanism and introducing a shear rate term. Ritter's (37) rate theory is based on a consecutive reaction mechanism. This theory contains too many assumptions, and his method of obtaining equivalent shear stress from apparent viscosity-time curves is doubtful. Pinder (32) developed a general theory, and showed that the dispersions he was studying were best represented by a second order-zero order reaction mechanism.

This general kinetic approach has been carried a stage further by attempts to describe the viscosity variation with temperature by an Arrhenius equation (37,44), from which an apparent activation energy of viscous flow (44) or activation energies for thixotropic breakdown (37) were obtained.

THEORETICAL DEVELOPMENT

One of the objects of this series of investigations was to check the rate theory for thixotropic decay developed by Pinder (32) to see if it held for other thixotropic dispersions. A general outline of the development of this theory is given below.

Several workers in the field of thixotropy noticed that the viscosity-time curves approximate the concentration-time curves for a chemical reaction. It is from this analogy that the most recent theories for thixotropy have been developed.

Initially, particles in thixotropic dispersions, which have been at rest for an infinite time, are orientated in a random state. Upon shearing, the particles are forced to take a new average position which is in a lesser state of randomness, until an equilibrium ordered state is obtained. On leaving the particles at rest, with time they reorientate themselves into the random state. Thus the shear force is opposed by a natural force which tends to reorientate the particles from an ordered state to a random state. The rate at which these two forces are equilibrated varies for different particle shapes and sizes. Designating the two extremes of orientation, that is complete randomness and equilibrium order for any given shear field as M_1 , and M_2 in terms of apparent viscosity, the change can be compared to a chemical reaction.

with a forward rate constant k_1 and a reverse rate constant k_2 . Therefore, by assuming various reaction orders for the forward and reverse reactions, appropriate equations for the reaction orders,

- 1) Second order - second order
- 2) Second order - first order
- 3) Second order - zero order
- 4) First order - zero order

can be calculated. The nomenclature is listed in Appendix 1.

Let X , the viscous degradation, be the difference between the yield value M_o and the viscosity M at time t the solution for each of the reaction orders becomes:

1. Second order - second order, if the basic reaction rate equation is

$$dX = k_1 (M_o - X)^2 - k_2 X^2$$

the linear equation is:

$$\ln \frac{(X - X_e) M_o}{(2X_e - M_o) X - M_o X_e} = \frac{2 M_o (X_e - M_o)}{X_e} k_1 t$$

2. Second order - first order, if the basic reaction equation is

$$\frac{dX}{dt} = k_1 (M_o - X)^2 - k_2 X$$

the linear equation is:

$$\ln \frac{(X - X_e) M_o^2}{(X_e X - M_o^2) X_e} = \frac{(X_e^2 - M_o^2)}{X_e} k_1 t$$

3. Second order - zero order, if the basic reaction equation is

$$\frac{dX}{dt} = k_1 (M_o - X)^2 - k_2$$

the linear equation is:

$$\ln \frac{(2 M_o - X_e - X) X_e}{(X_e - X) (2 M_o - X_e)} = (2 M_o - 2 X_e) k_1 t$$

4. First order - zero order, if the basic reaction rate equation is

$$\frac{dX}{dt} = k_1 (M_0 - X) - k_2$$

the linear equation is:

$$\ln \frac{X_e}{(X_e - X)} = k_1 t$$

For the complete mathematical derivation of the above equations refer to Pinder's work (32). All the above mentioned reaction equations have a linear solution of the form $\ln ()$ versus t . To determine which reaction mechanism best represents the experimental data, the data are substituted into each equation to determine k_1 . The most constant value of k_1 will be given by the mechanism equation which best fits the data. The fitting of the straight lines can be carried out either by plotting graphically and comparing the resulting straight lines, or by means of least squares fitting.

Owing to the small angle of interception of the viscosity-time curve on the viscosity axis at zero time, many workers have encountered difficulty in obtaining values of the yield value by extrapolation. Pinder (32) found that a plot of the inverse of the viscosity versus time yielded a reasonably straight line over the first five to ten readings. This allows the calculation of the yield value and of the rate of change of fluidity after a short period of time by the method of least squares.

The equation used was

$$\frac{1}{\eta} = bt + a$$

where t = time from initiation of shear (secs)

$$a = \frac{1}{\eta_0} \quad \eta_0 \text{ is the yield value}$$

$$b = d \left(\frac{1/\eta}{dt} \right)$$

This method has been checked by Ritter (37) in his work and it gave good results. It has been used throughout this investigation giving good results.

EXPERIMENTAL

A. General

The experimental program was designed to investigate:

- (1) The effects of changing the particle shape, size and concentration, and the dispersing medium viscosity, on the time dependency of a thixotropic dispersion.
- (2) The rate theory developed by Pinder (32) using other thixotropic dispersions, with the hope of developing general flow equations for time dependent dispersions.

Previous authors (1,7,11,13,23,25,26,32,35,39,40,) have noticed that particle shape, size, and concentration effect the time dependency of dispersions. Attempts to measure the effects caused by particle properties have only been partially successful. The main difficulty has arisen from the variation of the shape, and the small size of particles in known thixotropic dispersion.

Two approaches were considered:

- (1) Using known thixotropic dispersions, separating the particles into a number of graded size increments by elutriation and obtaining an average shape and size factor for each size range by microscopic measurement.
- (2) To make up artificial time dependent dispersions using particles of a known shape and size. This entailed manufacturing particles of the same shape and size, and immersing them in a suitable dispersing medium, such that time dependent properties were obtained.

Previous workers have encountered difficulties in correlating size and shape factors using the first approach. This has been due to the small size and irregular shape of particles encountered in known thixotropic dispersions, or to the continued growth of irregular shaped crystalline

particles. The second approach was chosen, as known shape and size factors could be calculated and compared readily. The production of artificial thixotropic slurries has not been reported in the literature so that there were no guide posts for the choice of particle parameters, and dispersing mediums. Because of this considerable trial and error experimentation was necessary.

B. Preparation of Dispersions

The factors governing the time dependency of thixotropic dispersions are: temperature, particle shape and size, concentration, wettability of particles and dispersing medium viscosity. It was with these factors in mind that the primary selections of materials were made.

As this was the first attempt to make up artificial thixotropic slurries and there was no pertinent information regarding this problem in the literature, the development of an experimental technique for manufacturing artificial thixotropic slurries, therefore became a major part of this research project. Keeping in mind the above mentioned properties of thixotropic slurries it was desired to prepare a series of dispersions from the same material, such that all the above mentioned parameters could be varied independently of each other. Many materials were investigated during the course of experimentations, from which a number of properties directly related to the selection of materials emerged.

It was found that time dependent dispersions could be readily made up with high particle concentrations. But on trying to obtain this effect at low concentrations with the same materials, difficulties arose because the particles would not remain suspended. They were found to either settle or float depending on the density difference between the particles and the dispersing medium. On further investigation of high concentration dispersions this effect was also noticed. It had been partially

masked due to the close packing of the particles.

To prevent the particles from floating or settling, especially in low concentration dispersions, it was found necessary to carefully match the density of the dispersing medium to that of the particle material. This was achieved by selecting particle materials of low density, as near as possible to that of the dispersing medium, and adjusting the density of the dispersing material to that of the particle by addition of highly soluble mineral salts. The properties, governing the selection of materials, that became apparent in this investigation are summarized below.

Selection of materials for particle manufacture was governed by the following properties:

- (1) The ease with which the desired shape could be cut or punched from the material. The material had to be rigid and malleable, but not brittle.
- (2) Inertness, having no reaction with the dispersing medium.
- (3) Low density, preferably as near as possible to that of the dispersing medium.
- (4) Readily wettable by the dispersing medium.

Selection of materials for the dispersing medium was governed by the following properties:

- (1) Variable viscosity
- (2) Variable density
- (3) Exhibit Newtonian properties
- (4) Readily wet the particles
- (5) Non-corrosive to the particles.

A list of some of the more promising materials considered for the preparation of thixotropic dispersions appears in Appendix II. The

material finally selected for the particle manufacture was cellulose acetate. This material appears to have the best combination of previously listed properties. The particles can be easily punched to the desired shape, and are rigid, inert, of low density 1.3 gm/cc and are readily wettable by many liquids.

The most versatile dispersing medium was found to be made from a solution of Dow Polyglycol E9000, and water, which gave a possible viscosity range of 1 to 2,000 centipoise. Cupric nitrate, being readily soluble in small quantities of water, was used to make the density corrections. This solution was Newtonian over the whole range considered, readily wet the particles, and was non-corrosive to cellulose acetate.

The advantages of using dispersions prepared in this manner are:

- (1) The parameters, particle shape and size, concentrations and dispersing medium viscosity, could be varied independently of each other.
- (2) The desired dispersions could easily be made up and reproduced.
- (3) The particles and dispersing medium are easily separated and recovered by filtration.

C. Particle Shapes and Sizes

This being the initial study of artificial thixotropic dispersions there was little guide to the selection of regular particle shapes and sizes, as all previous work has been carried out on fairly irregularly shaped particles. Several factors that are well known and appear continuously in the literature, are that plate like particles and rod like particles exhibit a greater degree of thixotropy than do other shapes. The main particle parameters appear to be surface area, and the length to

width ratio.

For the initial investigation it was decided to manufacture smooth edged elliptical plate particles, varying the surface area whilst holding the length to width ratio constant. Later, rectangular plate particles with varying length to width ratio were tested. Throughout the literature it was noticed that the particle size was generally very small in thixotropic dispersions. The limiting size factor in this investigation was that of the smallest size of punch which could be accurately made for punching out a regular shaped particle. Details of particle sizes are given in Tables 1 and 2 below, the shapes are shown in Figure 1. Elliptical and rectangular plate-like particles were punched from cellulose acetate sheet of a uniform thickness of 0.005 inches. Five particle sizes were made in the elliptical plate shape, and four particle sizes in the rectangular plate shape.

TABLE 1

Elliptical Plate Particles, thickness 0.005 inches

Particle No	Length Inches	Width Inches	L/W ratio	Total Surface Area sq.inches
EP 1	.2350	.1550	1.52	.0938
EP 2	.2000	.1250	1.60	.0397
EP 3	.1400	.0850	1.65	.0198
EP 4	.1000	.0700	1.43	.0113
EP 5	.0500	.0350	1.43	.0044

FIGURE 1. PHOTOGRAPH OF PARTICLE SHAPES AND SIZES
SCALE: 1 DIV = 1 mm.

TABLE 2

Rectangular Plate Particles, thickness 0.005 inches

Particle No	Length inches	Width inches	L/W ratio	Total Surface Area sq. inches
RP 1	.2480	.0512	4.85	.0284
RP 2	.2008	.0512	3.92	.0231
RP 3	.1496	.0512	2.92	.0173
RP 4	.0984	.0512	1.92	.0116

Future references to individual particles will be made by referring to the particle number only.

It was hoped that the elliptical particles could have been made with a constant length to width ratio, but as can be seen from Table 1 this ideal was not attained. Slight variations were due to the difficulty in making similarly shaped elliptical punches.

The surface area of the elliptical particles was obtained by accurately weighing a known number of each set of particles, and dividing by the weight of a known surface area of cellulose acetate sheet of the same thickness as the particle. The length and width of both sets of particles was obtained by accurate measurement with a microscope. From these measurements the surface area of the rectangular plate particles could be obtained.

D. Experimental Equipment

A recording rotational viscometer was selected for the current study. Because of the time dependency of the viscosity of the dispersions, it was necessary to record viscosity readings at regular time intervals while the sample was subjected to prolonged shear at constant shear rate. A general view of the apparatus is shown in Figure 2. It consists of a Brookfield Rheolog viscometer coupled with a Foxboro 6" strip chart recorder. The

viscometer spindle is immersed in a thixotropic sample held in a calibrated glass tube. The sample is held at 20°C by a Calora constant temperature bath circulating water through the coils of the bath in which the sample tube is immersed.

a) Viscometer

The viscometer is a continuously indicating Brookfield Rheolog viscometer. This instrument employs a spindle, which is submerged in the material and rotated at a constant speed, as the viscosity sensitive element. The spindle is driven by an eight speed synchronous motor through a beryllium hair spring couple. The deflection of the spring is a measure of the torque caused by the drag on the surface of the cylinder. A flapper nozzle arrangement converts the spring torque to an air pressure in a completely linear fashion. The change in air pressure is sensed by the Foxboro indicating recorder. Five spindle sizes were supplied, which combined with the eight rotational speeds give a viscosity range of 1 to 64,000,000 centipoise. The viscometer was supplied by, Brookfield Engineering Laboratories Incorp., Stoughton, Massachusetts.

b) Recorder

The recorder used with the viscometer was a Model 40 Foxboro 6" strip chart recorder, with 18 chart speeds. The chart speed can be changed from inches per minute to inches per hour by flicking a switch, while other range changes are made by fitting different gears in the chart drive. The air pressure is sensed by a diaphragm pressure sensor, with a range of 9 to 65 inches of water. The sensitivity of the instrument on the pressure axis was $\frac{1}{2}$ scale division. Utilizing this instrument it was found possible to resolve time intervals as small as half a second.

E. Calibration Procedure

A set of sample holding tubes were made up from glass tubing (details Appendix II) of varying diameter. Constant filling marks were inscribed

FIGURE 2 PHOTOGRAPH OF APPARATUS

onto the tubes such that each spindle was immersed in the tubes to a constant depth.

The sample holding tubes were immersed in a constant temperature bath held to within $\pm 0.1^{\circ}\text{C}$ of 20°C . The tubes were aligned to the vertical using a 90° square, and checked by alignment lines inscribed at right angles on the perspex constant temperature bath. The spindle was aligned vertically and centrally by means of a leveling gauge on the viscometer and the alignment lines.

Standard Newtonian solutions of varying viscosity were made up from Glycerol and Polyethylene glycol. The viscosities of these solutions were determined using a set of Calibrated Cannon-Fenske viscometer tubes by De Verteuil's method. (9). Using standardized Newtonian solutions, sample holding tubes T3, T4, T5 and T6 were calibrated for spindles 1 and 2 with speeds 5, 10, 20 and 50 r.p.m. For details of the sample tube dimensions and spindle dimensions see Table 7 and 8, Appendix II. Sample tube T3, T4 and T5 were calibrated with spindle 1. at speeds of 5, 10 and 20 r.p.m., also sample tubes T4, T5, and T6 were calibrated with spindle 2 at speeds of 10, 20 and 50 r.p.m. Future reference to spindle and tube size will be given in the form 1-T4, which refers to measurements made with spindle 1 with sample holding tube T4.

Calibration charts have been drawn, and are shown in Appendix VI Figures 61 and 62. As can be seen from the calibration graphs, the calibration lines do not pass through the zero point but slightly to either side; this is due to the initial frictional inertia in the viscometer and Foxboro recorder.

F. Experimental Procedure

One of the properties of time dependent dispersions is that their yield value increases with the length of time they have been at rest, until a stable state is reached after an infinite time. This is due to a reorientation of the particle structure from an aligned to a random configuration. Because of this property most experimental work with time dependent dispersions reported in the literature deals with gels which have been at rest for considerable time. Thus a procedure of stirring the dispersion followed by a short period of rest prior to taking readings would appear to be out of line. However, dispersions which have been aged for considerable time are always sheared prior to the test, by the immersion of the spindle in the dispersion. Ideally the spindle would have to be immersed in the dispersion to the desired depth prior to aging. This procedure would be very time consuming and require a large number of spindles. Since the effect of aging is to produce a random structure, it was found that a random structure, from which decay curves could be obtained, could be produced by stirring with a twin bladed propeller type stirrer. Reproducible readings were obtained by following the procedure outlined below, which was adopted for all measurements.

- 1) Dispersions were made up by mixing the required weight of particles with dispersing medium to obtain the desired concentration. Care was taken to thoroughly mix the particles and dispersing medium to remove entrained air bubbles.
- 2) Dispersion and spindle were brought to a constant temperature of 20°C.
- 3) The spindle was removed from the dispersion. The dispersion was then thoroughly mixed using a twin bladed paddle for one minute.

- 4) The spindle was lowered into the dispersion, and centered by means of lines inscribed on the constant temperature bath.
- 5) A torque corresponding to the estimated yield value was applied to the spindle.
- 6) The dispersion and immersed spindle were held at a constant temperature of 20°C for five minutes.
- 7) A trial run was conducted to determine a closer approximation of the yield value.
- 8) Procedures 2 to 4 were repeated.
- 9) A torque was applied to the spindle of approximately the same order as that predetermined by the trial run.
- 10) The dispersion and immersed spindle were held at constant temperature for five minutes.
- 11) The spindle was released and the run was started at a high chart speed. For the infinite time reading the chart speed was reduced for the last part of the run.
- 12) Four to six runs were made on each sample at differing shear rates, spindle and tube sizes, using the above outlined procedure.

G. Experimental Accuracy

During the course of the initial experimentation and operation of the equipment, the experimental accuracy with which results could be recorded was found to be $\pm$ one scale division of the Foxboro recorder. From the calibration charts Figures 61 and 62 the value of one scale division in terms of viscosity for each combination of spindle, sample tube, and speed was obtained. The error is shown in terms of viscosity in Table 3. This error has resulted because of the following factors:

- 1) Frictional inertia and lack of sensitivity of the Foxboro recorder have resulted in a difference of ± 0.5 of a scale division. The frictional

Inertia was seen by a comparison of the value of constant viscosity obtained by approaching the value by moving up the scale and down the scale.

2) The recorder could be read only with an accuracy of ± 0.5 of a division because of its small size, 100 scale divisions to 6" of chart.

TABLE 3

Experimental Accuracy

Spindle	Tube	Speed r.p.m.	Error for one scale division in terms of viscosity
1	T4	5	± 29 cp.
1	T4	10	± 15 cp.
1	T4	20	± 8 cp.
1	T5	5	± 24 cp.
1	T5	10	± 13 cp.
2	T5	10	± 69 cp.
2	T5	20	± 36 cp.
2	T5	50	± 15 cp.
2	T6	10	± 63 cp.
2	T6	20	± 32 cp.
2	T6	50	± 14 cp.

Evaluation of the Largest Percentage Error. Initial experimentation showed that suitable time dependent dispersions for the particle size range considered (see Table 1 and 12) could be best made up within the dispersing medium viscosity range of 100-500 centipoise at 20 percent particle concentration. The lowest value of apparent viscosity recorded was the equilibrium apparent viscosity of 405 centipoise for EP5 particles in a dispersing medium viscosity of 130 centipoise. All other values recorded were greater than 405 centipoise. Thus with spindle, sample tube, and speed combinations of 2-T5-10 and 2-T6-10 the experimental error would be 16.8 percent. All other combinations give an experimental error of less than 9 percent. Experimental accuracy increases with the increase in dispersing medium viscosity, concentration and particle size.

Problems arose in the determination of equilibrium apparent viscosity and yield value apparent viscosity from the decay curves.

Equilibrium Apparent Viscosity

The apparent viscosity of thixotropic and false bodied dispersions upon shearing at constant shear rate decreases with time to an equilibrium value. The equilibrium apparent viscosity for thixotropic dispersions is independent of shear rate and spindle size whereas that of false bodied dispersions is dependent on shear rate and spindle size. The rheological state of the dispersions under consideration was indicated by a comparison of equilibrium apparent viscosities obtained with differing shear rates and spindle sizes. Dispersions were classed as thixotropic if the equilibrium apparent viscosity values at differing shear rates were within the experimental error range listed in Table 3. If the equilibrium apparent viscosities were outside this range they were classed as false

bodied.

Two difficulties arose in determining equilibrium apparent viscosities.

1. Because of the asymptotic approach of the decay curve to the equilibrium value, it was difficult to ascertain when a constant equilibrium value had been reached. The equilibrium values listed in Tables 4, 5 and 6 were obtained from the part of the decay curve that appeared to have reached a constant value.
2. For decay curves which exhibited a structure breakdown in the form of a ragged decay curve the equilibrium apparent viscosity was taken as the mean of the peaks on the part of the curve that appeared to have reached a constant value.

Yield Value

The yield value of a dispersion is the shear stress required to initiate shear. It is obtained by plotting $1/\mu$ versus t for the first 5-10 points on the decay curves, and extrapolating to zero time. This method was developed by Pinder (32) and has been checked by Ritter (37). It was used throughout this investigation, because a more accurate value of yield value could be obtained than by extrapolating an asymptotic decay curve to zero time. But even so, difficulties arose whilst using this method, increasing the errors due to the lack of sensitivity of the viscometer and recorder.

The viscometer was prestressed to an approximate predetermined value of the yield value to overcome the viscometer inertia. A major source of error arose depending on how close the determination of the approximate yield value was to the actual yield value. If the value was too large the initial few points when plotted in the form $1/\mu$ versus t would not be in a straight line and these were rejected. If the yield

value was too small a rounded top portion of the decay curve appeared and the whole curve was rejected.

The determination of approximate yield value became difficult when the rate of decay was very rapid so that insufficient data points were obtained over the initial portion of the curve. Equilibrium values only were obtained from these curves.

RESULTS

All the results have been obtained by recording the change in apparent viscosity with time at constant shear rate and temperature. They were obtained in graphical form on a Foxboro 6" strip chart recorder, connected to the Brookfield viscometer. The dispersions were made up of cellulose acetate particles of uniform shape and size, suspended in Newtonian solutions of the same density. The dispersion parameters investigated, were particle shape and size, particle concentration and dispersing medium viscosity. Particle shape and size were investigated over the range listed in Tables 1 and 2, particle concentration over the range 17.5 to 30 percent, and dispersing medium viscosity over the range 130-410 centipoise.

1. Particles EP1 to EP5 were tested over the dispersing medium viscosity range of 130-410 centipoise at a constant particle concentration of 20 percent.
2. Particles EP3 suspended in a dispersing medium viscosity of 170 centipoise were tested with particle concentration over the range 17.5 to 30 percent.
3. The particles RP1 to RP4 were used at a 20 percent concentration in a dispersing medium of 170 centipoise viscosity.

Viscosity measurements made on the initial dispersions have not been included in these data as they were obtained before the final development of a technique which would yield reproducible results.

The original decay curves have been reproduced from the recorder charts in Figures 15 to 60. From these, the effects of time and shear rate may easily be seen. Repeat readings have not been drawn on all the

curves, but are shown in Figures 37, 56, and 59, Appendix IV.

A. Decay Curves

On first testing the dispersions to ascertain whether they were time dependent, the initial run was made on a dispersion of the largest elliptical particles EPI. A ragged decay curve of the type illustrated in Figures 3 and 4 was obtained. This immediately indicated that the dispersion was time dependent, but there was no obvious reason for the ragged appearance of the curve. The viscometer and recorder were checked for oscillations, but only a very slight eccentric rotation of the spindle was found to be present. The viscometer bearings were checked and realigned such that there was no eccentric rotation at slow speeds. The same dispersion was again tested, but the ragged decay curve was still obtained. Tests were then conducted on dispersions made from the smaller size elliptical particles. A decrease in peak height with a decrease in particle size was observed, until smooth decay curves were obtained with the two smallest size particles. A test on a thixotropic dispersion of bentonite clay also produced a smooth decay curve. This indicated that the ragged decay curves were a function of the dispersion and not the viscometer.

B. Amplitude of Decay Curve Peaks

The amplitude of the decay curve peaks were found to be irregular, with no apparent periodicity. A mean value of the amplitude was measured for each run in which they appeared. The amplitude was converted into a force measured in terms of viscosity as shown in column 7, Table 4. (Note, Tables 4, 5 and 6 of rheological parameters are found in Appendix III and Figures 15 to 60 of decay curves are found in Appendix IV).

FIGURE 3 APPARENT VISCOSITY-TIME, DECAY CURVE

FIGURE 4 APPARENT VISCOSITY-TIME, DECAY CURVE

Little significance has been attached to the numerical values given to this force due to its irregularity and the lack of sensitivity of the recorder.

Some general observations may, however, be made.

- 1) The amplitude increased with the speed of rotation. This is a measure of the sensitivity of the instrument, as if shown in the calibration graphs.
- 2) The numerical values obtained for the amplitude appear to be independent of shear rate, for any constant set of parameters.
- 3) Amplitude was found to increase with:
 - (a) Particle surface area
 - (b) Length to width ratio
 - (c) Viscosity of dispersing medium for constant particle size and concentrations.
 - (d) Particle concentration for the same particle size and viscosity of dispersing medium.

C. Type of decay curve

Decay curves were obtained for each dispersion using two spindles at several speeds. See Figures 15 to 60. By a comparison of equilibrium apparent viscosities, it could be determined whether the dispersions were thixotropic or false bodied. The equilibrium apparent viscosity of thixotropic dispersions is independent of shear rate and spindle size, where as that of a false body dispersion is dependent on shear rate and spindle size.

Equilibrium apparent viscosities obtained with spindle, sample tube, and speed combinations of 2-T5-50 r.p.m. were lower than those obtained at slower speeds shown in Tables 4, 5 and 6. This was caused by a slight eccentric spindle rotation at this high speed and tube size, and consequently these results have been ignored throughout when distinguishing

between thixotropic and false bodied phenomena. At slower speeds there was no eccentric rotation. Eccentric rotation at this speed and spindle size was caused by a bad design in the spindle coupling, which no amount of aligning would eliminate. The thixotropic equilibrium apparent viscosity shown by one point in the graphs, is an average value of two spindle sizes and four speeds listed in Table 4, which are within the allowed experimental accuracy of Table 3.

It can be seen from Table 4, 5 and 6 that yield values have not been obtained for a number of runs, this has resulted because the yield values were outside the chart range for the particular spindles and speeds. However, equilibrium values were obtainable.

D. Observed effects

Due to the procedure of stirring the dispersions before testing, they were not solid gels, but in some intermediate state between that of the solid gel and the equilibrium state. However, dispersions left for several days did become solid gels, and the longer they were left at rest the greater was the shear force required to shear them. No actual measurements were made on age effects, because spindles would have had to have been immersed whilst aging, which is a very time consuming procedure.

Observations of structural changes were possible due to the construction of the apparatus and nature of the materials of the dispersions. After stirring, the structure appeared to be random, but on shearing with a rotating cylinder the particles reorientated themselves into an ordered state, lying in the vertical plane end to end, such that the particles could easily slip past each other. On leaving the dispersions in a state of rest overnight, the particles were seen to loose their ordered states, and within a few days the structure had become random again.

E. Effects of particle shape and size

Two particle shapes were considered, elliptical plate and rectangular

plate, both of the same thickness. The elliptical particles were made in five sizes EP1 to EP5, with a length to width ratio varying from 1.43 to 1.65. The rectangular plate particles were made in four sizes, RP1 to RP4, with a length to width ratio varying from 1.92 to 4.85. For fuller details of shapes and sizes see Figure 1 and Tables 1 and 2.

Equilibrium apparent viscosity values and yield values for dispersions are listed in Tables 4, 5 and 6, Appendix III. These results have been plotted in Figures 5 to 12, pages 37 to 45. All equilibrium values for thixotropic dispersions are an average value of two spindle sizes and four shear rates and are shown as one point, since all the points are within the allowable experimental error as given in Table 3. False bodied dispersions are shown by a series of points, indicating that equilibrium apparent viscosity is dependent on shear rate.

The initial investigation was carried out with dispersions of elliptical particles EP1 to EP5 with a dispersing medium viscosity range from 130 to 410 centipoise, at a constant particle concentration of 20 percent. Results are shown in Figures 5 to 9, and Table 4, Appendix III.

1) Figure 5 shows the increase in equilibrium viscosity with dispersing medium viscosity for dispersions made up with a 20 percent EP1 particle concentration. The dispersions are thixotropic with a dispersing medium viscosity of 130 centipoise, but with dispersing medium viscosities of 170 to 410 the dispersions became false bodied. This is shown by the equilibrium viscosity being dependent on shear rate.

2) Figure 6 shows the increase of equilibrium viscosity with dispersing medium viscosity for dispersions made up with a 20 percent EP2 particle concentration. The dispersions are thixotropic with a dispersing medium viscosity of 130 and 170

centipoise, but with dispersing medium viscosities of 190-410 centipoise the dispersions are false bodied. Equilibrium viscosity values of false bodied dispersions with dispersing medium viscosity of 360 centipoise appear lower than the other values, because the dispersing medium density correction was not close enough to the particle density.

3) Figures 7 and 8 show the increase of equilibrium viscosity with dispersing medium viscosity for thixotropic dispersions made up with 20 percent EP3, EP4 and EP5, particle concentrations. In both Figures 7 and 8 equilibrium viscosity increases linearly with dispersing medium viscosity for thixotropic dispersions made up with particle sizes EP3, EP4 and EP5.

4) Figure 9 shows the linear increase of equilibrium viscosity with elliptical particle surface area for thixotropic dispersion. With a dispersing medium viscosity of 130 centipoise the dispersions are thixotropic over the whole surface area range considered, but with increasing dispersing medium viscosities 170, 190, 215 and 260, thixotropic dispersions are only encountered with increasingly smaller surface area.

Results obtained from dispersions of rectangular plate particles RPI to RP4 with a particle concentration of 20 percent and dispersing medium viscosity 170 centipoise are shown in Table 5, and Figure 10 and 11.

1) Figure 10 shows the increase in equilibrium viscosity with length to width ratio. Thixotropic dispersions become false bodied between a length to width ratio of 2.92 and 3.92. The equilibrium value of a thixotropic dispersion of EP4 particles has also been plotted on the graph. These particles have approxi-

mately the same surface area as RP4. It is seen that it has nearly the same equilibrium value although its L/W ratio is smaller.

2) Figure 11 shows the increase in equilibrium viscosity with surface area for elliptical plate, and rectangular plate particles, for dispersions made up with a 20 percent particle concentration and with dispersing medium viscosity of 170 centipoise. This figure shows equilibrium viscosity and thixotropy to be more dependent on L/W ratio than on surface area.

Summary of General Observations

Results of equilibrium viscosity and yield value for the dispersions considered are shown in Tables 4, 5, and 6, and Figures 5 to 14. The rate of viscosity decay of a dispersion is the time it takes for the equilibrium viscosity to be reached after the initial shearing. The rate of viscosity decay is shown in Figures 15 to 60 Appendix IV.

- 1) The larger the surface area the larger the equilibrium value, Figures 5 to 9, and yield value, Figures 12 and 14.
- 2) The larger the L/W ratio the larger the equilibrium viscosity, Figure 10, and yield value, Table 5, Appendix III.
- 3) The larger the surface area or L/W ratio the lower the viscosity of the dispersing medium at which false bodied properties occur, Figures 9 and 10.
- 4) The larger the surface area or L/W ratio the slower the rate of decay, Figures 51 to 54, Appendix IV.
- 5) Equilibrium viscosity varies linearly with surface area for thixotropic dispersions of particles of the same shape, Figure 9.
- 6) The larger the surface area or L/W ratio the larger the amplitude, Tables 5, Appendix III.

FIGURE 5 INCREASE IN EQUILIBRIUM VISCOSITY WITH DISPERSING MEDIUM VISCOSITY FOR DISPERSIONS OF EPI PARTICLES

FIGURE 6 INCREASE IN EQUILIBRIUM VISCOSITY WITH DISPERSING MEDIUM VISCOSITY FOR DISPERSIONS OF EP2 PARTICLES

FIGURE 7 INCREASE IN EQUILIBRIUM VISCOSITY WITH DISPERSING MEDIUM VISCOSITY FOR DISPERSIONS OF EP3 AND EP4 PARTICLES.

FIGURE 8 INCREASE IN EQUILIBRIUM VISCOSITY WITH DISPERSING
MEDIUM VISCOSITY FOR DISPERSIONS OF EP5 PARTICLES

FIGURE 2 INCREASE IN EQUILIBRIUM VISCOSITY WITH PARTICLE SURFACE AREA FOR THIXOTROPIC DISPERSIONS

FIGURE 10

INCREASE IN EQUILIBRIUM WITH L/W RATIO FOR
DISPERSIONS OF RP PARTICLES WITH D.M.V. OF 170 cp.

F. The effect of particle concentration

The dispersions were made up with an EP3 particle concentration range from 17.5 to 30 percent and with a dispersing medium viscosity of 170 centipoise. Results are shown in Figure 12, and Table 6, Appendix III.

- 1) Figure 12 shows the effects of particle concentration on equilibrium viscosity for dispersions made from EP3 particles. For particle concentrations, 17.5 and 20 percent, thixotropic properties are shown; for concentrations from 22.5 to 30 percent all dispersions become false bodied.
- 2) Figure 12, shows an increase in equilibrium viscosity with particle concentration.
- 3) From Tables 6, yield value is seen to increase with particle concentration.
- 4) The rate of decay decreases with increase in particle concentration, for constant shear rate Figures 55 to 60, Appendix IV.

G. Yield Values

For Newtonian liquids the actual shear rate can be calculated from the spindle size and rotational speed, but with time dependent slurries in a concentric cylinder viscometer, this is impossible except at equilibrium. Hence a correlation between shear rate and the transient variables of yield value and slope 'b' is meaningless.

Some general observations, however, can be made from Tables 4, 5 and 6, and Figures 13 and 14.

- 1) The yield value decreases with rotational speed for any given spindle, shown in Tables 4, 5 and 6, Appendix III.
- 2) The smaller the viscometer spindle the higher is the yield value for the same rotational speed, shown in Tables 4, 5, and 6, Appendix III.

Yield value was found to increase with an increase in:

FIGURE 12

INCREASE IN EQUILIBRIUM VISCOSITY WITH PARTICLE CONCENTRATION FOR DISPERSIONS OF EP3 PARTICLES WITH D.M.V. OF 170 cp.

- (a) surface area, shown in Figures 13 and 14.
- (b) length/width ratio, shown in Table 5.
- (c) concentration, shown in Table 6.
- (d) linearly with dispersing medium viscosity, shown in figure 13.

The first five to ten points of the decay curves plotted in the form $1/\mu$ versus t gave a straight line, which was extrapolated to zero time to obtain the yield value. As the results were numerous a computer program employing a least mean squares fitting was used to obtain the intercept value and the slope 'b' (32).

Slope 'b'

The larger 'b' is, the more rapid is the fall in apparent viscosity when the slurry is sheared. 'b' may be considered as a rate constant for a non-reversible second order decay mechanism. Over the first few points no appreciable reverse mechanism will operate, hence the straight line. From Tables 4, 5 and 6 it can be seen:

- 1) The higher the rate of rotation the more rapid is the fall in apparent viscosity.
- 2) The larger the spindle for the same shear rate of rotation, the more rapid is the fall in apparent viscosity.
- 3) The smaller the particle size of the dispersion the more rapid is the fall in apparent viscosity.
- 5) The lower the concentration the more rapid is the fall in apparent viscosity.

1. Reaction Mechanisms

Equations for various rate mechanisms were developed in the theory from the basic equation, $M_1 \xrightleftharpoons[k_2]{k_1} M_2$. The rate equation which best fits the data was determined by substitution of the data into each equation to

FIGURE 13

INCREASE IN YIELD VALUE WITH DISPERSING MEDIUM
VISCOSITY FOR DISPERSIONS OF EP PARTICLES

FIGURE 14 INCREASE IN YIELD VALUE WITH PARTICLE SURFACE AREA FOR DISPERSIONS OF EP PARTICLES

see which one best described the data. Because of the volume of the data involved a computer program was written, using least mean squares fitting of the 'so-called' linear equations. The goodness of fit was determined by a coefficient of correlation which indicated how well the data was described by each equation. The second order zero order rate mechanism was found to best fit all the data. This is seen by comparing the coefficients of correlation for each equation considered, shown in Appendix 5. From the slope of the equation the forward rate constant k_f , can be calculated. This is a much better indication of the rate of decay than 'b', as it describes the whole decay process from the initial shearing to the final equilibrium. Even though k_f is a better indication of the rate of decay than 'b', the observations made concerning 'b' hold also for k_f .

DISCUSSION OF RESULTS

This investigation was an exploratory study made to determine a path of study for time dependent dispersions. A technique for producing artificial dispersions of known size parameters was developed to reduce the number of uncontrollable variables. The results obtained with these dispersions were not conclusive in any way, but many trends have been observed indicating a path for future research.

The results show that it is possible, by the consideration of the basic properties and parameters of thixotropic and false bodied phenomena, to make up artificial time dependent dispersions, with particles of known shape and size. The suspension of large particles at low concentrations was achieved by adjusting the dispersing medium density to that of the particle. This called for a careful selection of basic materials. The factors governing the selection of materials for making up dispersions have been outlined under the section headed Experimental.

Ragged decay curves were obtained for most of the tests carried out with dispersions of the larger particles. These curves seem to indicate that a structural breakdown was taking place. Several authors (13,25,26,37,44) have suggested that ragged decay curves should be obtained because of structural breakdown, but had not observed it themselves. However this phenomena has been reported once previously by Abduragimova et al (1) who were measuring the elastico-viscous properties of thixotropic structures in bentonite dispersions, with an instrument sensitive to small changes in viscosity.

The strength of the weak secondary bond forces exhibited by these dispersions would seem to be dependent on particle size and viscosity

of dispersing medium. The observation of structural breakdown was dependent on the sensitivity of the viscometer, which indicated that below particle size EP3 the structural breakdown could not be recorded due to the lack of sensitivity of the recorder. The probable reason for the observation of structural decay in this investigation was the large particle size and viscosity of dispersing medium. The particle size was much larger than normally encountered in natural thixotropic dispersions, suggesting larger bond forces were involved. The uneven peaks in the decay curve could be caused by a number of factors: unequal bond strengths, the number of cells being broken down at any one time not being constant, particle interference, or combinations of these factors. The most likely explanation for the ragged decay curves was that interference was taking place between the sheared and unsheared structure. The particles on shearing from a random structure to an ordered structure became temporarily jammed against each other and the unsheared structure, the result is a sudden increase in shear stress, which is relieved on the breakdown of the structure. Accurate measurements of the forces involved in the structural breakdown could not be made, because of the lack of sensitivity of the recorder (see Table 3), but a measure of the forces involved was obtained, from which it was seen that particle size, viscosity of dispersing medium, and concentration were the important parameters. The bond forces are known to be electrical but this study has not investigated the effect of adding various concentrations of ionic salts to the dispersing medium, which could have some effect on the bond strength.

Other authors (1,11,13,24,25,26,32,34,40) have found that the materials they were investigating exhibited different rheological states

with varying parameters, particle shape and size, concentration and dispersing medium viscosity. This investigation has shown that the rheological state was dependent on all the parameters considered. The thixotropic state was seen to change to the false body state by varying separately, particle shape and size, concentration and dispersing medium viscosity or combinations of these factors. A much more extensive study would have to be conducted to ascertain the degree of influence each parameter or combination of parameters has on changing the rheological state.

The results obtained indicate that the parameter of length to width ratio, which is one way of defining the particle shape, has the most pronounced effects. Pinder (32) found the dispersions he was investigating became false bodied when the length/width ratio exceeded 1.7. The results for artificial dispersions indicate that this transition occurs between a L/W ratio of 2.92 and 3.92. This difference can be accounted for by the fact that it has been shown in these results that other parameters of the dispersions also affect this transition from one state to another. Pinder's (32) work was carried out with different particle sizes, and concentrations, with nearly constant dispersing medium viscosity.

No general correlations were obtained since the study was exploratory and the subject too complicated to yield simplifying results from such a short study. Trends were noted, however, which would have to be verified by consideration of other particle shapes and sizes, before they could be considered applicable to all thixotropic dispersions.

The following trends were apparent for the particles under consideration:

- 1) For thixotropic dispersions of particles of approximately the same length to width ratio (i.e. the same shape), equilibrium viscosity

increases linearly with surface area, Figure 9.

2) For thixotropic dispersions of the same shape and size, equilibrium viscosity increases linearly with dispersing medium viscosity, Figures 7 and 8.

It should be noted that throughout this investigation particle thickness has been kept constant. The effect of this parameter should be investigated in subsequent research.

Certain problems arose in the technique for obtaining the yield value, which caused some of the data to be unanalyzable. These problems were outlined in the section on experimental accuracy. The first problem was the determination of the approximate yield value to which the spindle was preloaded. If the value was too large the initial few points when plotted in the form $1/\eta$ versus t would not be in a straight line and these would have to be rejected. If the yield value was too small a rounded top portion of the decay curve would appear, and the whole curve would have to be rejected. The determination of the approximate yield value became difficult when the rate of decay was very rapid, as insufficient data points were obtained.

No simple proportionality was found between the dispersion characteristics and 'b', because of the low accuracy with which 'b' could be measured. This factor 'b' is the rate constant for a second order non-reversible mechanism for the initial portion of the curve. As would be expected, shear rate and particle shape and size appear to be the main determinants of 'b'. The importance of this rate constant is limited to the initial portion of the decay curve. A more general rate constant can be obtained from the reversible reaction model equation.

The reaction mechanism that was found to fit the data best was that for a second order-zero order reversible mechanism. This mechanism fits the data regardless of the dispersion parameters. It also agrees

with Pinder's (32) results obtained with tetrahydrofuran and hydrogen sulfide-hydrate slurries. As this result has been obtained for artificial thixotropic dispersions, with widely varying parameters, and natural occurring thixotropic dispersions, it would appear that this rate mechanism would be applicable to most thixotropic dispersions. This could easily be confirmed by additional work with other naturally occurring thixotropic dispersions. The coefficient of determination, showing the goodness of fit of the mechanism equation varies from result to result. This can be explained by the accumulation of errors involved in obtaining the necessary data for substitution into the equations, particularly data that were obtained from ragged decay curves, with low instrument sensitivity.

The exact nature of the correlation existing between k_1 , the forward rate constant, and the particle parameters could not be determined due to the lack of accurate data. As in the case with 'b' the main parameters appear to be particle size and shape. Comparison of values of k_1 and 'b' for the same dispersions show a similar range of values, but the inaccuracies involved and lack of data are too great for any definite statement to be made.

Unfortunately the results from this investigation could not be used to evaluate and compare Pinder's (32) theoretical model with those developed by other workers. Eyring and co-workers' theoretical model (18,22) and also Denny and Brodkey's (6) theoretical model have been developed around the 'shear rate-shear stress' diagram, whereas the present work has been obtained from the 'shear stress-time' diagram. Ritter's (37) theoretical model was developed around the 'shear stress-time' diagram at varying temperatures, whereas the present work was carried out at constant temperature. These three theoretical models could be evaluated using

artificial thixotropic dispersions by obtaining the pertinent data for each model from the dispersions.

CONCLUSIONS

The initial object of this study was the investigation of the effects that the slurry parameters, particle shape, size, concentration, and dispersing medium viscosity, have on the time dependency of thixotropic dispersions. The main difficulty that had been encountered by previous workers was that they were unable to correlate particle shape and size to the other parameters, because of the small size and irregular shape of particles found in known thixotropic dispersions.

In this study a method was developed for making up thixotropic dispersions with artificial particles of constant shape and size, such that all the dispersion parameters could be investigated separately or together in any combination. As this was the first investigation using artificial time dependent dispersions, and as there was little guide to the selection of particle shapes and sizes in the literature, it became an exploratory study to determine a path for the study of time dependent dispersions. Each dispersion parameter was investigated over a wide range rather than in any specific area. Thus the results obtained in this initial study are not conclusive, but trends are illustrated indicating possible areas for future research.

The two time dependent rheological states exhibited by these dispersions, thixotropic and false bodied, were shown to be dependent upon the dispersion parameters. There was no clear cut transition from the thixotropic to the false body state, but it was found to be dependent on the particular combination of parameters present in the dispersion. The thixotropic state occurred with small particle sizes and length to width ratios over the complete dispersing medium range, 130 to 410 centipoise at low concentrations. The time dependency of thixotropic

dispersions was found to increase rapidly with increases in particle size, length to width ratio, and concentration, until the transitions to the false bodied state occurred. In general the dispersions were false bodied for large size particles, for large length to width ratios, for dispersing medium viscosities greater than 190 centipoise and for particle concentrations greater than 22.5 percent.

Ragged decay curves were obtained with large particle sizes, large length to width ratios, and at high concentrations, indicating a structural breakdown, or particle interference, or a combination of both was taking place. The actual breakdown mechanism could not be seen, as the first particles to be sheared were next to the spindle and were masked by the remaining unsheared structure, but particle orientation from a random structure to an ordered structure was observed. Accurate measurement of the forces involved in the breakdown were not possible due to the lack of sensitivity of the instrument. However, the amplitude of the decay peaks were found to be dependent on particle shape, size, concentration, and dispersing medium viscosity. A thorough study of the ragged decay curves should be undertaken using more sensitive instruments to determine, if possible, the order of magnitude of the bond strength. The effect of adding ionic mineral salts in varying concentrations to adjust the liquid density to that of the particles also should be investigated because the bonding forces involved are known to be of an electrical character.

Two particle shapes were considered, elliptical plate and rectangular plate. The elliptical plate particles were designed to investigate the variation of surface area with constant shape, whereas the rectangular particles were designed to investigate the effect of the variation of length to width ratio. For thixotropic dispersions, equilibrium viscosity was

found to increase linearly with total surface area for dispersions with constant particle shape, concentration, and dispersing medium viscosity. Also equilibrium viscosity was found to increase linearly with dispersing medium viscosity for dispersions with constant particle shape, size, and concentration. The parameter that appeared to have the most pronounced effect on the time dependency and rheological state of the dispersions was the length to width ratio. One parameter that was not investigated and should be in subsequent studies was the effect of particle thickness. This study was carried out with constant particle thickness.

The second objective of this investigation was to check the theoretical model developed by Pinder (32). The reaction mechanism for thixotropic decay, that was found to best fit the data regardless of dispersion parameters and rheological states, was that of a second order-zero order reversible reaction mechanism. This is in complete agreement with Pinder's findings. The forward rate constant ' k_1 ' for the thixotropic breakdown was found to be dependent upon the dispersion parameters of, particle shape, size, concentration, and dispersing medium viscosity. The relationship between the various parameters and k_1 could not be determined from the results, because of insufficient specific data for any one parameter and the lack of sensitivity of the apparatus. This should be determined in subsequent work with a more sensitive instrument. Pinder's theoretical model (32) could not be compared and evaluated with other workers models because of the different data obtained for the model. But the necessary data for the evaluation of other models could easily be obtained from the artificial dispersions used in this study.

The results show that the dispersion parameters considered affect the time dependency and rheological state, but unfortunately because of the number of variable parameters, trends have only been illustrated. A

more detailed study of the effects of each parameter should be undertaken. Only two particle shapes were considered in the present study, both of which were of the rigid plate type. Other particle shapes which can be prepared easily, are rod like particles, which can be made by cutting fibres of cylindrical and elliptical cross-sectional area into the desired lengths. The effects of flexible particles on slurries should also be studied. The temperature of the particle dispersions was kept constant at 20°C throughout the experiment. However, several properties of time dependent dispersions are known to be temperature dependent. A study should be made of the effect of temperature variation on the rate constant k_1 , the amplitude of the ragged decay curves, and the equilibrium viscosity with respect to the dispersing medium viscosity at the new temperature. By an extension of the kinetic analogy, it might be possible to calculate an activation energy of viscous flow from the variation of the rate constant k_1 with temperature. A change in bond energy might be obtained from the change of amplitude with temperature. This study has shown that the dispersion parameters of thixotropic slurries can be readily investigated using artificial dispersions prepared by the procedure outlined in this investigation.

From an engineering standpoint the three characteristic parameters of thixotropic dispersions, yield value, rate constant k_1 , and equilibrium apparent viscosity, are sufficient for design purposes if they are known under the exact conditions of concentration, particle shape and size, and shear rate as are pertinent to the design. The ultimate aim of the research is to correlate viscometer data with data obtained from pipeline tests with the same slurries, and to produce a flow equation which will fully describe thixotropic behaviour.

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APPENDIX I

NOMENCLATURE

- A - Amplitude, average peak height of ragged decay curves, (cp.)
- a - Intercept of inverse apparent viscosity-time curve, (cp.⁻¹).
- b - Slope of the inverse apparent viscosity-time curve, (cp.⁻¹sec⁻¹).
- D.M.V. Dispersing medium viscosity, (cp.)
- EP - Elliptical plate particles.
- k₁ - Rate constant for break-down of dispersion structure, (cp.⁻¹sec⁻¹).
- k₂ - Rate constant for build-up of dispersion structure, (cp.⁻¹sec⁻¹).
- L - Particle longest dimension, (ins).
- RP - Rectangular plate particles.
- t - Time from initiation of shear, (sec).
- W - Particle narrowest dimensions, (ins).
- X - Gel structure break-down ($\mu_o - \mu$), (cp.)
- X_e - Gel structure break-down at equilibrium ($\mu_o - \mu_e$), (cp.)
- μ - Apparent viscosity at any time 't', (cp.)
- μ_o - Yield value, (cp.)
- μ_1 - Original viscosity state, (cp.)
- μ_2 - Final viscosity state, (cp.)
- μ_e - Equilibrium apparent viscosity, (cp.)

APPENDIX II

MATERIALS CONSIDERED FOR ARTIFICIAL SLURRIES

Materials considered for artificial slurries

It was necessary to find suitable materials for particles and dispersing mediums, to make up time dependent slurries. Particle materials were considered in two forms, sheet form from which plate-like particles could be punched in any desired shape, and fibre form from which rod-like particles could be cut to any length. Dispersing medium materials were considered for variable viscosity and solubility for the density correction. A short list of the more promising materials considered is given below:

Particle Materials

Particle Materials

Sheet form		Fibre form	
1.	Paper, various grades	1.	Polyethylene
2.	Cellulose acetate	2.	Polypropylene
3.	Polyethylene	3.	Saran
4.	Perspex	4.	Nylon
5.	Aluminum foil	5.	Terylene
6.	Tin foil	6.	Hair

Dispersing Medium Materials

Viscosity variations		Density correction	
1.	Mineral Oils	1.	Cupric nitrate
2.	Vegetable oils	2.	Nickle chloride
3.	Complete range of polyglycols	3.	Copper sulphate
4.	Glycerol		
5.	Methyl cellulose		

Physical Properties of Materials for Slurries

Material	Density grms/cc	Form
Cellulose acetate	1.306	Transparent sheet
Polyethylene glycol E9000	1.212	White flaky solid
Cupric nitrate	2.047	Blue crystalline solid
Water	1.000	Clear liquid

TABLE 7

Sample Tube Dimensions

Approximate height of glass sample tube 6.25 ins.

Standard depth of the slurry in the sample tube with the spindle

Immersed 3.65 ins.

Tube No.	I.D.	Sample Volume S1 cc	Sample Volume S2 cc
T2	2.069	180	195
T3	1.700	118	123
T4	1.455	80	95
T5	1.223	53	68
T6	0.989	29	44

TABLE 8

Spindle Dimensions

	S1 ins	S2 ins
Total length	4.5	4.5
Diameter of shaft	.125	.125
Diameter of bob	.7418	.4037

TABLE 8 (cont...d)

	S1 In	S2 In
Length of bob	2.563	2.124
Depth Immersed to	3.188	2.624

APPENDIX III
RHEOLOGICAL PARAMETERS

APPENDIX III

TABLE 4

RHEOLOGICAL PARAMETERS

Part- icle No.	Spind- le Tube	Speed R.P.M.	M_e cp.	M_0 cp.	$'b' \times 10^4$ (cp.sec) ⁻¹	A cp.	$k_1 \times 10^5$ (cp.sec) ⁻¹	Order
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Particle concentration 20 percent.
Dispersing medium viscosity 130 cp.

EP1	1-T4	5	535	1318	.052	28	.382	2/0
EP1	1-T4	10	525	1188	.067	36	.460	2/0
EP2	1-T4	5	455	1254	.069	14	.774	2/0
EP2	1-T4	10	450	440	.109	26	.129	2/0
EP2	1-T4	20	435					
EP2	2-T5	20	415	1492	.162	30	.711	2/0
EP2	2-T5	50	385					
EP3	1-T4	5	435	1244	.106		1.559	2/0
EP3	1-T4	10	430	1049	.609		1.435	2/0
EP3	1-T4	20	430			16		
EP3	2-T5	10	440					
EP3	2-T5	20	435	1207	.581		7.366	2/0
EP3	2-T5	50	405			15		
EP4	1-T4	5	420	1231	.568		1.896	2/0
EP4	1-T4	10	405	1067	1.225		7.740	2/0
EP4	1-T4	30	390	809	1.670		13.285	2/0
EP4	2-T5	10	420	1140	.703		32.10	2/0
EP4	2-T5	20	420	1050	.470		2.761	2/0
EP4	2-T5	50	385	645	.1274		2.524	2/0
EP5	2-T6	10	405					
EP5	2-T6	20	405	894	3.460		5.038	2/0
EP5	2-T6	50	355	809	5.13		10.214	2/0

Particle concentration 20 percent.
Dispersing medium viscosity 170 cp.

EP1	1-T4	5	645	1957	.047		.349	2/0
EP1	1-T4	10	625	1346	.041	66	.748	2/0
EP1	2-T5	10	605	2881	.068		.385	2/0
EP1	2-T5	20	555	1887	.081	63	.391	2/0
EP1	2-T5	50	475	1299	.067	51	1.086	2/0
EP2	1-T4	5	590	1737	.067	21	.219	2/0
EP2	1-T4	10	555	1393	.087	33	.550	2/0
EP2	1-T4	20	535			39		
EP2	2-T5	10	540	1779	.042		.223	2/0
EP2	2-T5	20	530	1581	.086		.498	2/0
EP2	2-T5	50	460	1223	.127	40	1.206	2/0

TABLE 4 (Cont...d)

Part- icle No.	Spind- le Tube	Speed R.P.M.	M_e cp.	M_o cp.	$b' \times 10^4$ (cp.sec) ⁻¹	A cp.	$k_1 \times 10^5$ (cp.sec) ⁻¹	Order
EP3	1-T4	5	565	1504	.259		.723	2/0
EP3	1-T4	10	535	1145	.0451		1.303	2/0
EP3	1-T4	20	515			10		
EP3	2-T5	10	530					
EP3	2-T5	20	535	1240	.260		.858	2/0
EP3	2-T5	50	485	936	.433	15	2.061	2/0
EP4	1-T4	5	505	1422	1.156		4.368	2/0
EP4	1-T4	10	470	1327	.648		9.083	2/0
EP4	1-T4	20	465			4		
EP4	2-T5	10	520					
EP4	2-T5	20	500	1123	.668		3.639	2/0
EP4	2-T5	50	440	718	1.34		7.269	2/0
EP5	1-T5	5	500	1095	.6691		1.282	2/0
EP5	1-T5	10	475	905	1.814		1.868	2/0
EP5	1-T5	20	465					
EP5	2-T6	10	500					
EP5	2-T6	20	480					
EP5	2-T6	50	440					

Particle concentration 20 percent
Dispersing medium viscosity 190 cp.

EP1	1-T4	5	695	2102	.047		.267	2/0
EP1	1-T4	10	675			74		
EP1	2-T5	10	635					
EP1	2-T5	20	590	1840	.086	76	.630	2/0
EP1	2-T5	50	500	1104	.108	56	1.194	2/0
EP2	1-T4	5	620	1928	.107		.689	2/0
EP2	1-T4	10	585	1211	.102	24	.929	2/0
EP2	2-T5	10	600					
EP2	2-T5	20	535	1797	.134		.748	2/0
EP2	2-T5	50	470	1197	.412	27	.969	2/0
EP3	1-T4	5	605	1577	.253		1.294	2/0
EP3	1-T4	10	585	1531	.694		5.890	2/0
EP3	1-T4	20	590			15		
EP3	2-T5	10	590					
EP3	2-T5	20	570	1363	.270		1.250	2/0
EP3	2-T5	50	525	969	.318	20	2.092	2/0
EP4	1-T4	5	530	1244	.457		4.801	2/0
EP4	1-T4	10	510	1194	.922		16.355	2/0
EP4	1-T4	20	525			6		
EP4	2-T5	20	550	1149	.856		4.139	2/0
EP4	2-T5	50	515	833	.703		7.787	2/0

TABLE 4 (Cont....d)

Part- icle No.	Spind- le Tube	Speed R.P.M.	M_e cp.	M_o cp.	$\eta_b \times 10^4$ (cp.sec) ⁻¹	A cp.	$k_i \times 10^5$ (cp.sec) ⁻¹	Order
EP5	2-T6	10	500					
EP5	2-T6	20	500					
EP5	2-T6	50	485					

Particle concentration 20 percent
Dispersing medium viscosity 215 cp.

EP1	1-T4	5	780			48		2/0
EP1	1-T4	10	760			74		2/0
EP1	2-T5	10	700	2242	.049		.654	2/0
EP1	2-T5	20	640	2141	.091	86	1.686	2/0
EP1	2-T5	50	560	1290	.191	70	.162	2/0
EP2	1-T4	5	715	1873	.047		.626	2/0
EP2	1-T4	10	675			37		
EP2	2-T5	10	660					
EP2	2-T5	20	620	1928	.066		1.319	2/0
EP2	2-T5	50	540	1351	.107	29	1.781	2/0
EP3	1-T4	5	710	1643	.273		1.756	2/0
EP3	1-T4	10	665	1244	.296		1.831	2/0
EP3	1-T4	20	660			18		
EP3	2-T5	10	695					
EP3	2-T5	20	690	1561	.457		2.715	2/0
EP3	2-T5	50	640	991	.565	15	2.360	2/0
EP4	1-T4	5	605	1649	.457		6.104	2/0
EP4	1-T4	10	590	1210	.636		2.059	2/0
EP4	1-T4	20	575			8		
EP4	2-T5	10	635					
EP4	2-T5	20	620	1336	1.050		7.649	2/0
EP4	2-T5	50	585	912	.917	7	.900	2/0
EP5	1-T5	5	605	1378	.541		.880	2/0
EP5	1-T5	10	590	1094	.470		.130	2/0
EP5	2-T6	10	600					
EP5	2-T6	20	585					
EP5	2-T6	50	545					

Particle concentration 20 percent
Dispersing medium viscosity 260 cp.

EP1	1-T4	5	970	2927	.016	70	.185	2/0
EP1	1-T4	10	930			81		
EP1	2-T5	10	825	2753	.040		.373	2/0
EP1	2-T5	20	805	2926	.064	99	.019	2/0
EP1	2-T5	50	660			60		
EP2	1-T4	5	880	2041	.021	21	.191	2/0
EP2	1-T4	10	845	1650	.032	41	.382	2/0
EP2	2-T5	10	820			35		

TABLE 4 (Cont....d)

Part- icle No.	Spind- le Tube	Speed R.P.M.	cp.	cp.	$\eta' \times 10^4$ (cp.sec) ⁻¹	A cp.	$k_1 \times 10^5$ (cp.sec) ⁻¹	Order
EP2	2-T5	20	760	2260	.053	27	.771	2/0
EP2	2-T5	50	690	1488	.086	44	1.167	2/0
EP3	1-T4	5	835	2103	.233		.898	2/0
EP3	1-T4	10	825			37		
EP3	2-T5	10	820					
EP3	2-T5	20	810	1884	.175	18	1.821	2/0
EP3	2-T5	50	780			29		
EP4	1-T4	5	790	1810	.309		1.821	2/0
EP4	1-T4	10	770	1663	.497		4.492	2/0
EP4	2-T5	10	800	1775	.242		1.435	2/0
EP4	2-T5	20	800	1597	.506		.833	2/0
EP4	2-T5	50	785			22		
EP5	1-T5	5	787	1773	.246		.258	2/0
EP5	1-T5	10	765					
EP5	2-T6	10	780					
EP5	2-T6	20	770					
EP5	2-T6	50	725	1495	.595		.455	2/0
Particle concentration 20 percent Dispersing medium viscosity 302 cp.								
EP1	1-T4	5	1175			112		
EP1	1-T4	10	1080			103		
EP1	2-T5	10	980	3890	.023		.079	2/0
EP1	2-T5	20	925	2949	.042	90	.184	2/0
EP1	2-T5	50	835			102		
EP2	1-T4	5	1056			49		
EP2	1-T4	10	1040			59		
EP2	2-T5	10	910	2524	.012		.189	2/0
EP2	2-T5	20	815	2415	.052	30	.374	2/0
EP2	2-T5	50	730			51		
EP3	1-T4	5	940	2269	.0173		1.171	2/0
EP3	1-T4	10	915			37		
EP3	2-T5	10	945	2482	.087		.526	2/0
EP3	2-T5	20	960	2283	.189		.484	2/0
EP3	2-T5	50	870			22		
EP4	1-T4	5	920	2278	.246		1.438	2/0
EP4	1-T4	10	895			18		
EP4	2-T5	10	925	2121	.260		.985	2/0
EP4	2-T5	20	910	2021	.476		.611	2/0
EP4	2-T5	50	885			15		

TABLE 4 (Cont....d)

Part- icle No.	Spind- le Tube	Speed R.P.M.	M_e cp.	M_o cp.	$\eta' \times 10^4$ (cp.sec) ⁻¹	A cp.	$k_1 \times 10^5$ (cp.sec) ⁻¹	Order
Particle concentration 20 percent Dispersing medium viscosity 360 cp..								
EP1	1-T4	5	1315			126		
EP1	1-T4	10	1190			103		
EP1	2-T4	10	1115	.042		53	.243	2/0
EP1	2-T4	50	920			73		
EP2	1-T4	5	1100	2560	.065	70	.183	2/0
EP2	1-T4	10	1005			59		
EP2	2-T5	10	1015	2451	.038		.283	2/0
EP2	2-T5	20	805	2413	.061	28	.271	2/0
EP2	2-T5	50	735			39		
EP3	1-T4	5	1170	2465	.146	28	.778	2/0
EP3	1-T4	10	1090			37		
EP3	2-T5	10	1020	2382	.101		.370	2/0
EP3	2-T5	20	975	2267	.154	18	.477	2/0
EP3	2-T5	50	905			29		
EP4	1-T4	5	965	2213	.223		2.149	2/0
EP4	1-T4	10	950			20		
EP4	2-T5	10	1015	2188	.133		1.031	2/0
EP4	2-T5	20	990	1929	.304		.991	2/0
EP5	2-T6	10	925	1925	.446		.883	
EP5	2-T6	20	880	1750	1.001			
EP5	2-T6	50	765					
Particle concentration 20 percent Dispersing medium viscosity 410 cp.								
EP1	1-T4	5	1525			140		
EP1	1-T4	10	1380			102		
EP1	2-T5	20	1255	4606	.037	108	.105	2/0
EP1	2-T5	20	1145	3513	.055	80	.219	2/0
EP1	2-T5	50	1075					
EP2	1-T4	5	1320	2917	.027	78	.091	2/0
EP2	1-T4	10	1210			53		
EP2	2-T5	10	1080	3215	.024	65	.141	2/0
EP2	2-T5	20	1000	2805	.055	54	.188	2/0
EP2	2-T5	50	950			58		
EP3	1-T4	5	1285	2580	.129		.850	2/0
EP3	1-T4	10	1215			26		
EP3	2-T5	10	1220	2682	.106		.310	2/0
EP3	2-T5	20	1205	2401	.270	18	.521	2/0
EP3	2-T5	50	1135			44		

TABLE 4 (Cont.....d)

3-7

Part- icle No.	Spind- le Tube	Speed R.P.M.	M_e cp.	M_0 cp.	$'b' \times 10^4$ (cp.sec) ⁻¹	A cp.	$k_1 \times 10^5$ (cp.sec) ⁻¹	Order
EP4	1-T4	5	1115	2491	.186		2.590	2/0
EP4	1-T4	10	1105			22		
EP4	2-T5	10	1165	2242	.147		.668	2/0
EP4	2-T5	20	1125	2163	.368		2.026	2/0
EP4	2-T5	50	1060			25		
EP5	1-T4	5	1110	2137	.205		.715	2/0
EP5	1-T4	10	1055					
EP5	2-T5	10	1050					
EP5	2-T5	20	1035	1998	.392		.320	2/0
EP5	2-T5	50	955					

TABLE 5

RHEOLOGICAL PARAMETERS

Part- icle No.	Spind- le Tube	Speed R.P.M.	M_e cp.	M_o cp.	$'b' \times 10^4$ (cp.sec) ⁻¹	A cp.	$k_1 \times 10^5$ (cp.sec) ⁻¹	Order
Particle concentration 20 percent Dispersing medium viscosity 170 cp.								
RP1	1-T4	5	1175			98		
RP1	1-T4	10	1010			101		
RP1	2-T5	10	850	2954	.034	105	.115	2/0
RP1	2-T5	20	750	2635	.104	108	.346	2/0
RP1	2-T5	50	655	1565	.124	88	.351	2/0
RP2	1-T4	5	725			42		
RP2	1-T4	10	660	1556	.036	33	.349	2/0
RP2	1-T4	20	600			32		
RP2	2-T5	10	675					
RP2	2-T5	20	620	2094	.125	36	.646	2/0
RP2	2-T5	50	515	1285	.179	27	1.201	2/0
RP3	1-T4	5	570	1759	.230		.373	2/0
RP3	1-T4	10	530	1186	.141		.268	2/0
RP3	1-T4	20	515			11		
RP3	2-T5	10	550					
RP3	2-T5	20	510	1298	.130		.578	2/0
RP3	2-T5	50	450	1011	.124	11	.448	2/0
RP4	1-T4	5	520	1734	.705		1.727	2/0
RP4	1-T4	10	480	1178	.986		1.997	2/0
RP4	1-T4	20	475					
RP4	2-T5	10	500					
RP4	2-T5	20	465	1280	.566		.692	2/0
RP4	2-T5	50	425	850	1.29		2.067	2/0

TABLE 6

Particle EP3
Dispersing Medium Viscosity 170 c.p.

Spindle Tube	Speed R.P.M.	Part- icle conc. %	M_e cp.	M_o cp.	$\eta_{sp} \times 10^4$ (cp.sec) ⁻¹	$k_1 \times 10^5$ (cp.sec) ⁻¹	Order
1-T4	5	17.5	475	1399	.834	2.807	2/0
1-T4	10	17.5	445	1078	.118	12.72	2/0
1-T4	20	17.5	430				
2-T5	10	17.5	485				
2-T5	20	17.5	460	1431	2.22	4.158	2/0
2-T5	50	17.5	425			7	
1-T4	5	20.0	565	1635	.772	2.020	2/0
1-T4	10	20.0	550	1280	1.24	1.667	2/0
1-T4	20	20.0	535			15	
2-T5	10	20.0	545				
2-T5	20	20.0	515	1691	1.24	2.069	2/0
2-T5	50	20.0	470	1028	1.53	2.608	2/0
1-T4	5	22.5	735	2048	.297	.789	2/0
1-T4	10	22.5	695	1501	.472	3.897	2/0
1-T4	20	22.5	660			30	
2-T5	10	22.5	610				
2-T5	20	22.5	555	1879	1.33	1.832	2/0
2-T5	50	22.5	520	1270	1.58	3.718	2/0
1-T4	5	25.0	885			42	
1-T4	10	25.0	820			38	
1-T4	20	25.0	775			46	
2-T5	10	25.0	680				
2-T5	20	25.0	625	2162	.480	.938	2/0
2-T5	50	25.0	570	1333	.425	1.410	2/0
2-T5	10	27.5	845				
2-T5	20	27.5	770	3086	.514	1.117	2/0
2-T5	50	27.5	695			59	
2-T5	10	30.0	1155			69	
2-T5	20	30.0	1015	3975	.386	.724	2/0
2-T5	50	30.0	910			88	

APPENDIX IV

APPARENT VISCOSITY-TIME, DECAY CURVES

FIGURE 16

FIGURE 17

FIGURE 18

FIGURE 19

FIGURE 20

FIGURE 21

FIGURE 22

FIGURE 23

FIGURE 24

FIGURE 25

FIGURE 26

FIGURE 27

FIGURE 28

FIGURE 30

FIGURE 31

FIGURE 33

FIGURE 34

FIGURE 35

FIGURE 36

FIGURE 37

FIGURE 38

FIGURE 39

FIGURE 40

FIGURE 41

FIGURE 42

FIGURE 43

FIGURE 44

FIGURE 45

FIGURE 46

FIGURE 47

FIGURE 48

FIGURE 49

FIGURE 50

FIGURE 51

FIGURE 52

FIGURE 53

FIGURE 54

FIGURE 55

FIGURE 56

FIGURE 57

FIGURE 58

FIGURE 59

FIGURE 60

APPENDIX V
COMPARISON OF COEFFICIENTS OF CORRELATION
FOR VARIOUS REACTION ORDERS.

TABLE 9

COMPARISON OF COEFFICIENTS OF CORRELATION OF GOODNESS OF FIT

FOR THE REVERSIBLE REACTION

MECHANISMS

Particle No	Spindle -tube	First-zero	Second-zero	Second-First	Second-second
<u>130 Centipoise 20%</u>					
E P1	1-5	0.9944	0.9977	0.9972	0.9955
E P1	1-10	0.9737	0.9765	0.9762	0.9748
E P2	1-5	0.9591	0.9706	0.9689	0.9655
E P2	1-10	0.9955	0.9976	0.9975	0.9974
E P2	2-20	0.9652	0.9771	0.9743	0.9677
E P3	1-5	0.9754	0.9881	0.9870	0.9852
E P3	1-10	0.9937	0.9959	0.9958	0.9953
E P3	2-20	0.9760	0.9842	0.9825	0.9791
E P4	1-5	0.9735	0.9817	0.9806	0.9784
E P4	1-10	0.9947	0.9980	0.9977	0.9971
E P4	1-20	0.9810	0.9895	0.9880	0.9851
E P4	2-10	0.9970	0.9987	0.9983	0.9971
E P4	2-20	0.9102	0.9306	0.9273	0.9208
E P4	2-50	0.9009	0.9214	0.9174	0.9093
E P5	2-20	0.9041	0.9162	0.9115	0.8965
E P5	2-50	0.8755	0.8970	0.8917	0.8800

<u>170 Centipoise 20%</u>					
E P1	1-5	0.6744	0.6969	0.6915	0.6801
E P1	1-10	0.9789	0.9884	0.9872	0.9849
E P1	2-10	0.9989	0.9991	0.9971	0.9986
E P1	2-20	0.9590	0.9829	0.9812	0.9783
E P1	2-50	0.9629	0.9836	0.9821	0.9791
E P2	1-5	0.9990	0.9995	0.9981	0.9989
E P2	1-10	0.9395	0.9563	0.9540	0.9497
E P2	2-10	0.9718	0.9843	0.9820	0.9772
E P2	2-20	0.9387	0.9605	0.9580	0.9535
E P2	2-50	0.9632	0.9815	0.9793	0.9753
E P3	1-50	0.9768	0.9870	0.9854	0.9820
E P3	1-10	0.8685	0.8955	0.8905	0.8811
E P3	2-20	0.8776	0.8944	0.8899	0.8800
E P3	2-50	0.9105	0.9306	0.9262	0.9170
E P4	1-5	0.9596	0.9678	0.9654	0.9588
E P4	1-10	0.9472	0.9593	0.9572	0.9534
E P4	2-20	0.9608	0.9746	0.9723	0.9681
E P4	2-50	0.9196	0.9380	0.9336	0.9240
E P5	1-5	0.9812	0.9849	0.9835	0.9777
E P5	1-10	0.8267	0.8483	0.8430	0.8309

<u>190 Centipoise 20%</u>					
E P1	1-5	0.7567	0.7742	0.7686	0.7544
E P1	2-20	0.9877	0.9890	0.9885	0.9888

TABLE 9 (cont...d)

5-3

Particle No	Spindle -tube	First-zero	Second-zero	Second-first	Second-second
EP1	2-50	0.9789	0.9933	0.9920	0.9895
EP2	1-5	0.9952	0.9957	0.9955	0.9954
EP2	1-10	0.9489	0.9692	0.9666	0.9619
EP2	2-20	0.9842	0.9845	0.9849	0.9844
EP2	2-50	0.9572	0.9749	0.9729	0.9695
EP3	1-5	0.9820	0.9916	0.9900	0.9864
EP3	1-10	0.9100	0.9250	0.9221	0.9167
EP3	2-20	0.9750	0.9692	0.9670	0.9626
EP3	2-50	0.9291	0.9443	0.9413	0.9366
EP4	1-5	0.9500	0.9593	0.9564	0.9477
EP4	1-10	0.9804	0.9889	0.9872	0.9833
EP4	2-20	0.9946	0.9925	0.9933	0.9944
EP4	2-50	0.9558	0.9652	0.9627	0.9567

215 Centipoise 20%

EP1	2-10	0.9851	0.9944	0.9936	0.9920
EP1	2-20	0.9843	0.9925	0.9917	0.9903
EP1	2-50	0.9877	0.9883	0.9886	0.9883
EP2	1-5	0.9380	0.9561	0.9528	0.9464
EP2	2-20	0.9910	0.9942	0.9941	0.9937
EP2	2-50	0.9880	0.9942	0.9932	0.9908
EP3	1-5	0.9551	0.9694	0.9662	0.9594
EP3	1-10	0.9213	0.9348	0.9307	0.9203
EP3	2-20	0.9141	0.9306	0.9266	0.9175
EP3	2-50	0.9286	0.9362	0.9328	0.9207
EP4	1-5	0.8657	0.8859	0.8822	0.8755
EP4	1-10	0.9556	0.9657	0.9629	0.9562
EP4	2-20	0.7951	0.8152	0.8099	0.7983
EP4	2-50	0.9342	0.9422	0.9387	0.9258
EP5	1-5	0.7551	0.7726	0.7683	0.7595
EP5	1-10	0.7530	0.7700	0.7644	0.7494

260 Centipoise 20%

EP1	1-5	0.9816	0.9913	0.9896	0.9858
EP1	2-10	0.6101	0.9314	0.9216	0.9010
EP1	2-20	0.9739	0.9883	0.9865	0.9831
EP2	1-5	0.3835	0.1944	0.1514	0.0047
EP2	1-10	0.9591	0.9700	0.9668	0.9584
EP2	2-20	0.9833	0.9925	0.9914	0.9890
EP2	2-50	0.9888	0.9952	0.9938	0.9901
EP3	1-5	0.9269	0.9461	0.9423	0.9348
EP3	2-20	0.8539	0.8749	0.8701	0.8601
EP4	1-5	0.8871	0.9051	0.9009	0.8920
EP4	1-10	0.9539	0.9639	0.9614	0.9556
EP4	2-10	0.9434	0.9576	0.9543	0.9467
EP4	2-20	0.7216	0.7424	0.7363	0.7215
EP5	1-5	0.8048	0.8258	0.8208	0.8100
EP5	1-20	0.8408	0.8599	0.8548	0.8422

TABLE 9 (cont....d)

Particle No	Spindle -tube	First-zero	Second-zero	Second-first	Second-second
<u>302 Centipoise 20%</u>					
EP1	2-10	0.9510	0.9743	0.9723	0.9693
EP1	2-20	0.9102	0.9350	0.9317	0.9260
EP2	2-10	0.9819	0.9857	0.9854	0.9844
EP2	2-20	0.9892	0.9969	0.9960	0.9942
EP3	1-5	0.9598	0.9718	0.9693	0.9641
EP3	2-10	0.9560	0.9708	0.9684	0.9633
EP3	2-20	0.8639	0.8868	0.8820	0.8722
EP4	1-5	0.5238	0.6878	0.6664	0.6111
EP4	2-10	0.9168	0.9321	0.9286	0.9211
EP4	2-20	0.8579	0.8785	0.8733	0.8622
<u>360 Centipoise 20%</u>					
EP1	1-5	0.9705	0.9794	0.9770	0.9708
EP1	2-10	0.9602	0.9776	0.9760	0.9733
EP1	2-20	0.9813	0.9916	0.9907	0.9890
EP2	1-5	0.9179	0.9383	0.9338	0.9241
EP2	2-10	0.9900	0.8959	0.9950	0.9925
EP2	2-20	0.9549	0.9715	0.9692	0.9651
EP3	1-5	0.9357	0.9470	0.9441	0.9371
EP3	2-10	0.8820	0.8955	0.8926	0.8863
EP3	2-20	0.8784	0.8945	0.8910	0.8833
EP4	1-5	0.9740	0.9836	0.9815	0.9768
EP4	2-10	0.9552	0.9681	0.9650	0.9575
EP4	2-20	0.8724	0.8886	0.8837	0.8713
EP5	2-10	0.7823	0.7984	0.7940	0.7838
<u>410 Centipoise 20%</u>					
EP1	2-10	0.9325	0.9580	0.9556	0.9515
EP1	2-20	0.9538	0.9740	0.9712	0.9664
EP2	1-5	0.9393	0.9548	0.9510	0.9426
EP2	2-10	0.9683	0.9831	0.9812	0.9775
EP2	2-20	0.9637	0.9796	0.9772	0.9725
EP3	1-5	0.9405	0.9538	0.9503	0.9421
EP3	2-10	0.8554	0.8700	0.8665	0.8585
EP3	2-20	0.9021	0.9191	0.9142	0.9019
EP4	1-5	0.9903	0.9951	0.9941	0.9916
EP4	2-10	0.8928	0.9057	0.9018	0.8915
EP4	2-20	0.9195	0.9313	0.9276	0.9183
EP5	1-5	0.8135	0.8290	0.8241	0.8116
EP5	2-20	0.7932	0.8101	0.8052	0.7930
<u>170 Centipoise 20%</u>					
RP1	2-10	0.9173	0.9462	0.9431	0.9379
RP1	2-20	0.9150	0.9446	0.9414	0.9361
RP1	2-50	0.9089	0.9296	0.9251	0.9159
RP2	1-10	0.9616	0.9718	0.9696	0.9649
RP2	2-20	0.9694	0.9731	0.9731	0.9728
RP2	2-50	0.9853	0.9926	0.9913	0.9884
RP3	1-5	0.9245	0.9512	0.9476	0.9412
RP3	1-10	0.6483	0.6513	0.6505	0.6488

TABLE 9 (Cont....d)

Particle No	Spindle -Tube	First-zero	Second-zero	Second-First	Second-second
RP3	2-20	0.9622	0.9768	0.9742	0.9686
RP3	2-50	0.9584	0.9712	0.9683	0.9616
RP4	1-5	0.8171	0.8477	0.8436	0.8369
RP4	1-10	0.7813	0.7968	0.7936	0.7871
RP4	2-20	0.8417	0.8678	0.8635	0.8556
RP4	2-50	0.9355	0.9493	0.9454	0.9355

EP3 170 Centipoise

Spindle Tube	Concen- tration %	First-zero	Second-zero	Second-First	Second-second
1-5	17.5	0.8631	0.8886	0.8844	0.8772
1-10	17.5	0.9526	0.9632	0.9609	0.9563
1-5	20.0	0.9118	0.9357	0.9318	0.9247
1-10	20.0	0.8083	0.8331	0.8274	0.8156
1-5	22.5	0.8211	0.8482	0.8435	0.8350
1-10	22.5	0.9563	0.9671	0.9643	0.9581
2-20	17.5	0.8492	0.8719	0.8684	0.8626
2-20	20.0	0.8218	0.8484	0.8448	0.8390
2-50	20.0	0.8486	0.8655	0.8613	0.8519
2-20	22.5	0.8374	0.8805	0.8753	0.8668
2-50	22.5	0.9391	0.9575	0.9538	0.9462
2-20	25.0	0.9043	0.9311	0.9538	0.9462
2-50	25.0	0.9711	0.9821	0.9821	0.9231
2-20	27.5	0.8926	0.9310	0.9275	0.9223
2-20	30.0	0.8411	0.9795	0.9754	0.8693

APPENDIX VI
CALIBRATION CHARTS FOR FOXBORO RECORDER.

FIGURE 62, SPINDLE S 2.