# Rheology of suspensions : a study of dilatancy and thixotropy

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# Rheology of Suspensions

A STUDY OF DILATANCY
AND
THIXOTROPY

by

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# RHEOLOGY OF SUSPENSIONS
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## PROEFSCHRIFT

TER VERKRIJGING VAN DEN GRAAD VAN DOCTOR IN DE WIS- EN NATUURKUNDE AAN DE RIJKSUNIVERSITEIT TE UTRECHT, OP GEZAG VAN DEN RECTOR-MAGNIFICUS Dr TH. M. VAN LEEUWEN, HOOGLEERAAR IN DE FACULTEIT DER GENEESKUNDE, VOLGENS BESLUIT VAN DEN SENAAT DER UNIVERSITEIT TEGEN DE BEDENKINGEN VAN DE FACULTEIT DER WIS- EN NATUURKUNDE TE VERDEDIGEN OP MAANDAG 3 JULI 1939, DES NAMIDDAGS TE 4 UUR

DOOR

HUGO LEVIN RÖDER

GEBOREN TE GRAFT

AMSTERDAM — H. J. PARIS — MCMXXXIX

AAN MIJN OUDERS
AAN M. A. S.

*„Nicht in der Ruhe des Besitzes sondern in der steten Vermehrung der Erkenntnis liegt die Befriedigung und das Glück des Forschers.“*

MAX PLANCK

# VOORWOORD

De techniek van het schrijven brengt met zich mede dat wat voor U als lezer het voorwoord is, voor mij als schrijver het slot vormt van de redactie van het onderzoek waarop mijn aandacht langen tijd is geconcentreerd geweest. Het schrijven van deze regels richt onze blik achterwaarts en bij het als in vogelvlucht overzien van de periode die met dit proefschrift afgesloten wordt dringen zich gedachten op waarvan een enkele hier een plaats moge vinden.

Het onderzoek dat in de volgende pagina's behandeld wordt heeft, met mij, eenige malen van domicilie gewisseld, doch waar de voorbereiding er toe, en de afsluiting er van, onafscheidelijk met Utrecht verbonden zijn kan ik niet nalaten uitdrukking te geven aan een gevoel van diepe dankbaarheid jegens de Alma Mater voor het vele dat mij het verblijf binnen Hare muren geschonken heeft; een gevoel van dankbaarheid dat, naar mij in het afgeloopen jaar duidelijk geworden is, in intensiteit toeneemt naarmate de afstand in de tijd die ons scheidt van de periode van dagelijksch contact met de Universiteit toeneemt, waarbij weliswaar de details van het beeld in onze herinnering vager worden, doch waarbij wij ons tevens scherper bewust worden van de resultante van alle invloeden die in de studententijd in bonte mengeling op ons ingewerkt hebben.

Zoozeer valt voor mij hierbij de nadruk op de invloed die wij ondervonden hebben van de Academie als geheel dat ik er van wil afzien het aandeel dat verschillende personen hiertoe bijgedragen hebben nader te analyseeren. Een enkele uitzondering zij het mij vergund hierop te maken.

Dat ik U, Hooggeleerde Kruyt, Hooggeachte Promotor, daarbij in de eerste plaats wil noemen moge U geen verwondering baren. Aan weinigen Uwer leerlingen zal het in dier mate vergund geweest zijn met U in contact te komen, zoowel binnen als buiten de muren van het Laboratorium, als voor mij het geval was. Een qualitatieve uitdrukking te vinden voor de groote waarde die dit contact met U voor mij gehad heeft is een te omvangrijke taak om binnen het kader van deze regels adequaat ten uitvoer gebracht te kunnen worden; hoeveel te zwaarder derhalve de taak deze grootheid ook quantitatief te benaderen en onder woorden te brengen! Zoozeer dringt zich de mate van Uw vermogen om uit een veelheid van materiaal de essentieele elementen uit te lichten op aan diegenen wien het gegeven is onder Uw leiding zich een weg te banen tot het begrijpen van hetgeen zich binnen de grenzen der chemische verschijnselen kan afspelen, dat geen Uwer leerlingen, en wel in de laatste plaats de schrijver van deze regels, zich kan onttrekken aan het streven te trachten zich Uw werkwijze eigen te maken en het door U gegeven voorbeeld als ideaal voor oogen te houden.

Dear Professor Freundlich, the more ardently I attempt to give expression to the feeling of gratitude towards you which has steadily grown during the period in which I was engaged in these investigations, the less I fear I shall succeed in doing so. The bare fact that your presence in London enabled me to combine carrying out research under your supervision with a prolongued visit to England, would in itself have been sufficient to make me feel deeply indebted to you. How much more so where in addition you have displayed towards me such a continuous and stimulating interest in the results of these investigations; an interest interrupted neither by distance nor by time. Please accept the expression of my sincere gratitude for the invaluable guidance which you lent to my steps in the domain of the intricate systems under discussion and for the generous way in which you have never ceased to put at my disposal your extensive knowledge of colloid-chemical phenomena.

Dear Professor Donnan, I feel sincerely indebted to you for the hospitality which I experienced in the Sir William Ramsay Laboratories and for the encouraging interest which you have shown in the progress of my work.

So very much do I owe to all those whose frienship I shared during my stay in England, without whose continuous sympathy I should have found it difficult, if not impossible, to complete the drafting of this investigation in its present form that I can not refrain from tendering these few lines to all of them as a token of cordial gratitude. Our contacts, though for the moment interrupted, remain a perpetual source of the most pleasant souvenirs to me, and will, I am sure, never cease to do so.

My sincere thanks are due to Mrs. D. Kuenen-Wicksteed for kindly having revised the manuscript.

Ede - Bennekom
Juni 1939.

# CONTENTS

# INTRODUCTION

It has been our aim to investigate the properties of systems which show the phenomenon of dilatancy [1], in particular the relations between dilatant and thixotropic systems. In this form the problem originally formed a subject of investigation undertaken by the author under the supervision of Prof. H. Freundlich at *The Sir William Ramsey and Ralph Forster Laboratories, University College, London.*

From the beginning it has been our intention to develop a technique which should enable us to reduce the measurements of dilatant as well as thixotropic phenomena to the appropriate units, since it has been in particular the lack of an adequate technique for quantitative investigation which has increasingly hampered the extension of our knowledge of thixotropic phenomena.

However valuable the "time of solidification" may have been for the development of a schematic knowledge of thixotropic systems, and still may be for a qualitative characterisation of such systems, it has been the authors aim to correlate dilatant as well as thixotropic systems only with their behaviour in connection with flow.

After preliminary investigations had supplied us with sufficient information to outline the scope of the experimental method to be applied, a design was made of an apparatus for the measurement of the systems in the required way.

This apparatus was constructed at the Instrument workshop of the *van 't Hoff Laboratorium, Utrecht,* and all further experimental work has been carried out in this laboratory.

In chapter I a short summary will be given of the principles underlying the measuring of flow in general; chapter II will deal with the apparatus above referred to, while in chapter III and IV the measurements of dilatant and thixotropic systems respectively will be reported and examined. In chapter V thixotropic systems will be subjected to a somewhat broader

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[1] For a description of the phenomenon c.f. page 29.

treatment, whereas chapter VI aims at providing a coordinating discussion of all the various phenomena involved. Eventually a concise summary of relevant papers in the contemporary literature will be offered in chapter VII.

For literature, books as well as papers, concerning the subjects which are dealt with in the following pages we refer to the list of literature at page 85.

# CHAPTER I

# INTRODUCTORY SURVEY

## § 1 - GRAPHIC REPRESENTATION OF FLOW

As has been pointed out in the introduction, we decided to look for an unambiguous criterion for the degree of dilatancy and the degree of thixotropy of our systems in their behaviour under various conditions of shearing stress. In the literature dealing with thixotropic systems again and again the terms "highly thixotropic" or "weakly dilatant" are met with, but, unfortunately, the criterion according to which these qualifications are attributed to the systems under observation seems to vary from one author to another.

Now the whole subject of the behaviour of systems under various conditions of flow can ultimately be reduced to the relation between rate of shear and the shearing stress exerted on the system under observation. The various possibilities which are met with in practice are shown in

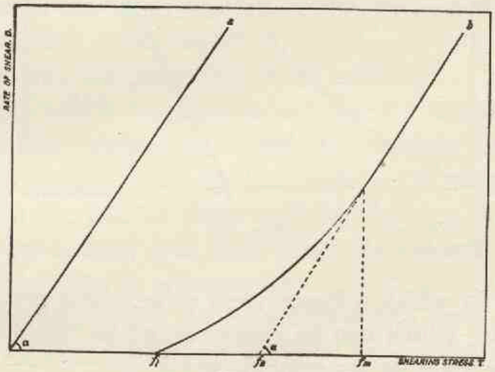

Fig. 1

Fig. 1. and Fig. 2. Curve *a* represents a system in which the rate of shear is linearly proportional to the shearing stress. This type of flow will be

referred to as "viscous flow". The tangent of the angle between this curve and the abscissa represents the mobility of the system i.e. the reciprocal value of the viscosity. Curve *b* represents a system which behaves differently according to the value of the shearing stress; for stresses below $f_l$ (the lower yield value)[1] no flow occurs at all. For stresses larger than $f_m$ ordinary "viscous" flow takes place, while for intermediate stresses the mobility shows a strong dependance upon the shearing stress, the viscosity i.e. $\frac{d\tau}{dD}$ rapidly decreasing with increasing shearing stress.

Attention must be drawn in particular to the characteristic values on the abscissa denoted by $f_l$, $f_B$ and $f_m$, each of which is called a yield value. The lower yield value $f_l$ and the maximum yield value $f_m$ were mentioned above. The yield value $f_B$ (Bingham's yield value) represents the (purely theoretical) value of the shearing stress which would be necessary to just produce flow of the system in case this should exhibit "viscous flow" at each value of the rate of shear. The type of flow represented by curve *b* will be referred to as "plastic flow".

Two more special cases of plastic flow are shown in Fig. 2. Curve *c* represents a case in which a lower yield value is not present, while curve *d* represents a case which can be characterised as "ideal plastic flow"; in this case the three yield values coincide at f.

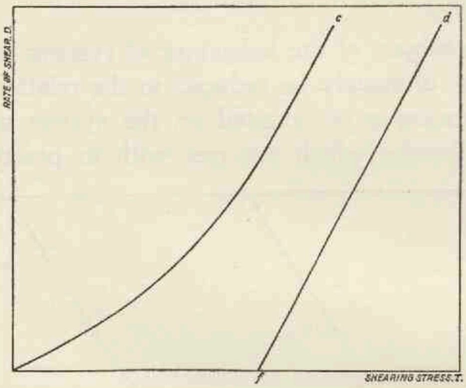

Fig. 2

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[1] Throughout the following pages we will use the nomenclature suggested — and applied — in the First Report on Viscosity and Plasticity of the Academy of Sciences, Amsterdam, 1935.

Eventually a third type of curve must be taken into consideration, which is drawn in Fig. 3, showing a curvature concave to the abscissa. From the theoretical point of view we may distinguish between curve *e* and *g*, according to the abscence of a yield value or not.

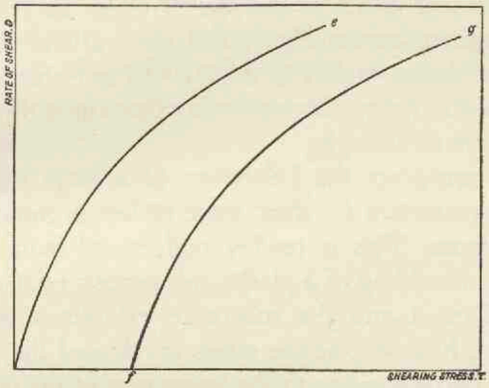

Fig. 3

## § 2 - RELATION BETWEEN GRAPHIC REPRESENTATION AND PHYSICAL PROPERTIES OF VARIOUS SYSTEMS

The question arises which is the physical meaning of the curves of the preceding section, i.e. which systems exhibit curves like the ones just shown and what is the interpretation of the physical mechanism causing either one type of flow or the other?

Curve *a* represents the properties of an ordinary — a so called "Newtonian" — liquid which is characterised by the abscence of any yield value while its $D/\tau$ relation is a perfectly straight line. A Newtonian liquid is entirely characterised by the angle $\alpha$ i.e. by its mobility. By a simple calculation the rate of shear and the shearing stress can be calculated from the experimental data, from which the viscosity i.e. the reciprocal value of the mobility can be enumerated.

Curve *d* Fig. 2, represents a system which over a certain range of shearing stresses shows no flow at all, i.e. behaves as a solid. From f onwards, however, purely viscous flow suddenly sets in. It is not so easy, from the physical point of view to understand what kind of system would behave as represented by this type of curve which shows such an abrupt change in behaviour from a solid to a Newtonian liquid at one particular shearing stress. In addition it is often doubted whether systems showing this type of $D/\tau$ relation do really exist, the difficulty being to determine a $D/\tau$ relation for very small values of the rate of shear. So it is often supposed that in actual practice curves like *d* will always tend to degenerate into the type of curve shown in *b*. Fig. 1. We will not enter into a discussion of this point here. Let it be sufficient to say that curve *d* may be considered as an idealised form of curve *b*.

The curve *b* represents the behaviour of a large number of systems which are all characterised by their more of less pronounced character of a "plastic" substance. This is readily understood from the form of this curve. During the moulding of a plastic substance a relatively high shearing stress is exerted on it and the substance exhibits a comparatively low viscosity; as soon, however, as the stress is released the substance regains its high viscosity corresponding to the lower part of the curve subsequently an infinitely great viscosity represented by the part of the curve which coincides with the abscissa for stresses below $f_l$. This means that after the stress has ceased to act the substance will retain the shape it had adopted during the moulding. In order to characterise a plastic substance four quantities should be specified, namely, $f_l$, $f_B$, $f_m$ and the angle $\alpha$ i.e. a quantity proportional to the viscosity of the linear part of the curve.

## § 3 - INTERPRETATION OF THE MECHANISM CAUSING THE VARIOUS PROPERTIES OF FLOW

Let us try to realise the physical meaning of these various yield values. The lower yield value $f_l$ (c.f. curve *b*, Fig. 1) apparently is the minimum stress necessary to cause the system to break somewhere; since the system will contain bonds of different strength the lower yield value apparently corresponds to the weakest of these bonds. The maximum yield value, on the other hand characterises that stress onward from which the force applied to the system is consumed to produce viscous flow only, i.e. that type of flow which occurs in systems with relatively independent rheological units like a Newtonian liquid.

For any value $f_x$ of the stress between $f_l$ and $f_m$ the force applied to the system is apparently consumed for two purposes, an amount equal to to $f_l$ is used for breaking the weakest bonds which are present in the system while an amount equal to $f_x$—$f_l$ is available for the mutual shearing of the lumps into which the system has been broken down. Since these lumps themselves are liable to be further reduced in size during this shearing-process the total force applied to the system will at any value of the shearing stress be consumed for these two purposes: breaking down of bonds, thus producing lumps of system, and shearing of the lumps of system. At any point of the D/$\tau$ curve these two amounts may be graphically determined as it has been done for the point P in Fig. 4, which shows a curve similar to the curve b of Fig. 1. The tangent in P has been drawn (P—$f_a$). In this Fig. O—$f_a$ represents the part of the stress consumed for the breaking down process (consists of part $f_l$ for breaking down of the weekest bonds plus $f_a$—$f_l$ for breaking down of further bonds), while the part of the force equal to $f_A$—$f_a$ produces the flow of the remnants of the system.

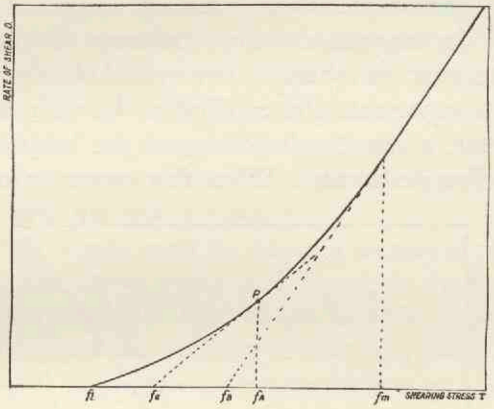

Fig. 4

On continually increasing the shearing stress applied to the system a value must be reached at which no further breaking down of the system is possible, since it has been reduced to the smallest possible particles. This is the value indicated by $f_m$, curve *b*, fig 1. At the same time we can now realise the meaning of $f_B$, this being the stress necessary to reduce the system to the smallest possible rheologically active units at a rate of shear of zero, provided such a condition were possible. The remaining part of the stress $f_m$—$f_B$, Fig. 1, curve *b* is the force necessary to produce that rheological condition at which the smallest possible active units mutually influence each other as if they were the "molecules" of an ordinary liquid.

So far we have assumed that when the system had been partially broken down no tendency whatever to reunite should be present in the disintegrated remnants of the system. If, however, in a particular type of system such a tendency should actually exist then the aspect will necessarily be affected. Let us consider, in addition to the two tendencies taken into account in the preceding lines, n.l. the breaking down action of the stress and the mutual resistance against shear of the lumps of system, a third factor, namely the tendency of the lumps of the system to reunite after the shearing has ceased. In that case each point of the $D/\tau$ curve represents the equilibrium between a breaking down action of the shear, a reuniting tendency of the lumps of system and a certain "viscous-flow-resistance". What this means in terms of the $D/\tau$ curve may be discussed in connection with Fig. 5. Let curve *a* represent a $D/\tau$ curve for a system, the particles of which do not exhibit the tendency to reunite after having been broken down by the action of a stress greater than $f_l$. Let us for instance take the point p at a shearing stress $f'$; now let us endow the particles of the same system with a vigourous tendency to reunite after having been disunited. In that case the same force $f'$ will result in a smaller rate of shear of the system. Let us assume a rate of shear $p'$ to be reached in this case; a similar kind of reasoning may be applied to the other points of the curve and in this way the whole curve *a* shifts to curve *b*. Each point of curve *b* now represents the equilibrium between: rate of break down by shear, rate of reunion and "viscous resistance". In curve *b* the value of $f_m$ represents that shearing stress which

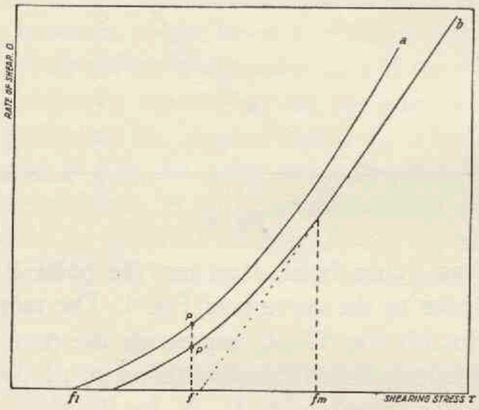

Fig. 5

produces a rate of shear at which the rate of break down to the smallest possible particles is just balanced by their tendency to reunite.

Now if we ask under which conditions a curve like *b* of Fig. 1 will pass into a curve like *d* of Fig. 2 the answer automatically follows from the preceding discussion. Since we have considered the portion of the curve between $f_l$ and $f_m$ to be an indication of the breaking down of bonds of different strength it must be reduced to a single point if only one type of bonds should exist in the system. If such a system might be discovered it would show the behaviour of an ideal plastic substance. On the other hand we will consider the amount of divergence of any curve from that of an ideal plastic curve as an indication of the degree of complexity of the bonds which keep the system together.

Eventually, a few words must be devoted to curves of the type which is represented by the curves *e* and *g* of Fig. 3; in the literature curves of this type are seldom met with. Their shape, however, in the case of curve *e* suggests a behaviour just the opposite to that of a plastic substance, since in the former case at low shearing stresses the system will show similarity with a Newtonian liquid, i.e. will flow spontaneously, while at higher shearing stresses an increasing "viscosity", i.e. an increasing resistance against change of shape will occur. Curve *g* represents a system which exhibits the character of an ideal plastic substance at small values of the shearing stress while at higher shearing stresses an opposite tendency is exhibited similar to that of curve *e*. This type of systems will be dealt with more extensively in § 9.

## § 4 - APPARATUS USED FOR THE MEASURING OF FLOW IN GENERAL

Having dealt with the graphic representation of the properties of various systems in the preceding section, a few lines should be devoted to a description of the measuring apparatus by means of which such graphs may be obtained in practice. Since the object of all such measurements is the establishment of a relation between a rate of shear and a shearing stress two ways are open from the start: either a certain rate of shear can be specified and the shearing stress propagated by the system under observation registered, or the shearing stress can be given and the rate of shear recorded. So with an apparatus of the first group the method comes down to the measurement of a force, while with the second group a speed is recorded, i.e. the method is reduced to the measurement of a time interval. All the different viscometers, plastometers etc. which are used in practice do belong to either of these two groups. The best known representatives of the first group are: The Couette viscometer and its various modifications.

To the second group belong:

1 - The Ostwald viscometer, and other capillary- or efflux-viscometers.
2 - The Searle viscometer, and its modifications (Mc. Michael viscometer, Stormer viscometer, Wolffs turboviscometer).
3 - Falling sphere viscometers, including the Höppler viscometer.
4 - Various extrusion plastometers.

Neither the measurement of a force nor that of a speed offers insuperable difficulties in practice. Difficulties, however, arise in the evaluation of the numerical data in terms of a rate of shear. The dimension of rate of shear is $(T^{-1})$ i.e. a difference of two speeds divided by the distance separating the two planes of different speed. (This applies to laminar flow). With systems consisting of rheological units which are very small compared with the dimensions of the measuring apparatus, as in the case of ordinary liquids, the distance between the two planes can be made very small, namely of the order of magnitude of 1—2 millimeter, as is the case in an ordinary Couette viscometer. In that case the rate of shear in one plane is the speed at which the rotating part of the apparatus revolves while the speed of the other plane is assumed to be zero, and calculation of the rate of shear is easy.

## CHAPTER II

# APPARATUS AND EXPERIMENTAL TECHNIQUE

### § 5 - PRELIMINARY MEASUREMENTS

Owing to the fact that it was dilatant systems, which formed the starting point of our investigations any apparatus we intended to make use of must be appropriate to cope with the properties characteristic for these systems. In chapter III these particular properties will be dealt with comprehensively, but at this place we will mention only those few points which narrowed our choice of the type of apparatus to be used. The greatest difficulty we had to deal with was the tendency of the systems to settle. It seemed most appropriate to us to use an instrument of the Stormer-viscometer type, which allows a determination of the speed of a cylinder, rotated by a specified force, to be made, since it is just the change in behaviour resulting from a variation of the speed which characterises dilatant systems. In its earliest form the apparatus we used consisted of a glass rod kept in position by a piece of glass tube; at the lower end of the rod a paddle — made of wood — was fixed while at the upper end a kind of drum was fixed upon which a string had been wound; at the end of the string, which ran over a pulley a pan had been fixed on which weights could be placed. In course of time this type of instrument was developed to a slightly higher state of craftmanship, the apparatus being made of brass, while a ball-bearing provided adequate guiding of the axis. By means of a screw paddles of various size could be fixed at the lower end of the axis; the system itself was contained in a beaker kept in position by a contrivance allowing the beaker to be removed and replaced in the same position; a scala on top of the axis allowed the number of revolutions during a certain time to be determined.

Apparatus of a similar type, though of varying shape of the paddle are occasionally met with in the literature; c.f. the Turboviscosimeter of Droste and Wollf[1], Kämpf Viscosimeter[2] and a modification of it by Elliot Mc Millen[3].

When the angular speed of the rotating paddle was determined it was found that this speed increased during the first rotations and finally reached a constant value. At a slightly higher weight this constant speed was reached after a larger number of revolutions. Only the constant value of the speed was considered as a criterion for the rheological behaviour of the system under observation. On increasing the weight, however, an increasing number of rotations was required in order to reach this constant speed. Since the number of rotations of the apparatus is determined by the length of the thread the apparatus was altered in so far that it could be worked continually by employing two pans, one of which went up while the other descended.

In Fig. 6 measurements of a 40,5 % dispersion of starch in a mixture of 70 % glycerine and 30 % of water have been reproduced. The angular speed has been plotted against the number of revolutions of the paddle for various weights. The lenght of the thread allowed the paddle to make about 26 revolutions; then the weight was transferred to the other pan and another 26 revolutions were examined. It is seen that at a force of 15 g a

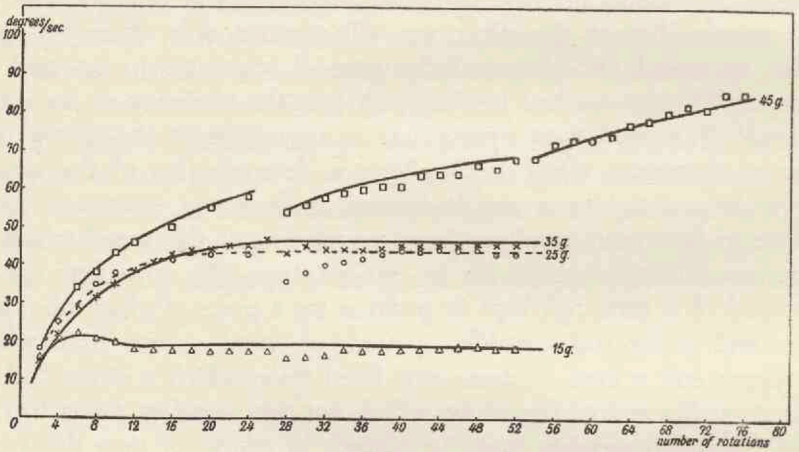

Fig. 6

Results of early experiments with Stormer-type of viscometer.

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[1] Droste und Wollf, Z. angew. Chem. **43**, 1002 and 1022 (1930) Kolloid-Z. **55**, 81 (1931).

[2] Kämpf, Kolloid-Z. **51**, 165 (1930).

[3] Elliot Mc Millen, Ind. Eng. Chem. **23**, 676, (1931).

perfectly constant speed is reached after about 10 revolutions; at 25 g about 20 revolutions are required for this stage to be reached but then the speed remains quite constant. About the same speed is attained at a weight of 35 g; at 45 g, however, a constant speed is not reached even after 80 revolutions. The determinations can be repeated at will.

We asked ourselves what might be the meaning of this slow increase of the speed at consecutive rotations. Apparently the conditions are slightly different after each rotation of the paddle, i.e. the system is seriously affected by the measuring method itself.

So the conclusions we have come to are obviously this: that in order to obtain a reliable impression of the rheological behaviour of a dilatant system the measurement should be carried out in such a way as to allow the system to be subjected to a shearing motion only once; each following shearing of the system will bring it in a different condition and should therefore be discarded.

The most obvious solution for this problem seemed to be the construction of some type of apparatus which should enable us to closely imitate the test by which hitherto dilatant systems used to be tested qualitatively, namely the moving of a spatula through a few cc's of the system on a watch glass. Two more conditions which should be fulfilled by the apparatus were: 1 - the container of the system should allow the system to be easily accessible to being stirred just before starting the measurement, since dilatant systems show a strong tendency to settle; 2 - the container should be as long as possible in order to secure sufficient length for reaching the constant speed while its content should not be too large in order to avoid the necessity of a large quantity of system for each determination.

## § 6 - CONSTRUCTION OF A NEW APPARATUS

The form in which the apparatus, embodying these various requirements has eventually taken shape is shown in pictures I to V, and figures 7, 8, 9, 10 and 11.

Essentially the instrument consists of a "canal"-shaped container which can be closed by a cover on top of which a small "car" moves, guided by two grooves; a slot in the cover allows a metal sphere, fixed underneath the car to be drawn through the centre of the container. This sphere acted as the spatula in our qualitative test and therefore forms the essential part of the instrument. The force required to draw the sphere through the system after this has been introduced into the "canal" is provided by weights which are placed on a scale connected to the "car" by means of a thread.

In picture I the apparatus is shown ready for making a measurement; the "car" may be seen on the extreme left, while the scale is visible on the extreme right of the apparatus. Picture II shows the container, empty, while the cover separately is shown in picture IV; in this picture the cover is suspended in a special frame which we used in later experiments (c.f. page 26). The pictures III and V give further details of the position of the "car" on top of the cover, of the construction of the pulley and of the "car" itself. The small hook on top of the car (c.f. picture V) served for attaching the thread, by means of a small ring at the end of the thread, which allowed the thread to be easily detachable from the car if necessary.

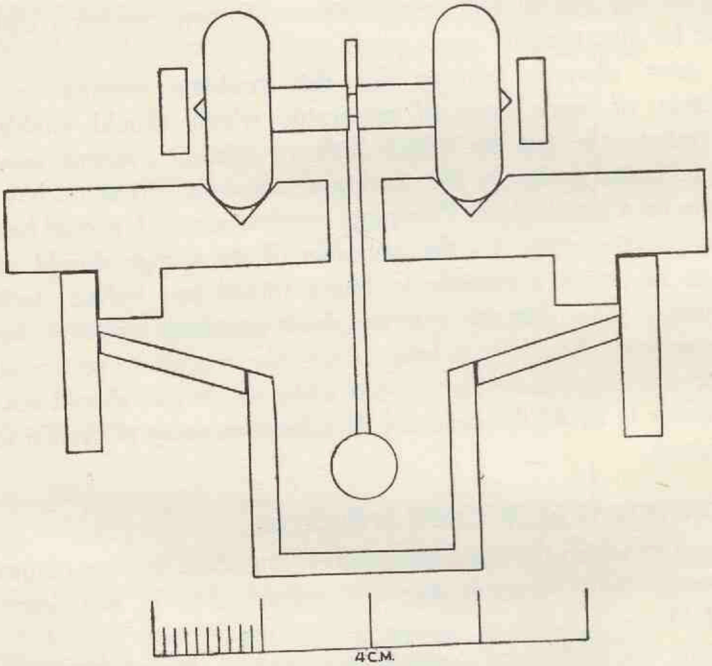
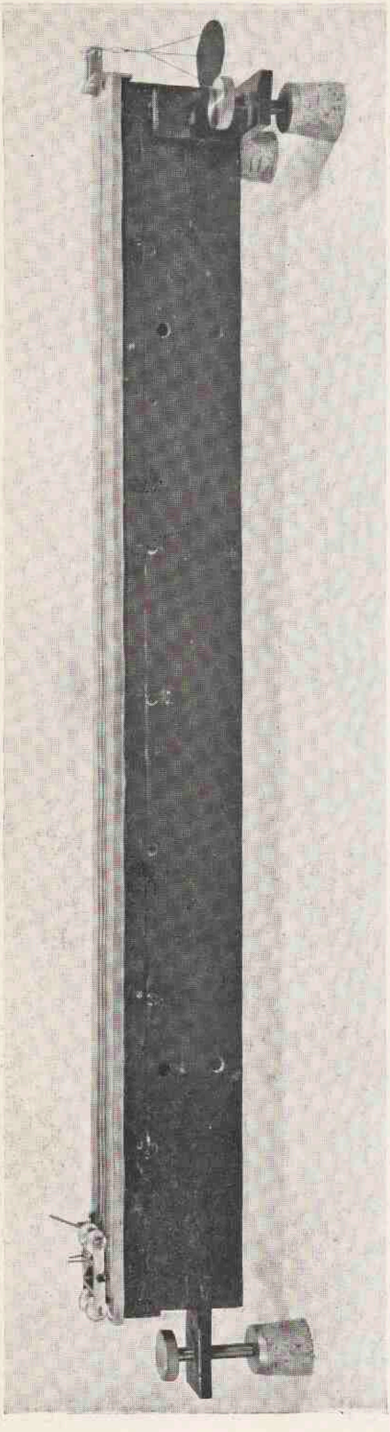


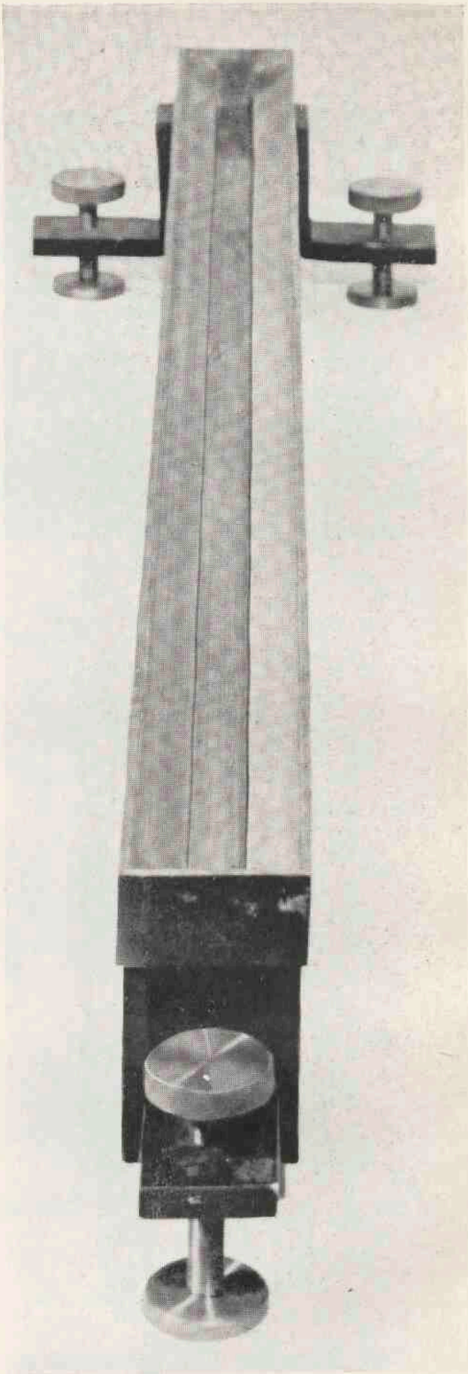
Fig. 7

Cross-section of part of the apparatus, showing the situation of the "canal", the cover and the "car" when in operation.

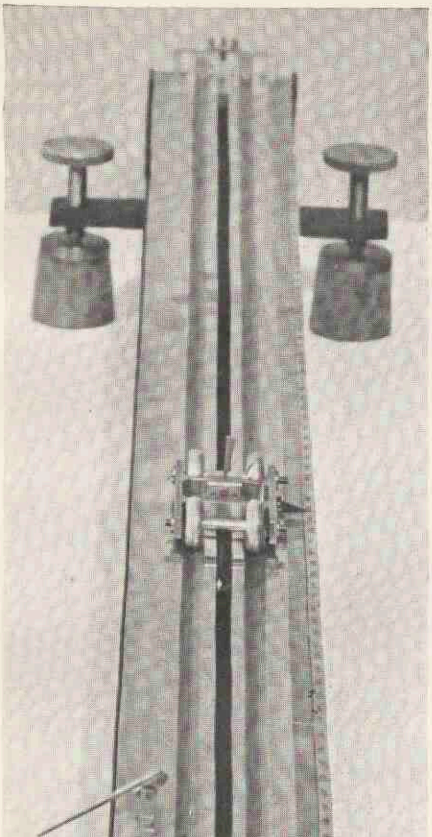
Figure 7 shows a cross section of the container with the cover and the car in the position for carrying out a measurement. Originally the con-



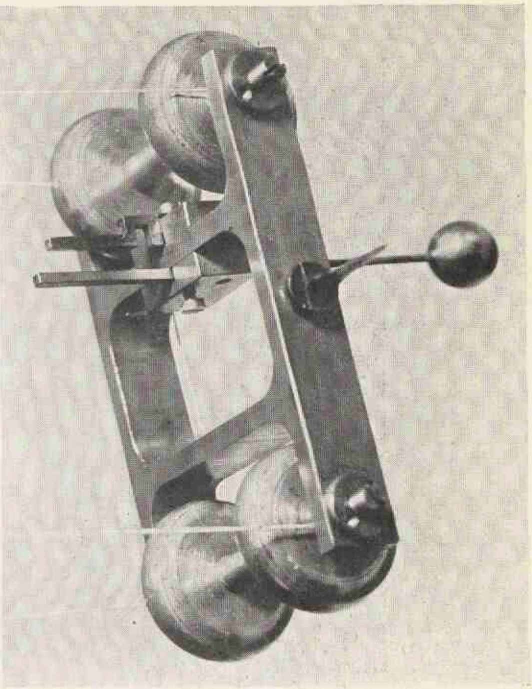
Picture I; Apparatus for the measuring of dilatant and thixotropic systems.



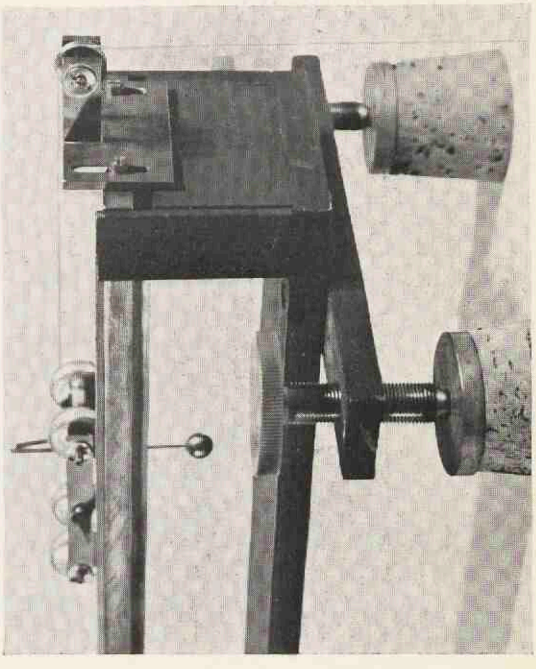
Picture II; The container.



Picture IV; The cover.

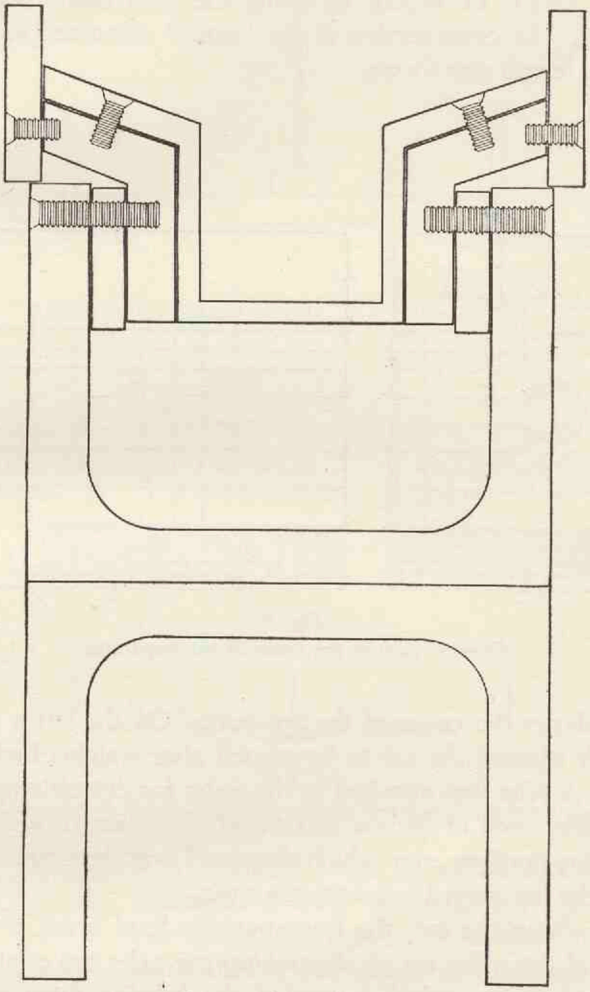


Picture V; The "car".



Picture III; Detail of the cover.

tainer consisted of a brass ⊔ shaped tube with the two oblique brims attached to it. Since the structure in this way was too weak to sustain the cover the tube was suspended in a H shaped profile iron; this is shown in the cross section of figure 8.



Same scale as fig. 7.

Fig. 8

Cross-section of total apparatus, showing the "canal" suspended in iron frame.

The oblique brims are attached to the side-walls of the container by the aid of supporting clamps (6 of them on either side soldered to the walls). Additional clamps secured the container to be firmly fixed inside the profile iron, details of which, including the dimensions may be gained from figure 8. The cross section of the "canal" amounted to 17×17 mm, while its total length was 85 cm.

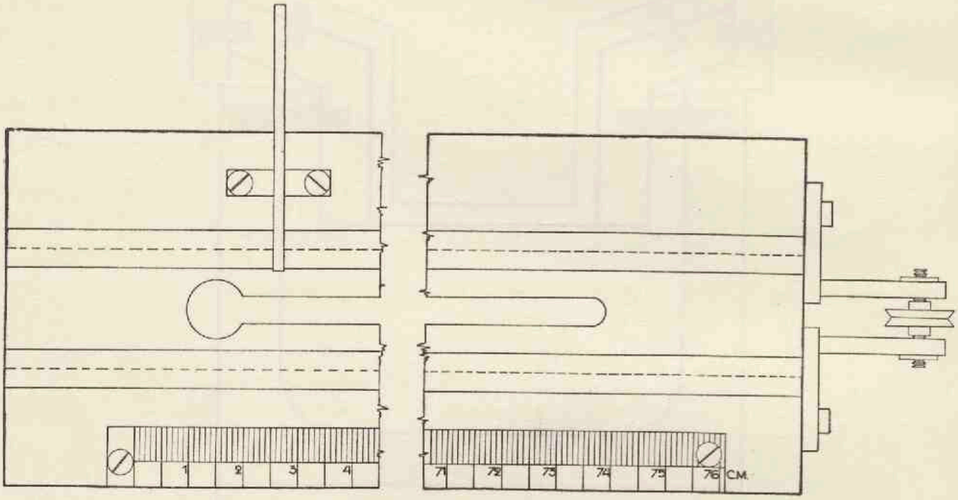


Fig. 9
General view of the cover of the apparatus.

Figure 9 shows the cover of the apparatus. On the left a small lever is shown which allowed the car to be started after weights had been placed on the scale. A ruler was attached to the cover for determining the distance over which the speed of the car was timed. By means of a chalk mark we used to fix the portions over which the speed was determined. The arrow attached to the car moved just over the ruler.

Figure 10 shows the car; the frame was made of brass, the wheels and the guiding of the axles are of aluminium; the axles are of steel while the conical-topped screws which provided the bearing were also made of steel. Details of this construction may be gained from figure 11. The weight of the car was 54 g.

Originally the dilatant systems were directly introduced into the canal; later glass cuvets were made fitting inside the container since thixotropic systems are very sensitive to traces of electrolytes. This apparatus allows us to investigate the behaviour of any kind of fluid system upon deformation, the properties of the system being the decisive factors which determine the speed at which the sphere moves through the system under the action of a specified force. In actual fact our apparatus represents a kind of "horizontal" modification of the falling-ball type of viscometer, the difference being that in our apparatus the force acting on the system can be modified by simply adding weights to the scale while the shearing surface — i.e. the sphere — remains constant. At first a circular plate was used instead of a sphere of the same radius but it was found that there was hardly any difference between the effect of either of these, so the sphere was chosen. Another point of difference is the fact

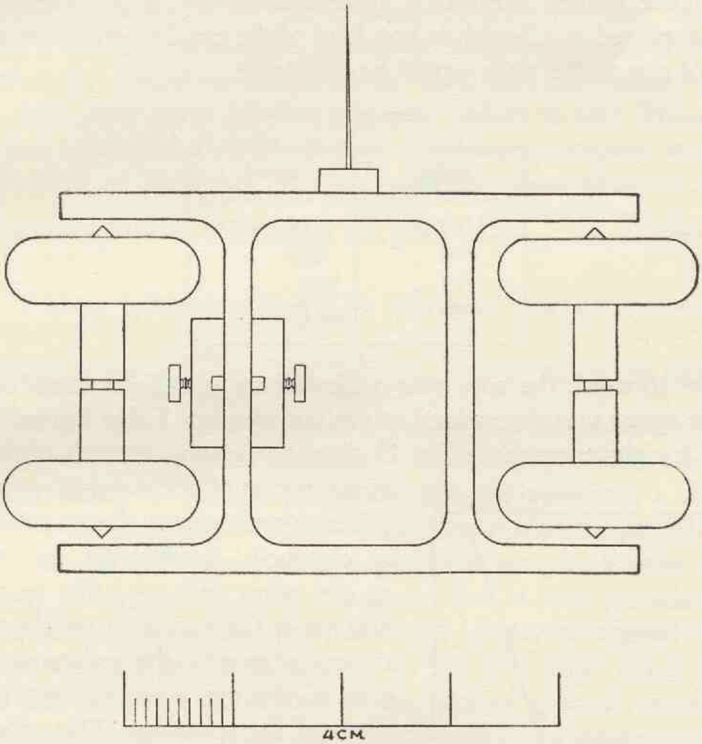


Fig. 10
General view of the car; (details of axle bearings have been omitted).

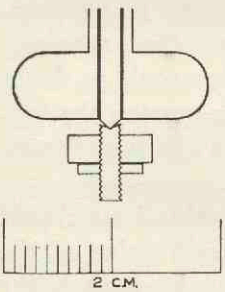


Fig. 11
Detail of axis of the car.

that it was the aim of this apparatus to let the sphere move in an "infinite" quantity of system, the motive being that if we should try to determine the resistance against shear of a system consisting of particles of 1—10 micron, dispersed in a liquid, in any kind of the usual viscometers a certain amount of slip at the walls would be inevitable.

TABLE I

| weight | speed |
|---|---|
| 1100 mg | 6,38 cm/sec. |
| 1300 „ | 9,68 „ |
| 1700 „ | 15,6 „ |
| 1900 „ | 18,1 „ |

In order to check the apparatus a Newtonian liquid was introduced into it and the speed was determined at various weights. Table I gives the data obtained for glycerine while Fig. 12 gives the graphic records of the speed as a function of the weights.

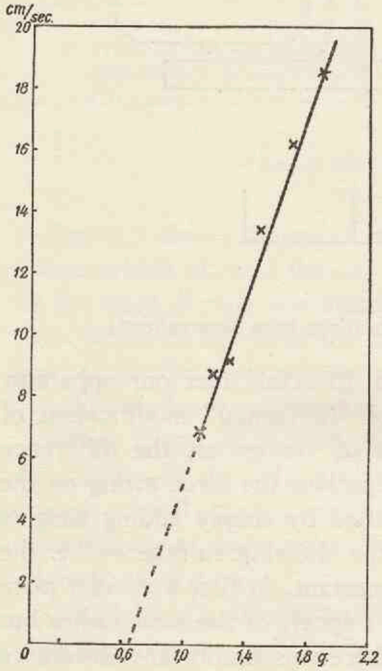


Fig. 12
Speed/weight curve of glycerine.

This graph shows that a straight line is obtained, intersecting the abscissa at the point 660 mg; this means that 660 mg is the minimum weight required to just overcome the resistance of friction of the car when moving over the cover of the apparatus. This value is not constant since the friction of the car is not a perfectly reproducable magnitude, owing to the craftmanship of the axle bearings; Had these been of agate instead of ordinary steel then a smaller and more constant value would no doubt have been attained. In practice the friction turned out to have a fairly stationary value of circa 600 mg.

In connection with table I we should like to remark that each value of the speed for one particular weight is the average value of 10 single determinations. These single determinations have not been inserted in this table; On page 22, however, an example in detail will be given of this way in which each measurement was carried out.

From the data of Fig. 12 the viscosity of glycerine may be roughly calculated if certain assumptions are made. The dimensions of the apparatus under the conditions of the above mentioned determinations were: cross section glass cuvet 14 mm; diameter sphere 8 mm. From fig. 12 we see that a weight of 2000—660 = 1340 mg is required to give the sphere a speed of 20 cm/sec. If we assume the shear to reach from the surface of the sphere to the wall of the glass cuvet — i.e. $\frac{14-8}{2} = 3$ mm the rate of shear is found to be $\frac{20}{0,3} = 66,6\ \text{sec}^{-1}$ ; now the viscosity can be calculated to be $\frac{1,340}{4.\pi.(0,4)^2} .\ 981 .\ \frac{1}{66,6} = 10$ poise. Since the viscosity of glycerine at 18° is 12 poise this results proves that the apparatus gives us data of the correct order of magnitude for substances of a viscosity of 10 poise or larger. If water is introduced into the apparatus a very steep curve is obtained, while it is by no means certain that the recorded speed actually is the constant speed at that particular weight. A value is found of about 1, i.e. about 100 times too large. This is very probably due to the fact that the sphere does not move in a cylindrical shaped container — as was assumed in the calculation — but in a glass cuvet, while in addition it is even inprobable that in the case of a highly mobile liquid as water the shear should reach from the surface of the sphere to the walls of the cuvet.

For a highly viscous syrup a viscosity of 1800 poise was found.

These numerical data have been inserted as a rough quantitative guide rather than a rigorously reliable method for the determination of viscosity. The main point we want to emphasize is the fact that Newtonian liquids are characterised by a straight speed/weight relation in this apparatus, the curves of which intersect the origin. Further results of our measurements will be used for a qualitative and semi-quantitative interpretation respectively of the phenomena under observation in such a way that any deviation of a speed/weight curve from a straight line will be attributed to the pecularities of the system under observation.

The limits of the measuring capacity of our apparatus can be summed up as follows: The maximum speed which could be recorded was about 20 cm/sec. At larger speeds it was not possible to time the passing of a certain mark by the car without making appreciable errors. Towards the smaller speeds, there is no limit in principle, since the slower the motion of the car the easier it is to obtain accurate readings of the time needed to cover a specified portion of the apparatus. In practice, however, a difficulty arose; namely that, when the car moves at small weights at a small speed the slightest resistance may seriously affect the speed of the car, causing it to stop. Because of the fact that the weights are small the force exerted on the car will in such a case be insufficient to overcome the initial frictional resistance of the car, in consequence of which the sphere will persist to stop. With systems of higher viscosity this limit lies at a much lower rate of shear since in that case a relatively high weight is required for even moving the sphere with a relatively small speed. Any resistance which in such a case may occur will be more easily overcome. The following figure may serve to illustrate this:

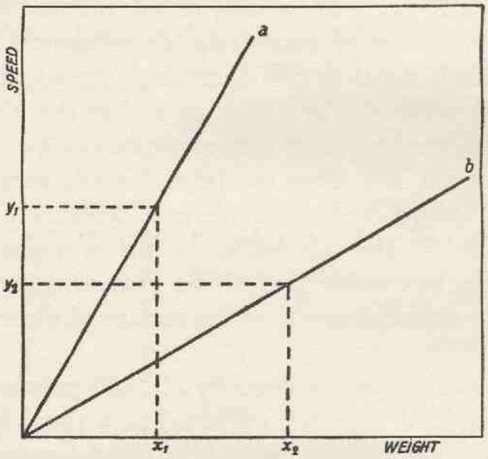


Fig. 13

With curve *a* (representing a liquid of low viscosity) — Fig. 13 — $x_1$ may be the weight required to just allow the car to move continuously, at speed $y_1$. In the case of curve *b*, it is weight $x_2$ wich serves this purpose, at speed $y_2$. According to the preceding discussion no points of curve a can be determined lower than point $x_1y_1$, nor of curve b lower than $x_2y_2$. This means that the area in which actual readings can be obtained with our apparatus is confined to the region A in fig. 14. The limiting curve *a* on the left was obtained after examination of thirty speed/weight curves and recording the smallest concurrent values of speed and weight. To the right, region A is limited by the strength of the thread connecting the car with the pan supporting the weights; the second factor limiting the region on this side being the fact that at high weights the torque acting on the sphere becomes so large that the sphere is partially lifted out of the system; this turned out to occur at weights over ± 50 g. The situation of curve a is determined purely by the mechanical qualities of the apparatus. Reduction of the weight of the car and of the friction would displace the situation of the curve to the left, i.e. enhance the accuracy of the apparatus.

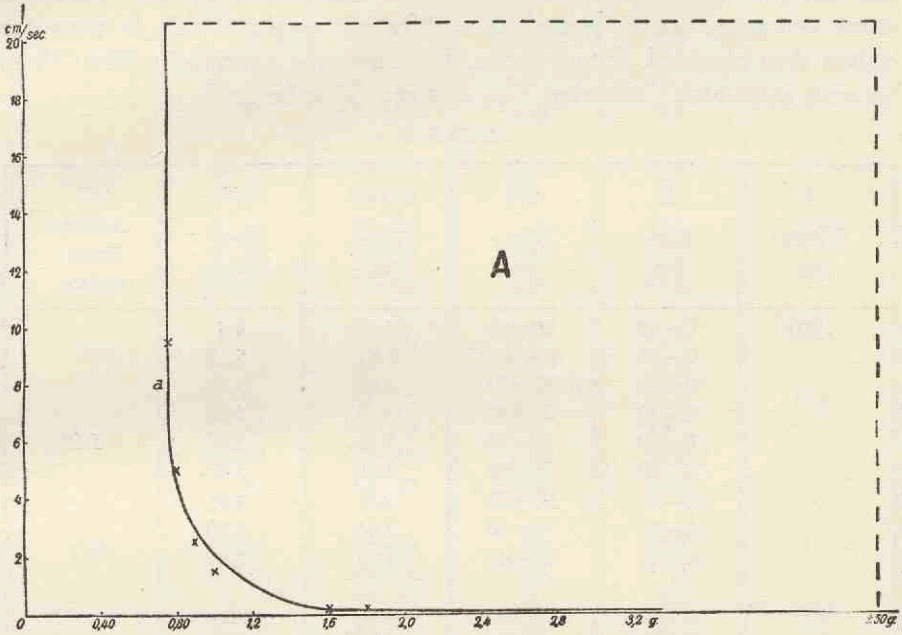


Fig. 14
Figure showing the area in which measurements could be obtained. (A)

## § 7 - ACCURACY OF THE DETERMINATIONS

An impression of the accuracy of the readings obtained with our apparatus may be gained from the following lines. In order to justly appreciate the accuracy a number of considerations have to be taken into account. First of all, the frictional resistance met by the car varies over each portion of the cover of the apparatus owing to imperfections of the grooves which keep the car in position. By systematic experiments we were able to trace those parts of the "track" which apparently offered a somewhat higher resistance to the car. These experiments were made by checking the speed over varying portions of the track at a specified weight: e.g. the portion from 20—30 cm, 20—40 cm, 20—50 cm etc. Then the same procedure was repeated at a different weight. Table II gives the values thus obtained. for glycerine. The time was measured with a "three seconds stopwatch", allowing $^{1}/_{100}$ of a second to be read.

TABLE II

| I<br>Weight: mg | II<br>Run: cm | III<br>Dist.: cm | IV<br>Time: sec. | V<br>Speed: cm/sec. | VI<br>Average Speed: cm/sec. |
|---|---|---|---|---|---|
| 1100 | 0—40 | 40—60 | 4,18 | 4,8 | 5,60 |
| | 0—30 | 30—60 | 5,82 | 5,15 | |
| | 0—30 | 30—20 | 3,68 | 5,43 | |
| | 0—20 | 20—40 | 3,55 | 5,63 | |
| | 0—20 | 20—50 | 5,30 | 5,66 | |
| | 0—20 | 20—60 | 7,05 | 5,67 | |
| | 0—50 | 50—60 | 2,02 | 4,95 | |
| | 0—10 | 10—30 | 3,84 | 5,20 | |
| | 0—10 | 10—40 | 5,50 | 5,45 | |
| 1200 | 0—10 | 10—40 | 4,20 | 7,14 | 7,36 |
| | 0—10 | 10—50 | 5,59 | 6,79 | |
| | 0—20 | 20—40 | 2,66 | 7,52 | |
| | 0—20 | 20—50 | 4,05 | 7,40 | |
| | 0—30 | 30—50 | 2,80 | 7,15 | |
| | 0—30 | 30—60 | 4,30 | 6,98 | |
| | 0—40 | 40—60 | 2,85 | 7,01 | |
| | 0—50 | 50—60 | 1,55 | 6,45 | |
| 1300 | 0—20 | 20—50 | 3,35 | 8,95 | 8,74 |
| | 0—40 | 40—60 | 2,35 | 8,51 | |
| | 0—20 | 20—40 | 2,20 | 9,09 | |
| | 0—30 | 30—50 | 2,34 | 8,50 | |
| | 0—10 | 10—30 | 2,31 | 8,66 | |
| 1400 | 0—20 | 20—50 | 2,67 | 11,2 | 11,14 |
| | 0—20 | 20—60 | 3,65 | 10,9 | |
| | 0—30 | 30—60 | 2,65 | 11,3 | |
| | 0—10 | 10—40 | 2,89 | 10,4 | |
| | 0—10 | 10—50 | 3,80 | 10,5 | |

| I<br>Weight:<br>mg | [illegible]<br>Run:<br>cm | III<br>Dist.:<br>cm | IV<br>Time:<br>sec. | V<br>Speed:<br>cm/sec. | VI<br>Average<br>Speed:<br>cm/sec. |
|---|---|---|---|---|---|
| 1400 | 0—40 | 40—60 | 1,87 | 10,7 | |
| | 0—30 | 30—50 | 1,82 | 11,0 | |
| | 0—20 | 20—50 | 2,70 | 11,1 | |
| 1500 | 0—20 | 20—50 | 2,42 | 12,4 | 12,4 |
| | 0—30 | 30—50 | 1,61 | 12,4 | |
| | 0—40 | 40—20 | 1,63 | 12,3 | |
| | 0—10 | 10—30 | 1,80 | 11,1 | |
| | 0—30 | 30—60 | 2,37 | 12,6 | |
| 1600 | 0—20 | 20—50 | 2,15 | 14,0 | 14,3 |
| | 0—30 | 30—60 | 2,01 | 14,9 | |
| | 0—30 | 30—50 | 1,35 | 14,8 | |
| | 0—40 | 40—60 | 1,44 | 13,9 | |
| | 0—20 | 20—40 | 1,43 | 14,0 | |
| | 0—10 | 10—40 | 2,26 | 13,3 | |
| 1700 | 0—20 | 20—50 | 1,97 | 15,2 | 15,9 |
| | 0—40 | 40—60 | 1,26 | 15,9 | |
| | 0—20 | 20—40 | 1,23 | 16,3 | |
| | 0—30 | 30—60 | 1,84 | 16,3 | |
| | 0—30 | 30—60 | 1,94 | 15,5 | |
| | 0—20 | 20—50 | 1,98 | 15,3 | |
| | 0—10 | 10—40 | 2,15 | 14,0 | |
| 1800 | 0—30 | 30—60 | 1,76 | 17,1 | 16,7 |
| | 0—40 | 40—60 | 1,21 | 16,5 | |
| | 0—20 | 20—60 | 2,39 | 16,7 | |
| | 0—10 | 10—40 | 1,90 | 15,8 | |
| | 0—20 | 20—50 | 1,81 | 16,6 | |
| 1900 | 0—30 | 30—60 | 1,49 | 20,— | 19,7 |
| | 0—20 | 20—60 | 2,05 | 19,5 | |
| | 0—10 | 10—60 | 2,34 | 17,1 | |
| | 0—40 | 40—60 | 1,02 | 19,6 | |
| | 0—20 | 20—50 | 1,74 | — | |

Column I shows the weight, col. II represents the portion of the track over which the car was allowed to move before the speed was checked, col. III represents the portion over which readings of the speed were made, while col. IV shows the time — in seconds — and col. V the speed calculated from these data. From these data two conclusions may be drawn: first, that with this particular system a "run" of about 10 cm is sufficient to guarantee a constant speed up to a value of the speed of about 9 cm/sec.; at higher speeds at least 20 cm is required before a constant speed is reached. Second: the portion of the grooves from cm 40—50 exerts a resistance larger than that of the rest of the track.

In col. VI the average values of the speed are recorded, in the calculation of which the values for a "run" of 0—10 cm and those including the portion of the track from 40—50 cm have been left out of consideration. The data of Col. VI have been plotted in Fig. 15 against the weights.

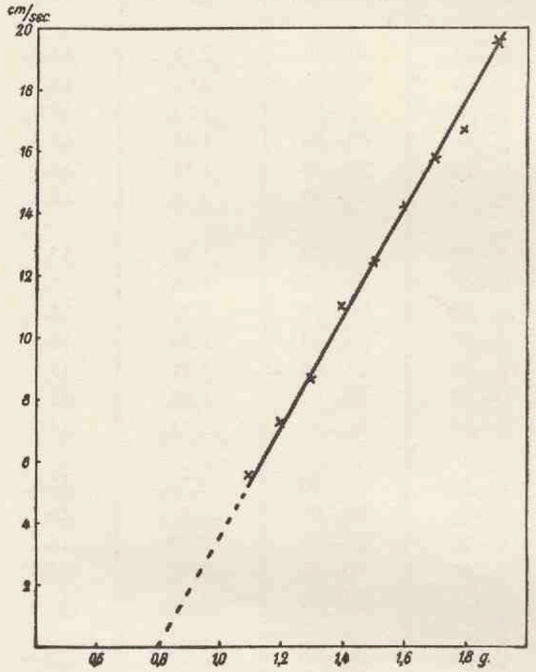


Fig. 15
Speed/weight curve of glycerine in ordinary cuvet.

From table II the average error of the average result of the determinations may be calculated; this turns out to be ± 1 % in this case.

*Influence of the dimensions of the cuvet.*

In order to check the influence of the walls of the cuvet, i.e. of the thickness of the layer of substance between the sphere and the walls a somewhat larger cuvet was made measuring 25×25 mm cross-section. This cuvet filled with glycerine yielded the data of table III while the curve representing these data is shown in Fig. 16. This curve practically coincides with the curve representing the behaviour of glycerine in the small cuvet as shown in Fig. 12.

TABLE III

| Weight: mg | Run: cm | Dist.: cm | Time: sec. | Speed: cm/sec. | Average Speed: |
|---|---|---|---|---|---|
| 1100 | 0—20 | 20—30 | 1,42 | 7,05 | 6,87 |
| | 0—20 | 20—35 | 2,25 | 6,68 | |
| 1200 | 0—20 | 20—40 | 2,12 | 9,45 | 8,75 |
| | 0—10 | 10—40 | 3,29 | 9,15 | |
| | 0—30 | 30—40 | 1,30 | 7,70 | |
| | 0—20 | 20—40 | 2,23 | 8,99 | |
| | 0—20 | 20—40 | 2,37 | 8,46 | |
| 1300 | 0—30 | 30—55 | 3,02 | 8,30 | 9,14 |
| | 0—20 | 20—45 | 2,51 | 10,0 | |
| | 0—10 | 10—30 | 1,95 | 10,3 | |
| | 0—30 | 30—40 | 1,09 | 9,20 | |
| | 0—30 | 30—40 | 1,13 | 8,88 | |
| | 0—30 | 30—55 | 3,07 | 8,18 | |
| 1500 | 0—30 | 30—55 | 1,92 | 13,0 | 13,4 |
| | 0—20 | 20—45 | 1,84 | 13,6 | |
| | 0—30 | 30—50 | 1,48 | 13,5 | |
| | 0—20 | 20—50 | 2,20 | 13,6 | |
| | 0—30 | 30—50 | 1,52 | 13,2 | |
| 1700 | 0—30 | 30—55 | 1,57 | 15,9 | 16,2 |
| | 0—20 | 30—45 | 1,46 | 17,1 | |
| | 0—30 | 30—45 | 0,95 | 15,8 | |
| | 0—20 | 20—40 | 1,30 | 15,4 | |
| | 0—20 | 20—45 | 1,47 | 17,0 | |
| 1900 | 0—30 | 30—55 | 1,37 | 18,3 | |
| | 0—30 | 30—55 | 1,36 | 18,4 | |
| | 0—20 | 20—55 | 2,15 | 16,2 | |
| | 0—10 | 10—55 | 2,49 | 18,1 | |

| Weight: mg | Run: cm | Dist.: cm | Time: sec. | Speed: cm/sec. | Average Speed: |
|---|---|---|---|---|---|
| 1900 | 0—20 | 20—45 | 1,38 | 18,1 | 18,5 |
| | 0—10 | 10—45 | 2,00 | 17,5 | |
| | 0—10 | 10—55 | 2,49 | 18,1 | |
| | 0—30 | 30—55 | 1,24 | 20,2 | |
| | 0—30 | 30—55 | 1,25 | 20,0 | |
| | 0—20 | 20—55 | 1,79 | 19,6 | |
| | 0—20 | 20—55 | 1,84 | 19,0 | |

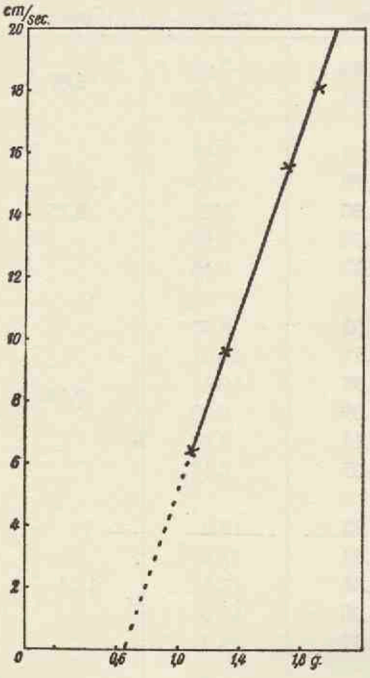


Fig. 16
Speed/weight curve of glycerine in large cuvet.

Of course it was not possible to fix the large cuvet inside the container which measured only 17×17 mm. In order to overcome this difficulty a frame was made in which the cover of the apparatus could be suspended. This frame is shown in Picture IV (pag. 14). This frame in combination with the cover and a glass cuvet provides a complete equipment for carrying out measurements in the way we have described.

*Effect of diameter of sphere.*

The effect of the distance between the sphere and the wall of the apparatus was also checked by recording curves with spheres of various diameters while the dimensions of the cuvet remained unaltered. Table IV represents the data obtained in this way while the curves representing these figures are shown in Fig. 17.

Attention must be paid to the fact that according to this Fig. the extrapolated values on the abscissa are different from each other, which means that the friction of the car was different in each case. One explanation for the differences in frictional resistance may be found in differences in weight owing to the increasing weight of the car with increasing size of the sphere. In Fig. 18 the curves are shown after reduction on the same origin.

TABLE IV

| Weight mg. | $B_4$ |  |  | $B_6$ |  |  | $B_8$ |  |  | $B_{10}$ |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | I | II | F.S. | I | II | F.S. | I | II | F.S. | I | II | F.S. |
| 800 | 3,6 | 3,4 | 7,1 |  |  |  |  |  |  |  |  |  |
| 900 | 2,5 | 2,2 | 10,6 | 4,0 | 4,7 | 5,7 |  |  |  |  |  |  |
| 1100 | 1,6 | 1,4 | 16,6* | 2,3 | 2,2 | 11,1 |  |  |  | 6,8 | 7,4 | 4,2* |
| 1200 | 1,3 | 1,3 | 19,2 | 2,1 | 1,8 | 12,9 |  |  |  | 5,3 | 5,6 | 5,5* |
| 1300 | 2,4 |  | 20,9 | 1,8 | 1,6 | 14,7 | 2,3 | 2,3 | 10,9 | 4,5 | 4,7 | 6.5* |
| 1400 | 2,2 |  | 22,7 | 1,5 | 1,5 | 16,6 | 1,8 | 1,9 | 13,5 | 3,1 | 3,3 | 7.7 |
| 1500 | 2,0 |  | 25,0 |  |  |  | 2,1 | 1,9 | 15,0 | 2,7 | 2,8 | 9,1 |
| 1600 |  |  |  | 2,4 |  | 20,8 | 1,8 | 1,6 | 17,6 | 2,4 | 2,3 | 10,6 |
| 1700 |  |  |  |  |  |  | 1,4 | 1,2 | 19,2 | 2,1 | 2,0 | 12,2 |
| 1900 |  |  |  |  |  |  | 2,2 |  | 22,7 | 1,7 | 1,7 | 15,0 |
| 2000 |  |  |  |  |  |  | 2,1 |  | 23,8 | 1,6 | 1,4 | 16,4* |

Column I: number of seconds necessary for covering first 25 cm (sec.s.)
" II: " " " " " " second 25 cm (sec.s.)
F.S. means: Final Speed, calculated from second portion of 25 cm.
* means: 30 cm instead of 25 cm.
$B_4$, $B_6$, $B_8$, $B_{10}$ means: sphere of 4, 6, 8, 10 mm diameter.

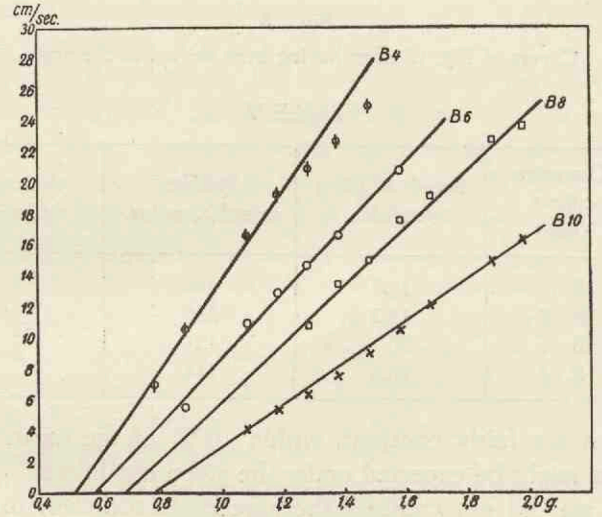


Fig. 17
Speed/weight curves of glycerine with various spheres.

From these data may be computed whether our apparatus agrees with

Stokes' law. According to Stokes' law the product of speed × radius of the sphere should be constant at a constant force. From Fig. 18 the values of the speed for one constant force — i.c. 1,00 g — have been graphically determined. In Table V the result is shown.

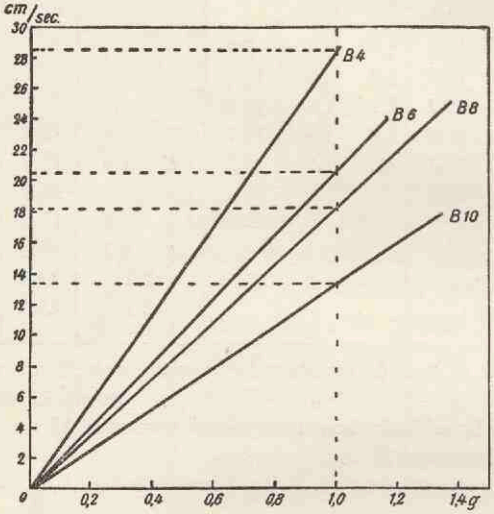


Fig. 18

Curves of Fig. 17 after having been shifted to the origin.

TABLE V

| Diameter sphere (mm) | Speed at 1,0 g cm/sec. | Product speed × radius | Mean value: |
|---|---|---|---|
| B 10 | 13,6 | 136 | 130 |
| B 8 | 18,2 | 146 | |
| B 6 | 20,7 | 124 | |
| B 4 | 28,6 | 114 | |

The values are fairly constant, within 10 % of the mean value which is as good as might be expected under the given conditions.

However we did not consider the agreement sufficient to allow us to convert values of different spheres to the unit of surface; thus, when curves for different systems are compared they will always have been determined with the same sphere.

## CHAPTER III

# MEASURING OF DILATANT SYSTEMS

### § 8 - HISTORIC REVIEW OF DILATANCY

An investigation of the properties of various samples of quicksand by Freundlich and Juliusburger[1] drew the investigators' attention to the peculiar behaviour of some of the samples of sea sand wich had been taken from the neighbourhood of places where the quicksand samples had been collected. This behaviour can be easily demonstrated by the following experiment: 20 g quartz powder of an average particle size of 1—5 $\mu$ which is carefully freed from electrolyte by prolonged treatment with hydrochloric acid and subsequent washing with water, is mixed with 8,5 $cm^3$ of water on a watch glass.

When stirred with a spatula the system exhibits the following pecularities: when undisturbed, the system will spread out like a drop of an ordinary liquid. When slowly stirred it will behave in the same way; as soon, however, as the spatula is moved through the system quickly a disproportionately high resistance sets in while the system becomes "dry" and ceases to behave like a drop of liquid. Immediately after the stress is released the system will recover its previous appearance and flow easily; it is possible in this way to cut out a piece of the system with a spatula, but as soon as this has been done the "solid piece" will return to its fluid state again and trickle down the spatula like a viscous liquid. The phenomenon is entirely reversible and can be repeated at will.

It was found by the investigators that the peculiar behaviour of systems consisting of sandgrains and water have been the subject of an investigation bij Osborne Reynolds as early as the year 1885[2]. This author

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[1] H Freundlich and F. Juliusburger, Quicksand as a thixotropic system, Trans. Faraday Soc. 168, **31**, 769, (1935).

[2] Osborne Reynolds, Phil. Mag. (5), **20**, 469, (1885); Nature, **33**, 429, (1885).

describes the following experiment which is highly instructive as well as puzzling at the first sight: A rubber ball, which is fitted with a glass tube on top of it is filled with ordinary sand of an average particle size of 1—2 mm after which water is added until the whole ball is completely filled. Now if the ball is softly squeezed at the place indicated by the arrows — c.f. Fig. 19 — the water level will immediately fall, the meniscus being lowered proportionally to the squeezing. The explanation of this startling phenomenon should be this that the content of the rubber ball, when filled with sand and water does not decrease upon squeezing — as it does when filled with water only — but increases, in consequence of wich the water level wil fall. The reason why the volume of the rubber ball increases upon squeezing is this: at the beginning the sand grains inside the ball will be in a condition of close packing, each particle touching a number of other particles. Upon squeezing, however, this condition of close packing will be disturbed, the particles are removed from each other, causing the interstices to increase. This will result in an increase of the total volume of grains and water and water will be drawn into the enlarged interstices. It was this behaviour which Osborne Reynolds characteristically denoted as "dilatancy", owing to the dilating effect of the sand-water system on the rubber ball. Since the mechanism responsible for the behaviour of the quartz in the experiment of Freundlich and Juliusburger is obviously the same as the one in the experiment of Osborne Reynolds the term "dilatancy" (adiectiv: dilatant) was reintroduced by the former authors.

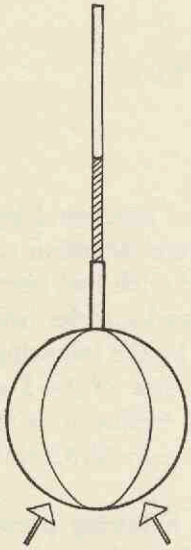

Fig. 19
Experiment
of Osborne Reynolds.

It must be mentioned that there is a difference between the experiment of Freundlich and Juliusburger and the one of Osborne Reynolds in so far that the former experiment can be done only with small particles while the latter can be carried out with large sand grains only. If a rubber ball is filled with quartz powder of 1—5 micron it is impossible to squeeze the ball since the system is far too consistent. On the other hand no effect will be noted when sand grains of 1—2 mm diameter are stirred with water on a watch glass.

One more experiment may be inserted in order to illustrate the remarkable properties of dilatant systems: when a beaker of 100 c.c. is partly filled with a dilatant paste the mass can be easily stirred with a glass rod by gently moving it through the mass. When, however, the glass rod is dropped into the system the mass will solidify at the sudden impact of the rod, thus reducing the speed of the rod to almost zero, after which the rod will quietly sink to the bottom of the beaker. Whether dropped from one or ten feet height does not make any difference, in no case will the bottom of the beaker be broken by the falling rod.

At the start of our investigations a number of dilatant systems had already been traced; in the first place a number of powdered minerals were examined by Freundlich and Jones[1] who mention the following substances to show dilatancy in a marked degree:

*a* - quartz
*b* - corundum
c - diamond
*d* - monax glass

while dilatancy in a somewhat lesser degree was observed in the following cases:

*a* - mica
*b* - gypsum
c - pure calcium carbonate
*d* - Iceland spar
*e* - galena
*f* - mosaic gold
*g* - limestone
*h* - aragonite
*i* - marble

An interesting system, which turned out to be a case of dilatancy was found to be reported bij Bon[2] who described the behaviour of a paste of wheat starch with a mixture of glycerine and water; we found that a mixture of rice starch and water exhibits the phenomenon equally well as quartz and water. Recently a system consisting of carbonyl iron suspended in carbon tetrachloride which exhibits dilatancy on addition of a drop of oleic acid has been described by Verwey and De Boer[3].

## § 9 - DESCRIPTION OF EXPERIMENTAL RESULTS

As has been pointed out in the introduction it has been our aim to

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[1] H. Freundlich and A. D. Jones, J. Phys. Chem., **40**, 1217 (1936).

[2] W. F. Bon, Chem. Weekblad, **33**, 45 (1936).

[3] E. J. W. Verwey and J. H. de Boer, Rec. trav. chim., **57**, 383 (1938).

investigate the properties of these dilatant systems and it was decided to start with an investigation of the influence of particle size upon the phenomenon. As our object we choose quartz-water, later rice starch-water suspensions. A quantity of Kahlbaum quartz powder (Quarz, geglüht und gepulvert) was chosen as the material for these experiments. The crude material does not show dilatancy on addition of water, obviously owing to its content of electrolyte. In order to purify the quartz it was treated with concentrated chloric acid on a water bath until no more iron could be extracted and subsequently washed with water until the washing water showed no acid reaction to lacmoid. The quartz was then separated into various fractions by allowing the particles to settle during various periods. The average size of the particles in the various fractions was checked by measurement under the microscope. Fractions were obtained containing particles of:

smaller than 1,5 micron
1,5—5 „
5—10 „
15—30 „
30—55 „
larger than 50 „

In addition we had at our disposition samples of larger quartz particles namely: quartz sand, which was obtained by grinding of big particles in a mechanical agate mortar. These portions were purified in the same way as mentioned above, and subsequently divided in various fractions by sieving through cotton sieves. The fractions thus obtained ranged from

55— 75 micr.
75—100 „

Qualitative experiments showed us that dilatancy was exhibited in a different degree according to the size of the particles. The following summary may give some idea of this:

| size of particles | degree of dilatancy: |
|---|---|
| 200—100 $\mu$ | no dilatancy |
| 100— 75 | " " |
| 75— 50 | very weekly dilatant |
| 50— 30 | " " " |
| 30— 15 | rather " |
| 15— 10 | distinctly " |
| 10— 5 | very well " |
| 5— 1,5 | highly " |
| < 1,5 | weakly " |

The difference between the behaviour of particles of 5 $\mu$ and 50 $\mu$ is very marked; the system consisting of the 5 $\mu$ particles becomes quite dry and hard upon quick stirring while it turns liquid immediately after the stress is released. In the 50 $\mu$ system, however, dilatancy is much less pronounced; Upon stirring the increase in consistency is considerably less than with the 5 $\mu$ particles while after release of the stress the mass does not reacquire the fluid character until the watch glass has been slightly tapped. It was this behaviour which was indicated as "passive dilatancy" by Freundlich and Jones (loc. cit. pag. 31).

From these experiments it was learnt that the range of 1,5—5 $\mu$ shows dilatancy the most obviously, so it was decided to first investigate the properties of this system in detail. In the first place we wished to examine the flowing properties of quartz suspensions as a function of the concentration. To that purpose to 90,5 g of quartz 42,3 c.c. of water was added, and the system well mixed — conc. 44,7 % by volume —. The system behaves as a consistent mass; after having been transferred into the apparatus determinations were made of the speed at various weights. The same procedure was repeated after addition of water to final concentrations of 42,9 and 41,6 %. The data are shown in Table VI. The speed was determined over portions of 14 cm; each determination was repeated two or three times. Fig. 20 shows the curves representing the data of Table VI.

TABLE VI

Speed at various weights for suspensions of quartz (1½—5 $\mu$) in water; cm/sec.

| sphere | conc. | weight: (grams) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 0,700 | 0,800 | 0,900 | 1,13 | 2,13 | 3,13 | 4,13 | 5,1 | 6,1 | 7,1 | 9,1 | 11,1 | 15,1 | 16,1 |
| B4 | 44,7 | | | 1,2 | 1,9 | 2,5 | 2,4 | 2,3 | 2,4 | | 2,5 | 2,5 | 2,4 | 2,6 | 2,4 |
| B4 | 42,9 | | 3,0 | 3,1 | 3,5 | 4,8 | 4,8 | | | 4,7 | | 5,0 | 4,5 | | 4,7 |
| B4 | 41,6 | 2,8 | | 8,2 | 11,7 | | | | | | | | | | |
| B8 | 41,6 | | | 5,0 | 7,0 | 7,7 | 8,2 | 8,7 | | 7,7 | | | 8,7 | | 8,7 |
| | | weight: | | 0,630 | 0,680 | 0,780 | 0,880 | 0,980 | | 1,08 | 1,28 | | | | |
| B8 | 40,6 | | | — | 4,3 | 7,0 | 8,7 | 10,7 | | 11,7 | 15,5 | | | | |

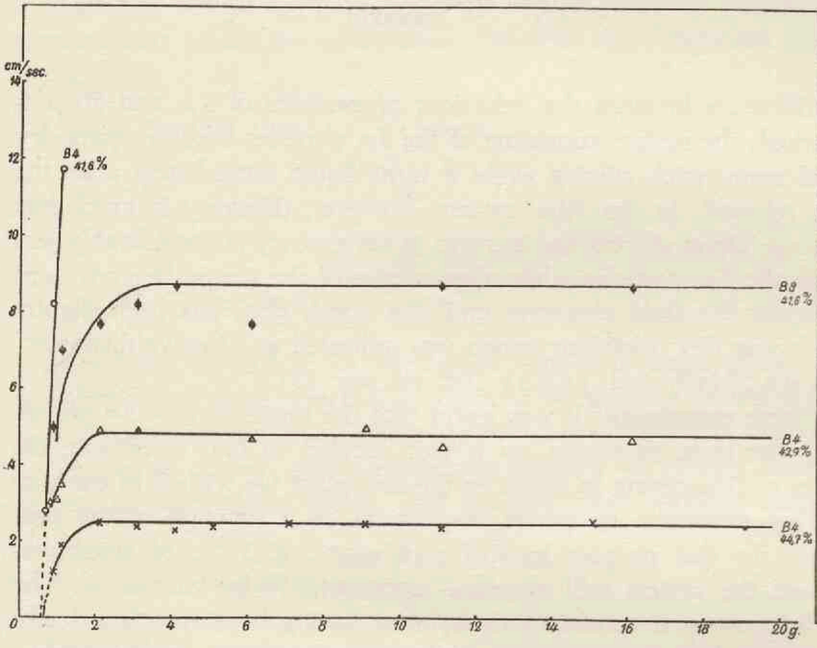

Fig. 20

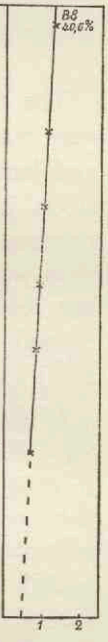

Fig. 20*a*

Speed/weight curves of suspensions of quartz in water.

From these graphs we see that at small speeds there is proportionality between the speed and the weight but at a certain speed no further increase in the speed is obtained on increasing the weights. This "maximum" speed is higher the lower the concentration of the suspension. At 41,6 % this maximum speed is so high that it can not be registered anymore under application of the sphere of 4 mm diameter. When this system was investigated by means of the sphere of 8 mm diameter the curve B8 (Fig. 20) was obtained. On dilution to 40,6 % this system gave the curve of Fig. 20a.

For rice starch similar curves were obtained. Fig. 21 shows a curve for a 44 % — by volume — suspension of rice starch in water. The curves which are reproduced are just a few examples of the many dozens of curves of quarz and starch systems which have been determined with various spheres in course of time. They all exhibit the same shape as the curves of Fig. 20 and Fig. 21.

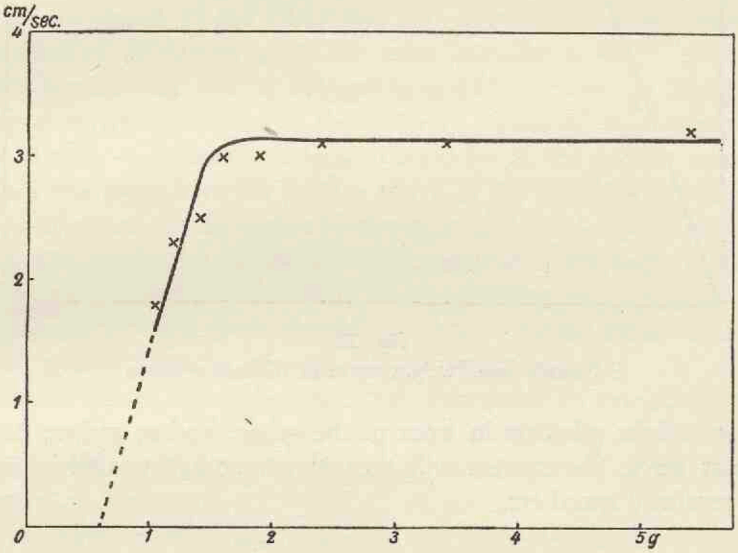

Fig. 21
Speed/weight curve of 44 % suspension of rice starch in water.

In order to understand what they mean attention should be drawn to one pecularity which does not find adequate expression in the curves. It is this: Let the diagrammatic shape of the curves be as shown in Fig. 22. Now if we observe the motion of the sphere at small speeds, i.e. the points of part a. of the curve then the motion is perfectly smooth. At the speed of the horizontal part b. of the curve, however, the sphere does not move smoothly but with periodical variations of speed. Since the speed was always measured over a distance of 15—25 cm each point of the part b of the curve represents the mean value of this periodically varying speed. The reason of this behaviour is the following: when a large force is applied to the sphere it will tend to acquire a high speed; the system, however, will be piled up in front of the sphere and so reduce its speed to almost zero. The system will then flow out again, after which the sphere regains it speed etc.

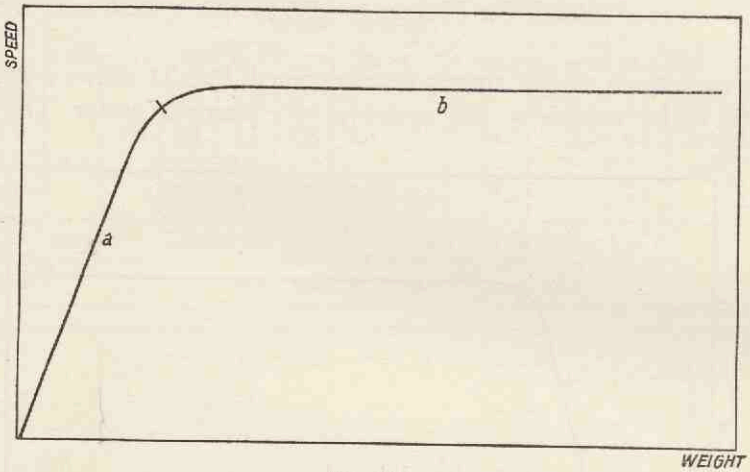

Fig. 22
Schematic speed/weight curve of dilatant systems.

## § 10 - DISCUSSION OF EXPERIMENTAL RESULTS

In this section we will attempt to deduce the meaning of the curves which have been reported in the preceding one. It seems reasonable to us to emphasize three points:

1st: Dilatant systems show no yield value whatever.

2nd: Dilatancy is confined to a rather narrow range of concentrations; for quartz-water ± 41—45 % by vol.; for rice starch-water ± 38—44 %.

3rd: Dilatant systems are characterized by a speed/weight curve which is concave to the weight axis.

On close inspection of the speed/weight curves we come to the conclusion that two different mechanisms must give rise to the two sharply distinguished parts a and b. During the slow motion, represented by part a the particles apparently are able to slide along each other. When a certain speed is reached, however, they are forced against each other and thus form a solid obstacle; immediately after the stress is released they retake their original position. The predominant condition for allowing this behaviour being that the particles do not show the least tendency to adhere to each other, but remain absolutely individual.

These results having been obtained, let us return to our initial problem, being the question how to find an unambiguous criterion for the degree of dilatancy of a system. Apparently it is not quite correct to consider the value of the speed of the horizontal part of the curves as a measure of the degree of dilatancy; since we must consider a 40 % quartz-water mixture qualitatively just as dilatant as a 44 % system, — though quantitavely different according to the different values of the horizontal part of the curves — it seems obvious to consider as the correct criterion for dilatancy the angle between parts a and b of the speed/weight curve. The more pronounced the difference in direction of these two parts the stronger the dilatant tendencies of the system. Apparently this angle represents a criterion for the degree of stability of the particles in suspension.

The next step to be taken should have been a measurement of a suspension of quartz particles of say 10—15 $\mu$ average size. Unfortunately, however, it turned out to be practically impossible to make any measurement of such a system since the particles immediately settle down, thus preventing the possibility of making any determination of the rheological behaviour of the system.

In this connection it may be well to say a few words about the expression, hitherto used of: "a 45 % quarz suspension". It would be quite wrong to think of such a system in terms of a 45 % solution of sugar in water for instance. The latter is a homogeneous system while the former is quasi-homogeneous only when it is kept in vigorous stirring motion and during a number of seconds after the stirring has ceased; a number which depends entirely upon the size of the particles. With particles of 1—5$\mu$ it may be for 30—60 seconds while it may be 1—2 seconds for 15—30$\mu$ particles. It is this circumstance which seriously interfered with our attempts to establish a ratio between speed and weight with particles larger than 5 $\mu$.

Another point of importance with dilatant systems is the fact that there is no influence of time apart from the tendency to settle. Other changes do not seem to occur. A dilatant system exhibits its behaviour independently of the time elapsed since its preparation.

# CHAPTER IV

# MEASURING OF THIXOTROPIC SYSTEMS

## § 11 - HISTORIC REVIEW OF THIXOTROPY

Originally the word "thixotropy" was chosen to characterize those systems which are liable to an isothermal gel-sol transformation by the influence of shaking, while the gel condition redevelops on standing[1].

In course of time, however, the conception was extended to all those systems which are liable to a temporary change of consistency upon mechanical deformation. During the last decade an appreciable amount of research has been carried out on the nature of the phenomenon and the optimum conditions under which thixotropy occurs. After the first extensive investigations of the ferrice-oxyde sol by Freundlich and coworkers dealing with the influence of electrolytes on the rigidity of the systems under investigation, numerous other systems have been described showing the phenomenon in all varying grades of intensity and inconspiciousness. These many substances may be classified, roughly, within a few classes of kindred systems[2], e.g.

*a* - systems which show real sol-gel transition ($Fe_2O_3$ sol; copper-ferrocyanide sol, aluminiumhydroxide)

*b* - suspensions of small distinct particles in various vehicles (bentonite, clays, paints, ceramic masses)

*c* - numerous hydrophylic systems like dyestuff solutions, honey.

Numerous investigations have taught us that the thixotropic condition is intermediate between the sol condition and the condition of a flocculated system. Naturally the concentration is a factor of decisive importance. Most of the investigators have made their experiments on the basis of

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[1] c.f. Thixotropy, by H. Freundlich. Paris, Hermann & cie. 1935.

[2] For a comprehensive treatment of various systems c.f. Scott Blair's book mentioned on page 85.

the "time of solidification", i.e. the time required by a certain system to reach such solidity as to just prevent the system from flowing down the walls of a testtube, upon turning it upside down. It need hardly be said that this criterion is a relative one, in consequence of which it is quite usefull for comparing differences brought about in one system, but hardly suitable for comparison of different systems. The reason why measurement of the time of solidification must be considered insufficient for completely caracterizing a thixotropic system is this: Apparently thixotropy is characterized by the increase of consistency in course of time; So, from the start only the increase of some magnitude proportional to the consistency of the system as a function of time will be able to convey a complete picture of the properties of the system under observation. The time of solidification can be considered as just one point of this imaginary consistency-time curve, namely the time at which the consistency of the system is just sufficient to overcome the tendency of the system to flow down the walls of the tube in which the system happens to be contained.

Now the difficulty of finding a suitable criterion for the consistency of a thixotropic system is this: apparently the increase in consistency of the liquified system only effects an increase in the viscosity of the system. Viscosity, however, can only be measured by shearing the system, while this very shearing reduces the consistency of the system. So, whatever determination of the viscosity is made the measuring method itself will always interfere with the condition of the system. For this reason all measurements of thixotropic systems with the Couette type of viscometer are rendered doubtful. In a few cases only authors have tried to circumvent the difficulty hinted at; Pryce Jones[1] constructed an apparatus in which the movement over a small angle of a cylinder immersed in the system under observation is registered, while observations are made as a function of the time elapsed after stirring of the system has ceased. This method of observation is undoubtedly able to provide some information concerning the changes occurring in thixotropic systems, the difficulty being, however, to translate the results obtained in this way in terms of a $D/\tau$ relation. The movement of the cylinder namely is produced by the recoil of a torsion wire; which implies that the shearing stress continually decreases during the movement of the cylinder. Even though it is theoretically not impossible to obtain by calculation the concurring values of shearing stress and rate of shear, this method hardly seems suitable to give

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[1] Pryce Jones, J. Oil and Colour Chem. Assoc., **19**, 295 (1936).

more than qualitative results. Various authors have made investigations on similar lines, thus compromising between the determination of viscosity according to the Couette method and the requirement of the thixotropic system of not being altered by a disturbing shearing motion. We refer to the papers of: Freundlich & Rawitzer[1] and Wolarowitsch & Borinowitch[2].

## § 12 - DESCRIPTION OF EXPERIMENTAL RESULTS WITH THIXOTROPIC SYSTEMS

Since it was our aim to compare the behaviour of dilatant systems with that of thixotropic systems an investigation was started concerning the behaviour of thixotropic system in our apparatus. This apparatus namely enabled us to measure a system at any time after shaking of the system had ceased, while the breaking down of the system owing to the shearing motion of the moving sphere does not affect the results since the sphere moves continually through a fresh — i.e. an undisturbed — portion of the system. This, however, implies that the sphere should be allowed to move through the system only *one* time; after it has travelled through the system from one end of the apparatus to the other the apparatus should be emptied, the content thouroughly stirred, the apparatus refilled and allowed to stand for the same specified time as with the previous measurement, and then a second measurement could be made with a different weight on the scale.

This method could be carried out in practice by making use of glass cuvets which just fitted inside the canal-shaped container of the apparatus. Cuvets of 45 and 65 cm length at an inside cross section of 1,4×1,4 cm were constructed by cementing together long strips of object-glass with de Khotinsky cement. In this way even electrolyte-sensitive systems like $Fe_2O_3$ could be safely manipulated. Measurements were made in the following way: The thixotropic system, contained in a stopp-bottle was vigorously shaken during a standard period of 15 seconds. Immediately after shaking had been stopped the cuvet(s) was (were) filled to the brim and allowed to stand for a specified time. This time will be referred to as the "time of rest" (R). In order to avoid evaporation during times of rest the cuvets were kept in glass tubes which just fitted around the cuvets

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[1] Freundlich and Rawitzer, Kolloidchem. Beihefte. **25**, 231 (1927).

[2] Wolarowitsch and Borinowitch, Kolloid-Z. **77**, 93, (1936).

and which were closed with a cork on each end. As soon as the time of rest had passed the cuvet was placed in the apparatus, the cover adjusted, a certain weight placed on the scale and the time needed to cover a certain distance was determined. This gave us *one* point of the speed/weight curve. In order to determine other points of the speed/weight curve with the same time of rest the cuvet had to be emptied and the process was started all over again, only a larger weight now being placed on the scale. A minor modification of this method was applied at small values of the speed. At small speeds namely, a smaller portion of the system sufficed for the determination of the speed since a run of a few cm's was sufficient for the car to reach a constant speed. Thus a portion of 5—10 cm being sufficient, up to 4 determinations could be made in a cuvet of 45 cm length.

The minimum time of rest after which determinations could be made turned out to be 60 seconds, this being the minimum time required for adjusting the apparatus.

In the first place betonite and $Fe_2O_3$ will be dealt with, since they number among the best known and most characteristic representatives of thixotropic substances. A bentonite suspension 6,2 % by weight was made by adding 300 c.c. of water to 20 g of bentonite. (Bentonite A).

The substance immediately swells and after 24 hours standing at room temperature a macro-homogeneous system is obtained. The thixotropic $Fe_2O_3$ systems were made by mixing equal volumes of KCl solutions of various concentrations and $Fe_2O_3$ sol (Merck) stock solution.

The concentrations will be expressed in final concentrations of electrolyte in the system (i.e. half the concentration of added electrolyte solution). After mixing, the systems were left undisturbed for various times. Since time influences thixotropic $Fe_2O_3$ systems in the long run the date of preparing of the systems will be mentioned in each case.

## § 13 - RESULTS OF MEASUREMENTS OF BENTONITE

In figure 23 the results are shown for a 6,2 % bentonite solution after various times of rest. The numerical data are recorded in table VII.

TABLE VII

Bentonite 6,2 % (by weight).

Distance over which speed was measured: 20 cm

Diameter sphere: 0,8 cm.

| Weight: mg | Time: sec. | Speed: cm/sec. |
|---|---|---|
| Time of rest: 1 min. | | |
| 1400 | 2.90 | 6,9 |
| 1400 | 3,30 | 6,1 |
| 1600 | 1,90 | 10,5 |
| 1800 | 1,45 | 13,8 |
| 1800 | 1.45 | 13,8 |
| 2000 | 1,30 | 15,4 |
| Time of rest: 2½ min. | | |
| 1400 | 3,65 | 5,5 |
| 1400 | 3,00 | 6,6 |
| 1600 | 1,95 | 10,2 |
| 1600 | 2.15 | 9,3 |
| 1800 | 1,45 | 13,8 |
| 1800 | 1,55 | 12,9 |
| 2000 | 1,3 | 15,4 |
| 2000 | 1,30 | 15,4 |
| 2200 | 1,15 | 17,4 |
| 2300 | 1.10 | 18,2 |
| Time of rest: 10 min. | | |
| 1500 | 3,05 | 6,6 |
| 1600 | 2,60 | 7,7 |
| 1700 | 1,90 | 10,5 |
| 1800 | 1,65 | 12,1 |
| 1800 | 1,70 | 11,8 |
| 2000 | 1,40 | 14,3 |

(Table continued on next page).

The curves representing these data appear to be practically straight lines, which, upon extrapolation intersect the abscissa, i.e. a distinct Bingham yield value is present in these systems. This yield value appears to increase with increasing time of rest as may be seen from Table VIII. The data of col. III which have been obtained by abstracting 600 mg from the values of col. II have been plotted in Fig. 24.

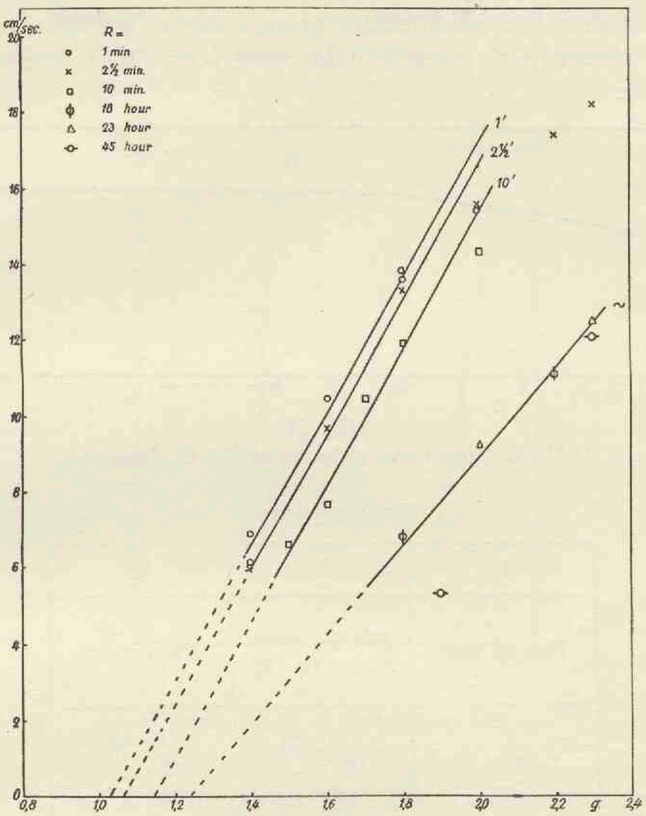

Fig. 23
Speed/weight curves of 6,2 % dispersion of bentonite as function of the "time of rest".

TABLE VII (continued)

| Time of rest: hours | Weight: mg | Time sec. | Speed: cm/sec. |
|---|---|---|---|
| 18 | 1800 | 2,95 | 6,8 |
| 18 | 2000 | 1,80 | 11,1 |
| 23 | 2000 | 2,15 | 9,3 |
| 23 | 2300 | 1,60 | 12,5 |
| 45 | 1900 | 3,80 | 5,3 |
| 45 | 2300 | 1,65 | 12,1 |

When we assume that no yield value is present during the shaking of the solution then the solidification process during the first minute after shaking is stopped will probably take place according to the dotted part of the curve.

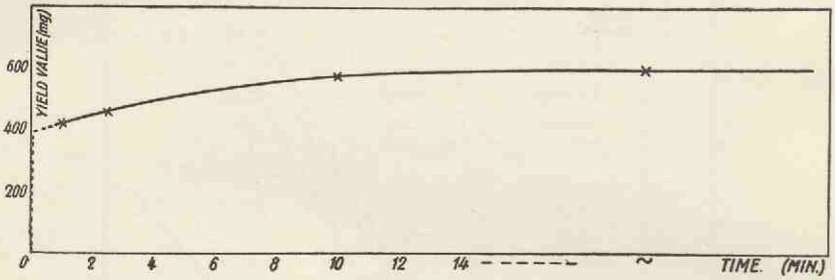

Fig. 24
Yield value/time curve of bentonite (6,2 % dispersion).

TABLE VIII

| I | II | III |
|---|---|---|
| Time of rest | extrap. values acc. to fig. 23 | Yield value |
| 1′ | 1030 mg | 430 mg |
| 2½′ | 1065 „ | 465 „ |
| 10′ | 1180 „ | 580 „ |
| ~ | 1200 „ | 600 „ |

The yield value/time curve does give us a complete picture of the solidification of the system: according to it there is a quick rise in consistency of the system *immediately* after shaking has ceased, followed by a slight increase during the first 10—15 minutes; no further increase in consistency is observed. Of course the question may arise whether it is allowable to extrapolate the speed/weight curves as has been done in Fig. 23. On page 6 this question has been dealt with and an explanation given of why it is difficult to obtain values at small rates of shear. There is, however, a way to check the physical meaning of the extrapolated Bingham yield values. If namely a weight is applied smaller than the extrapolated yield value no motion whatever of the car should be observed. This turned out to be the case indeed; even when the sphere was moved artifically it came to an immediate stop after release of this extra force.

The yield value of a bentonite suspension naturally depends of the concentration of the solid phase. Determinations were made of the final consistency of suspensions of various concentrations the results of which are shown in Fig. 25. The curves represent speed/weight relations after times of rest of 16, 28 and 17 hours respectively [1] for systems containing 5 %, 7 % and 8 % of bentonite by weight. According to these curves the yield value increases on increasing the concentration. There is no indication, however, that the mechanism of the process of solidification would be substantially influenced by an increase in concentration of the solid phase.

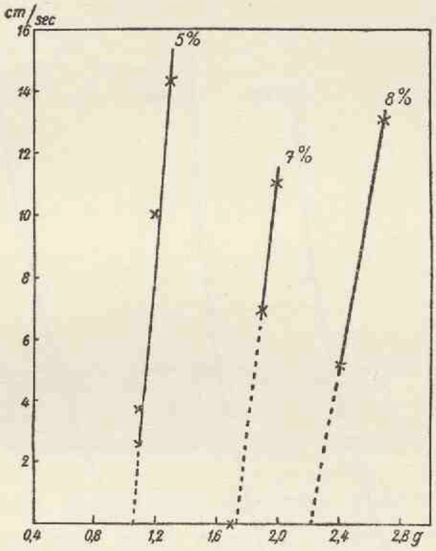

Fig. 25
Speed/weight curves of bentonite as function of concentration.

## § 14 - MEASUREMENTS OF $Fe_2O_3$ SYSTEMS

In Fig. 26 the results for an $Fe_2O_3$ solution with 150 mmol KCl are reproduced. Curves for times of rest of 4, 18, 27½ and 118 hours are shown. The first thing which strikes us is the fact that the solidification process apparently proceeds much slower than in the case of bentonite; after 4 hours the system has hardly developed any yield value and after 27½ hours the process has by no means reached its final state. The yield

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[1] this implies that the equilibrium condition has definitely been reached.

value-time curve which is shown in Fig. 27 has a shape which is definitely different from that of bentonite. (compare Fig. 24).

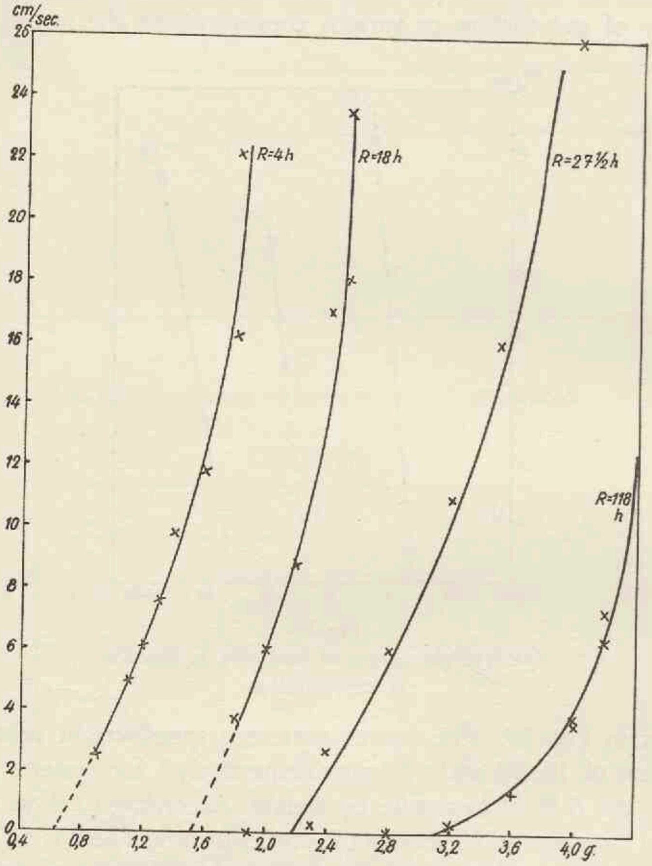

Fig. 26

Speed/weight curves of $Fe_2O_3$ "solutions" as function of the "time of rest".

## § 15 GENERAL DISCUSSION OF RHEOLOGY OF THIXOTROPIC SYSTEMS

On close inspection of Fig. 26 another problem arises: it appears namely that the shape of the curves changes with increasing time of rest; during the first period after shaking the curves are more or less straight lines while after 118 hours a very distinctly curved part has developed. According to our conception of pag. 9 this means an increase of bonds of different strength. However, a curve like the one for R = 118 h brings us in considerable difficulty as to the question which yield value should be taken as the correct criterion for the characterisation of the increase in consistency

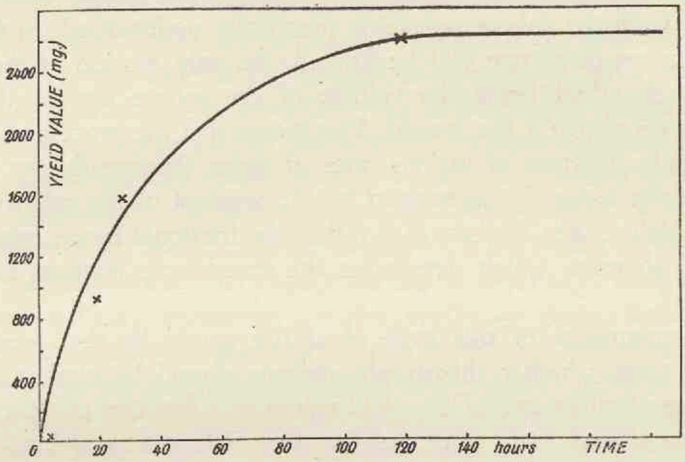

Fig. 27
Yield value/time curve of $Fe_2O_3$ "solutions".

of a thixotropic system. Should it be the lower yield value, the Bingham yield value or the maximum yield value? In order to find an answer to this question one more observation should be taken into consideration; it is this: on close inspection of cuvets with $Fe_2O_3$ systems, after the sphere has passed through them at a varying speed the following phenomenon is observed: if the sphere has travelled at low speed (± 1 cm/sec.) a broad track is left behind it. Cracks are present in the system and the whole content of the cuvet has been broken unto big lumps of system. When, however, the sphere has moved at relatively great speed (up from 15 cm/sec.) the only traces left by the sphere are just a faint line indicating where the system has been broken up by the thin metal rod to which the sphere is fixed. Neither cracks nor big lumps of system are present in the track behind the sphere.

So what apparently happens is this: when moving under the action of a small weight the sphere has to overcome the forces which keep the system together. The system will yield to the force exerted by the sphere at those places where its cohesive forces are smallest. This may be at any distance from the sphere. By this breaking-down process lumps are formed in a more or less haphazard way. When on the other hand a big weight is placed on the scale the sphere will be able to overcome even the strongest cohesive forces present in the system. Consequently the shearing will take place immediately at the surface of the sphere, the system even at short distances from the sphere remaining practically undisturbed. In the latter case no lumps of system will be formed, the only portion of the system which is disturbed being the volume of the sphere multiplied by the distance over which it has moved. This means that the process of shearing is essentially different at various rates of shear. Apparently the speed at small weights is mainly determined by the weakest of the cohesive forces while at higher rates of shear it is rather the frictional forces between the structural elements which determines the speed/force relation, i.e. a real "viscosity".

The consequence of this state of affairs would be that we can not definitely state whether thixotropic systems should be characterised by the change of either one of the yield values as a function of time but that the change of each yield value as a function of time may give us information about a different aspect of the properties of the system under observation. It is obvious that for comparing various systems the same yield value should be taken in each case.

In the following, however, we shall meet with systems which lend themselves easily for comparison since they possess only one yield value. Before dealing with that subject, however, let us return to the question we have raised at the beginning of this section, i.e. the question by what kind of a $D/\tau$ curve *thixotropic* systems are characterised in our apparatus. The first thing which is learnt from Fig. 26 is the fact that not one, but several curves all represent the same system; so if we want to express the behaviour in curves it will be the *shift of the $D/\tau$ curve as a function of time* that may give us information about the system. Leaving out of account for a moment the question which yield value should be taken as a representative point for each $D/\tau$ curve in order to be able to condense the sheaf of $D/\tau$ curves of one system to one yield value/time curve, we must notice the fact that an appreciable difference does exist between the bentonite and the $Fe_2O_3$ systems. The former show a rapid increase in consistency during the first 10—15 minutes but after that remain practically unaltered, while the latter very slowly develop their consistency, a process which has not yet reached its final state after as much as 118 hours.

Even though we do not exactly know the details of the solidification process we must accept the conclusion that this difference in behaviour between bentonite and $Fe_2O_3$ must of more than a quantitative nature only. When the rate of solidification varies in such an appreciable way as in this case it seems appropriate to distinguish between the bentonite type of thixotropy and the $Fe_2O_3$ type of thixotropy. Other investigators have come to a similar conclusion on account of experiments with thixotropic systems. Pryce Jones[1] mentions in his paper that there are certain systems which solidify rather slowly, while others exhibit a very rapid rise in consistency. The latter systems he calls "false body", this being a term taken from the painters terminology [2]. Even though at this moment it is not possible to trace out exactly the region where false body thixotropy stops and ordinary thixotropy — like $Fe_2O_3$ — starts, since no sharp limit separates the two phenomena, this distinction will turn out to be justified by strong evidence that causes of a different order of magnitude are responsible for both of the two types of thixotropy. It may be well, at this stage, to remember which definition was originally given of "thixotropy" i.e. which were the properties, for the designation of which the word "thixotropy" was originally coined. According to Freundlich, those systems are called thixotropic which are capable of an isothermal reversible sol-gel transformation. This means that, in order to obtain the epithet "thixotropic" two properties are required; first: the capacity of being liquified upon shaking, second: the capacity of spontaneously developing a certain amount of consistency in course of time. In a false body system, in which the final consistency is reached almost immediately after shaking has ceased, i.e. after the particles have come to rest from the externally imparted motion, the first required property is definitely present, the second however, is absent for there is no *gradual* increase in consistency, no gel-building mechanism like in a "real" thixotropic system such as the $Fe_2O_3$ sol. It just happens that the false body system has a certain consistency of its own, which, owing to the proportion of solid particles and liquid medium can be easily disturbed.

Now even in a bentonite system a short time up to ± 10 min. is required for reaching the final consistency; in the extreme case of a false body system it should take practically no time after shaking has ceased to reach the final condition.

It happened that we were fortunate in tracing a system which exhibits this false body thixotropy in a very striking way, while simultaneously

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[1] l.c. page 39.

[2] For a description of the behaviour of false body paints c.f. D. L. Gamble, l.c. page 73.

being of an extraordinary simple nature. Quite incidentally we became interested in the behaviour of quartz samples mixed not with water, but with organic liquids. The original idea was an attempt to eliminate the interfering tendency of the quartz-water suspensions to settle rapidly which we intended to circumvent by the application of a medium of the same density as quartz; to our surprise, however, a suspension of quartz in tetrabromoethane exhibited a behaviour entirely different from that of quartz in water. The system showed a rather paste-like behaviour and even at low concentrations of quartz the system tenaciously stuck to the walls of the testtube. Upon systematic investigation we found that the very quartz particles which used to supply us with such good dilatant systems when mixed with water, showed an entirely different behaviour when dispersed in any non-polar liquid. Let us take the system quartz-$CCl_4$ as an example to demonstrate the essential features of this peculiar behaviour. Suppose a few grams of quartz to be introduced into a testtube, $CCl_4$ to be added and the system to be well mixed by vigorous shaking; then the system will turn out to be a perfectly fluid mixture during the shaking but immediately after shaking has ceased the system sticks to the walls of the tube upon turning it upside down. The following table may give a complete picture of this test; Carbontetrachloride has been substitued by cyclohexane which behaves in the same way in this respect. The data between brackets are the number of cc's of liquid after reduction to *10* cc of quartz powder.

TABLE IX

Behaviour of quartz on addition of cyclohexane. 10 gr. quartz; average particle size 5—10 $\mu$.

| | | |
|---|---|---|
| 10 cc | (26 cc): | Paste-like system, non-fluid. |
| 14 cc | (37 cc): | Slightly thinner though not fluid. |
| 16 cc | (42 cc): | „ „ nearly fluid. |
| 20 cc | (53 cc): | relatively thin system, fluid upon shaking; immediately „solid" after shaking has ceased. |
| 22 cc | (58 cc): | Thin system, still sufficiently consistent to stick to tube upon turning upside down. |
| 24 cc | (64 cc): | Thin system, still sufficiently consistent to stick to tube upon turning upside down. |
| 26 cc | (69 cc): | Thin system; approaches limit of capacity to stick to walls of the tube upon turning upside down. |
| 30 cc | (79 cc): | At limit of consistency. |
| 32 cc | (85 cc): | Too diluted to stick to the walls of the tube; resembles collection of flocks dispersed in liquid; shows obvious syneresis upon standing within few minutes. |

This experiment has been repeated with the same quartz in several other organic liquids and completely the same result has been obtained with: carbontetrachloride, cyclohexane, benzene, ethylether, bromophorme and tetrabromoethane. With nitrobenzene only 12 cc were sufficient to give a perfectly fluid mixture with 10 g of quartz.

Rice starch behaves in the same way and quantitavely the results fall in the same order of magnitude as may be seen from the following table:

TABLE X

Behaviour of rice starch on addition of cyclohexane.
3g rice starch, average diameter of the grains 5—10 $\mu$. Numbers between brackets are quantities of liquid after reduction to 10 cc of rice starch.

4 cc (21 cc): Paste;
5 cc (26 cc): „
7 cc (37 cc): Still sufficiently consistent to stick to walls of the tube upon turning upside down.
8 cc (42 cc): Still sufficiently consistent to stick to walls of the tube upon turning upside down.
9 cc (48 cc): Approaches limit of consistency.
10 cc (53 cc): Limit of consistency just passed.

Apparently an obvious correlation exists between the dielectric constant of the liquid and the behaviour of the dispersion of quartz particles in the liquid. The higher the dielectric constant the higher we must make the concentration of quartz particles in order to reach a similar consistency of the system, i.e. the higher the diel. const. the more the system approaches the condition of dilatancy and consequently, the further it is removed from the thixotropic condition. With ethyl alcohol for instance the quartz behaves almost similarly to water.

The reason why this behaviour of quartz with organic liquids like $CCl_4$ is so striking is twofold: first because it represents such a remarkable example of the false body type of thixotropy; second because it drew our attention to the dominating influence which must be attributed to the interrelation of solid particle and dispersing liquid since the very same quartz particles behave so differently according to the nature of the liquid in which they are dispersed. The latter point will be considered in detail in § 17 while we deal with the former point below.

Since the dispersion of quartz in carbontetrachloride provides such a striking example of a false body system it seemed natural to check its rheological behaviour in our apparatus. Actually this experiment was carried out with a suspension of rice starch, since we had at our disposal a large quantity of the latter and only small portions of quartz powder. The behaviour of rice starch is entirely analogous to that of quartz when suspended in various media. In Table XI the data are recorded while curve *b* Fig. 28 represents these data.

TABLE XI

Speed/weight relation for system consisting of 100 g rice starch and 170 cc of $CCl_4$ Conc. by volume 27 %.

| Weight | Seconds for 25 cm | Speed. (cm/sec.) |
|---|---|---|
| 1,4 g | no movement | |
| 1,9 „ | „ | |
| 2,4 „ | „ | |
| 2,9 „ | 2,3 | 11 |
| 3,0 „ | 1,6 | 15 |
| 3,2 „ | 1,1 | 22 |
| 3,4 „ | 1,0 | 25. |

To make comparison easier the speed/weight relation for $CCl_4$ was also determined the result of which is shown in curve *a* Fig. 28. From curve *b* we learn two things: first that the system rice starch — $CCl_4$ is represented by one curve only. Whether a determination is made after a time of rest of 1, 10 or 60 minutes does not make any difference; the properties of the system do not alter with time; second: the curve is practically a straight line and a very obvious Bingham yield value is present, which amounts to just over 2,0 g; in accordance with this no movement of the sphere took place at a weight of 1,4, 1,9, and 2,4 g. This curve closely resembles the diagramatic one of Fig. 2, curve *d*. Obviously this system provides a striking example of the false body type of thixotropy; in systems like these the value of the yield value is determined only by the concentration of the solid phase. Increase of the concentration increases the yield value; this means that on increasing the concentration of the solid phase the $D/\tau$ curve shifts to the right; up to quite considerable concentrations the direction of the curve will remain practically unaltered. Not until higher concentrations (roughly ± 15—20 %) are reached the system will remain perfectly capable of being liquified by shaking.

Now how can we understand the reason why quartz behaves so differently in $CCl_4$ compared with its behaviour in water? The question will be approached in chapter VI; before doing so, however it is appropriate first to consider thixotropic systems from a somewhat broader point of view.

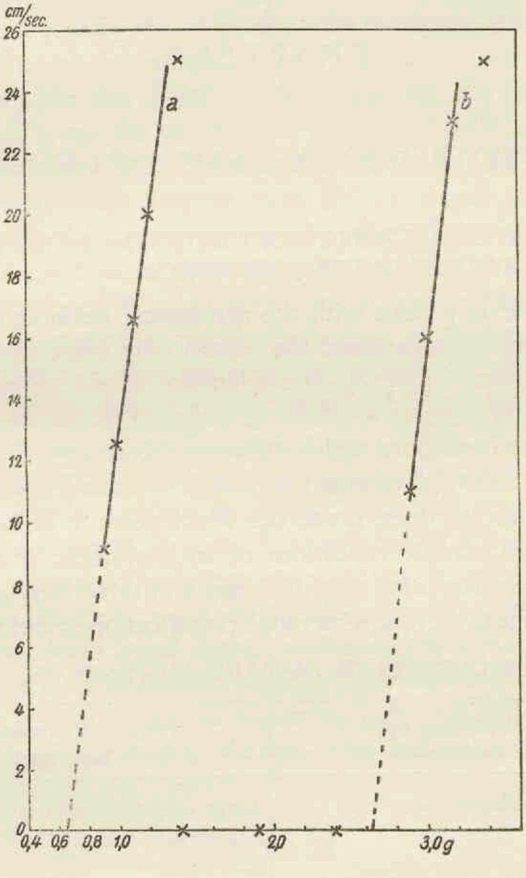

Fig. 28

Speed/weight curve of suspension of rice starch in $CCl_4$.

## CHAPTER V

# THIXOTROPIC SYSTEMS IN GENERAL

### § 16 - CORRELATION OF THIXOTROPY WITH OTHER PROPERTIES OF THE SYSTEMS UNDER OBSERVATION

Sofar we have only dealt with the *rheological* behaviour of thixotropic systems. In order to understand the reason why these systems show this particular behaviour, however, due attention should be paid to the properties of these systems as a whole, in order to get as complete a picture as possible of the conditions which influence thixotropy.

Careful observation of various thixotropic systems by numerous authors has resulted in tracing those properties which seem to be connected somehow with the thixotropic conditions of such systems. Freundlich[1] starting from the assumption that dilatancy and thixotropy are the opposite of each other came to the following rough classification of various suspensions:

PROPERTIES OF PAST-LIKE SUSPENSIONS.

| Properties depending upon close packing | Properties depending upon loose packing |
|---|---|
| Small volume of sedimentation<br>Dilatancy<br><br>no thixotropy<br>no plasticity | Large volume of sedimentation<br>Thixotropy<br>Plasticity<br>no dilatancy. |

This hypothetical correlation was checked with some 30 different minerals and generally speaking found to be satisfactory, though owing to the too qualitative criteria for each of the phenoma, the properties often appeared to overlap each other. Broadly speaking, however, this correlation holds.

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[1] H. Freundlich and A. D. Jones. J. Phys. Chem. **40**, 1217 (1936).

The idea of linking the properties of a system with the condition of packing of the particles is frequently met with in the literature concerning the behaviour of plastic substances.

Several authors propagate the opinion that the relation between solid matter and liquid vehicle should be the only dominant influence governing the total properties of any system.

However valuable this point of view may be, the conclusion seems inevitable that it is not the quantitative relation of solid and liquid matter only which determines the properties of a suspension, but that there must be another factor which may in even greater degree contribute to the final behaviour of the system as a whole. We will not go into a detailed consideration of the theories concerning the condition of packing but rather deal with those phenomelogical observations which may supply us with facts that are characteristic for the behaviour of suspensions in general. From the table on the preceding page we see that the volume of sedimentation is among these physical criteria that lend themselves for quantitative observation.

The volume of sedimentation as well as the speed sedimentation are both magnitudes which in many cases are easily accessible to quantitative measurement. It seemed appropriate to observe in this respect the behaviour of quartz in water and compare it with the behaviour of quartz in $CCl_4$ to find out if an equally dissimilar influence might be established as we have found in the rheological behaviour of these systems. To that purpose 40 g of quartz, 1—5 $\mu$, were dispersed in 25 cc of water resp. $CCl_4$, in ground-stoppered measuring cylinders and allowed to settle after having been vigorously shaken. The results are summarised in table XII.

TABLE XII

| I | II | III | IV | V | VI |
|---|---|---|---|---|---|
| Dispersion liquid | aspect of system | height of sediment | time required to reach this final cond. | Habitus of sediment | Concentration of solid phase in sediment |
| water | bright white | 8,5 mm | ± 6 hours | hard, compact | 54 % (by volume) |
| $CCl_4$ | bright white | 53 mm | ± 15 min. | lose, fluffy | 7 % (by volume) |

If a system is made up representing the conditions of the sediment of column VI what are its properties? A 54 % suspension of quartz in water is a hard dry clod, refusing even to be stirred with a spatula, owing to its consistency. When contained in a testtube the mass will naturally not flow down, but stick to the top when turned upside down. Upon dilution with water dilatancy appears at 45—40 % of solid, and at concentrations below 40 % the systems behaves perfectly fluid.

In addition there is one more feature of the quartz sediment which is very characteristic: when the cylinder which contains the settled quartz powder on the bottom of it is laid down horizontally the sediment will "flow" as if it were a heavy liquid, and slowly spread itself out in a horizontal layer in the lower portion of the cylinder; obviously any such tendency would be prohibited if the sediment exhibited a yield value, however small. Apparently this fact is in perfect agreement with the rheological features of the quartz suspensions. For similar observations as those just mentioned c.f. von Buzagh[1].

When $CCl_4$ is added to quartz, quite a different behaviour is observed. A mixture containing 7 % by volume of quartz particles 1—4 $\mu$ in $CCl_4$ will be just macro-homogeneous, i.e. the quartz will be homogeneously dispersed in the liquid phase. The system consists of flocks of particles loosely touching each other and enmeshing a large quantity of liquid in its interstices. The whole system, being so "porously" built up will easily flow when softly shaken. When the tube containing the system is laid down horizontally the mass will, however, hardly move; it remains in its original condition but does not acquire a horizontal level however long it is left in this position. The properties of this system do not essentially alter upon either increase or decrease of the concentration of the solid phase; in the former case the system gradually becomes more consistent, in the latter case it shows an increasing layer of clear liquid on top of the quickly settling flocks of solid particles.

The conclusion these experiments lead to is this that while the quartz particles may be dispersed in water at liberty they do not exhibit the slightest tendency to being capable of dispersion in an apolar vehicle; this behaviour causes immediate formation of flocks in any such liquid, which will settle quickly while giving rise to a large total volume of sediment plus liquid enmeshed in it.

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[1] Von Buzagh, Kolloidchem. Beihefte, **32**, 127, (1930).

## CHAPTER VI

# DISCUSSION OF THE REPORTED FACTS AND CHECKING OF THE CONCLUSIONS ARRIVED AT

### § 17 - GENERAL CONCLUSIONS CONCERNING PROPERTIES AND BEHAVIOUR OF SUSPENSIONS

In the preceding pages we have been dealing with the results of the observations on dilatant and thixotropic systems, in connection with flow as well as their behaviour in general. In the following lines we will try to deduce from these observations a picture which may make clear how to understand these phenomena. Already we have pointed out that the behaviour of the systems under discussion must be looked upon from the point of view of the relation between particles and the surrounding liquid medium. This relation may give rise to the particle behaving as a "stable" individual unit with no attraction for its fellow particles or an "instable" individual with the tendency to aggregate with neighbouring particles as soon as possible. From this point of view we are able to understand the rheological properties as well as the behaviour in general of these systems.

Since we are going to make frequent use of the words "stable" and "stability" in the following pages, it may be well to emphasise that what we are referring to is a "stability of *the particles*", definitely to be distinguished from the stability of the *system as a whole.* In colloid-chemical terminology the word "stable" originally used to be applied to indicate the capacity af a *system* to maintan macro-homogeneity for a prolongued period (of the order of a number of days or weeks at least). When we think of a hydrophobic sol, for instance, the condition of "stability" of the system owes its existence to a certain condition at the phase-boundary particle-dispersion medium; only when the resultant of the mutually attracting and repelling forces suffices to prevent the particles from aggregating, then the system as a whole will remain macro-homogeneous. Suppose, however, that it were possible to make a system in which, while everything remained the same as in the sol mentioned above, the particles grew larger and larger then a moment would arise at which the energy content of the particles, due to the Brownian motion might no longer be able to compensate their tendency of settling due to the force of gravity, even though the condition at the phase-boundary particle-dispersion liquid were still the same as before. In that case we would have in front of us a system which, though as a whole it did no longer deserve the qualification "stable", were still composed of "stable particles".

In the following pages we shall see that this case is actually present in certain quartz suspensions and for that reason we shall use the qualifications "stable" and "stability" irrespective of the fact whether the system as a whole happens to be macro-homogeneous or not[1].

According to the introductory lines of this section we were about to deal with the rheological behaviour of suspensions from the point of view of the degree of stability of the particles in their surrounding dispersion medium.

This issue comes down to the question: what are the consequences of the dispersion of solid particles in a liquid as far as the rheological properties of the vehicle are concerned? According to the experimental evidence reported in the previous sections we will distinguish between the two cases just mentioned, of: *a* - the particles possess a certain stability in the liquid under discussion, *b* - the particles are not stable under these conditions.

In case *a* the introduction of particles will hardly influence the movement of the liquid until the concentration of solid particles has become so great that they mutually touch each other and thus hamper the flow of the molecules of the liquid.

The particles will behave as a kind of mammoth-molecule amidst the rheological units of the liquid, but for the rest they will not dominatingly interfere with the movements of those. Consequently we shall find no great influence on the viscosity up to quite a considerable concentration. Neither will the influence show much difference at various rates of shear; when, however, the rate of shear becomes so large that the big particles are going to collide then an other factor enters into the system. At this moment, namely, the movement of the original constituents of the liquid

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[1] For a concise treatment of the dynamics of hydrophobic suspensions and emulsions c.f. "Hydrophobic Colloids", being the report of a Symposium on this subject held at Utrecht, Nov. 1937. Published by D. B. Centen's Uitg. Mij. Amsterdam.

vehicle may be hampered, in consequence of which the whole system locally acquires a certain degree of consistency. Apparently this is what happens in dilatant systems.

A priori it is not quite impossible that at much higher stresses the congested particles should be forced to be redispersed. In our experiments, however, we have not reached this condition.

Let us see how far the conditions will be altered when we rob the particles, which are to be dispersed, of their stability, i.e. case *b*.

Since the particles tend to aggregate, even in small concentrations they will form an impediment to the movement of the molecules of the liquid. Since, upon increase of the rate of shear the influence to redisperse the particles will equally rise, a relative decrease of the original increase in viscosity of the system as a whole may be anticipated in this case. This line of argument will a fortiori hold when the concentration of the solid phase is increased; so in this case there will be a *considerable influence* of the solid phase on the rheology of the liquid, and this influence will decrease with increasing rate of shear.

Now this is exactly what is observed in the flow of systems of the quartz-$CCl_4$ type and in those systems in general which are called "plastic". This trend of thought equally explains the properties of these systems in general. We have found the quartz particles when dispersed in water to settle slowly and to yield a sediment which "flows" upon the application of however small a shearing stress. Apparently the quartz particles remain individual beings even in the sediment where they may touch each other but, even so, do not cohere. The same quartz particles, dispersed in an apolar medium, however, lack the "stabilised individuality". They constantly tend to join each other and strongly cohere as soon as they have been able to satisfy this tendency.

By the application of small shearing stresses they do not come off, which is endorsed by the appearance of a yield value; when, however, the stress is sufficient to counterbalance the aggregating tendency then the flow of the system will equal that of the original medium in proportion to the annihilation of the aggregation of the particles.

Reasoning along this line, we may be able to understand why quartz gives a small, compact sediment in water and a loose fluffy mass in an apolar medium. In water the settling quartz particles fall down smoothly and, owing to their stability they will be able to arrange themselves in the condition of lowest energy, i.e. take up a position which is as near to that of close packing as possible. In $CCl_4$, however, the particles, devoid of any stabilizing influence, will immediately aggregate at random, fall down haphazardly and remain in that irregular disarrangement since they lack sufficient freedom of movement to approach the close packing condition. Microscopic observation supplies us with more evidence that the stability of the particles forms the conclusive property of their behaviour; the quartz particles, when dispersed in water show a lively Brownian motion; upon dispersion in an apolar liquid, however, not a trace of movement can be discovered since the particles can not be really incorporated in the liquid. The experiment is most striking when the particles are watched on a slide when dry, and after addition of a drop of liquid. With water the system gets into a state of general activity, while addition of $CCl_4$ does not alter the condition of the particles in any respect. The outcome of this trend of thought being the paradoxal conclusion that it is the stable particles which are capable of being wel dispersed but always retain their tendency to obey the force of gravity and sink to the bottom of the vessel in course of time, yielding a consistent sediment. Unstable particles on the other hand resist homogeneous dispersion since they constantly tend to join at random; therefore they "fill" a great volume of the liquid, though in a haphazard way, thus greatly affecting the consistency of the system as a whole.

Realising these correlations between the stability of a particle and its influence on the properties of the dispersing liquid, we are immediately inclined to apply this point of view to such systems as paints in which similar influences must be of paramount importance. Such systems are of much interest in connection with the systems under discussion in these pages because the classic paint industry constantly deals with dispersions of pigments in a liquid phase, while repeatedly it is noticed that a certain pigment may be very well suited to be dispersed but will settle in the container in course of time, while another pigment may require much more trouble for obtaining a homogeneous mixture but will have far more influence upon the rheological properties of the dispersing liquid. In § 19 we shall deal shortly with such systems.

It may be well to lay some emphasis on the property of the unstable particles to arrest a relatively large portion of dispersion-liquid in the spacious interstices that must necessarily follow the haphazard aggregation of the original particles.

There is one more feature which supports the argument pursued in the preceding pages, namely the fact that the quickly aggregating systems always exhibit the tendency to show syneresis. Apparently the particles, though mutually cohering, are still aiming at reaching the final state of minimum energy, supported by the impulses of the liquid-molecules. Syneresis is a feature which is encountered in practically all thixotropic and plastic systems.

So far the characteristic features of thixotropic systems, i.e. the $Fe_2O_3$ type of thixotropy, have been outside our attempts to understand the phenomena involved. Starting from the assumption that thixotropic systems belong to those which are composed of dispersions of unstable or partly destabilised particles, we are faced with the question why the consistency of these systems depends upon the amount of time elapsed after the dispersing influence has ceased to act.

A priori two possibilities seem to come into consideration. First: we might think of a partly destabilisation of the particles which has left them with sufficient repulsive forces to resist *immediate* aggregation but which will let them fall as victims to such tendencies in course of time. Second, we may think of a process in which there is a different influence exerted by the smaller particles compared with larger ones. It must not be forgotten that the false body type of systems mainly occur amongst the coarser suspensions of particles of say $1—10\mu$, while the "real" thixotropic systems mainly consist of particles of much smaller size, of the order of magnitude of $0{,}1\,\mu$. Since the degree of stability will undoubtedly be a strong function of the size of the particles this more or less comes to the same thing as the preceding suggestion. It seems quite possible that the initial quick rise in consistency of thixotropic systems — as expressed by the left hand part of the curve of Fig. 27 is due to the aggregation of the biggest among the particles, while the subsequent slow increase of the right hand part owes its existence to the smallest of the particles, gradually settling themselves in the interstices of the big ones. Since a difference in stability needs not necessarily be accompanied by a difference in size, we may say in general that it is the *divergence of degree of stability of the particles* that induces a system to acquire thixotropic properties, assuming that the relation solid phase/liquid phase is within the limits for allowing the system to reach sufficient consistency to exhibit thixotropic behaviour. From this point of view it becomes understandable why the false body systems behave in such a one-sided way, showing the transition "solid-fluid" and vice versa, but not showing the gradual rise in consistency of the $Fe_2O_3$ type of system; apparently they are composed of particles so utterly devoid of the least trace of stability that they must reach their equilibrium position immediately after shaking of the system has ceased.

Before proceeding to trace out in how far the various phenomena occurring in practise can be adequately explained from this point of view one point should be taken into consideration: namely the influence of the viscosity of the dispersing medium itself. Evidently there must be a difference between a medium of high viscosity in comparison with a low one. As shown above, however, the viscosity of the medium should never be considered without taking into account the specific influences of the medium on the stability of the particle. It is not so easy experimentally to investigate the influence of a change of viscosity without altering the system in such a way that the stability of the particle may be simultaneously affected. Since the viscosity of a liquid is the outward indication of its interior architecture — unfortunately a perfect understanding of this problem in itself is hardly available at present — differences of this property must per se influence the stability i.e. the relation between the particle and the surrounding liquid. So it may seem almost too simplistic to discuss the influence of an increase in viscosity as if it were a property that can be independently changed at will.

However, let us try to find out what influence might be expected from an increase in the viscosity, leaving everything else the same. Upon dispersion of stable particles in liquids of increasing viscosity the difference in mobility between the particles and the rheological units of the liquid will become smaller consequently the influence of the particles will tend to decrease upon increase in viscosity of the vehicle. In one respect there will be a difference: as the particles experience a higher resistance the settling tendency of the particles may be considerably reduced. So the result of the dispersion will tend to become of a more lasting effect in the case of a medium of high as compared with one of low viscosity. If there is a difference in density between the particles and the liquid the density of the total system will undergo the influence of the incorporation of the solid particles.

The question may arise if in a medium of high viscosity dilatancy can still occur. A priori there is no obvious reason why, at a sufficiently high concentration, the particles should not be forced together by mechanical movement and thus give rise to the local increase in consistency characteristic for dilatancy. However, the "reflow" of the system will be slower owing to the higher viscosity and therefore the behaviour of such a system will offer a less spectacular alternation of "solid" and "liquid" behaviour as compared with a dispersion in a vehicle of higher mobility. The suggestion has been launched [1] that an example of such a type of system might be found in the silica systems described by Bingham [2] which show properties very much resembling those of dilatant systems. In § 19 these systems will be dealt with shortly.

When unstable particles are dispersed in liquids of increasing viscosity a more or less similar effect will result as we have anticipated in the case of stable particles. Since the unstable particles affect the initial mobility of the liquid vehicle they will enhance the consistency of the system as a whole, and this effect may be relatively smaller in the case of a high as compared with a low viscosity of the medium. A higher viscosity of the medium will hamper the particles in their aggregation-tendency; so the behaviour of the system will be different in so far that, after it has been disturbed, it may take some time to reestablish the condition of aggregation of the particles which existed before the shear took place.

Consequently, an increase of the viscosity apparently tends to induce a "thixotropic" factor into a system which only exhibited the false-body variety of thixotropic behaviour at a low viscosity of the dispersion medium. Generally speaking, it seems that the influence of suspended particles which tend to form an additional contribution to the consistency of the dispersing liquid will be relatively smaller at higher viscosity of this medium (in comparison with a low viscosity), while the difference in behaviour between stable and unstable particles tends to be smoothed out at increasing viscosity.

## § 18 - MEASUREMENTS OF THE RHEOLOGICAL BEHAVIOUR OF QUARTZ IN ORGANIC LIQUIDS AND SALT SOLUTIONS

In the preceding section we have been dealing with the general aspect of our experiments and the conclusions they have lead to. Since these conclusions come down to the conviction that the degree of stability of the particles is at the root of their rheological behaviour as well as of their properties in general, it seems logical to check these conclusions by arti-

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[1] H. Freundlich and H. L. Röder, Trans. Faraday Soc. **34**, 308, (1938).

[2] E. C. Bingham & J. W. Robertson, Kolloid-Z. **47**, 1 (1929).

ficially inducing destabilisation or promoting stability and find out if this results in a corresponding change of the rheological properties of the systems under observation. Starting from this base, a decrease of the stability of the particles of a dilatant system should result in an alteration of the rheological properties in the direction of the false body type of systems. In order to realise any such investigations two ways are open from the experimental point of view. We can either investigate the rheological properties of a quartz suspension in salt solutions of various concentrations, or investigate suspensions of quartz in media of varying dielectric constant since we have found the stability to be a function of the d.c. of the dispersing liquid. We have made both these types of suspensions, choosing for the former KCl solutions and for the latter mixture of ethyl alcohol (d.c. 26) and benzene (d.c. 2,3).

Since electrolytes are known to have a destabilizing effect on hydrophobic sols a similar action may be anticipated in the case of quartz suspensions. A qualitative experiment quickly convinced us that this anticipated effect does exist. Upon addition of a solution of KCl or $BaCl_2$ the characteristic dilatant behaviour of the quartz particles entirely disappears. A plastic paste is what results.

TABLE XIII

Observation of the behaviour of:

| quartz | | | Rice starch |
|---|---|---|---|
| on addition of | | | |
| mmol. | KCl | NaOH | KCl |
| 0 | definitely dilatant | definitely dilatant | definitely dilatant |
| 25 | well ″ | ″ ″ | ″ ″ |
| 50 | ″ ″ | — — | — — |
| 100 | plastic mass; no reflow | ″ ″ | ″ ″ |
| 400 | very plastic mass | | ″ ″ |

Table XIII provides a record of these observations. From it we see that NaOH up till a concentration of 100 mmol. is of no influence on the behaviour of quartz, while rice starch remains unaffected by the addition of KCl solution.

In order to control these results it was decided to make an examination of the quartz-KCl system in the apparatus.

Let us see what kind of effect destabilisation of the quartz particles ought to have. In the first place, according to § 17 the concentration at which the solid particles influence the mobility of the liquid phase should be lower than in the case of electrolyte-free suspensions. In the second place, since we have been induced to consider the presence of a yield value a true criterion for the degree of destabilisation of the particles a yield value may be expected to be developed by the system.

Fig. 29 represents the curves for two concentrations of quartz in a 100 mmol KCl solution. From these curves it may be seen that the mobility of the system is far less at the same concentration of solid in the case of KCl solution as compared with water. C.f. Fig. 20.

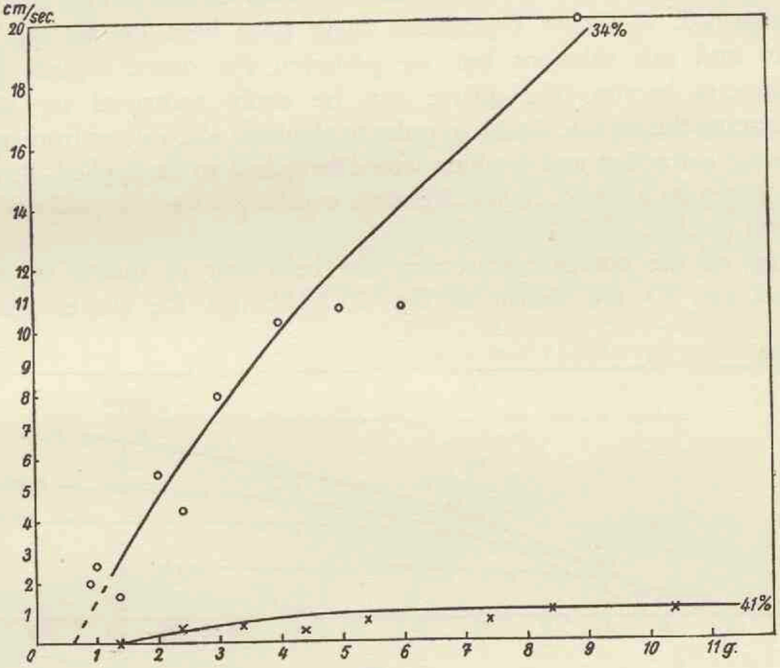

Fig. 29

Speed/weight curves of quartz in 100 mmol KCl.

There is no pronounced indication of the presence of a yield value in Fig. 29. In addition no vibrating motion of the sphere could be observed in the quartz-KCl system. From these graphs we see that the typical "dilatant" shape of the curves has been considerably reduced and has degenerated into a weakly concave curvature towards the weight-axis. Apparently this experiment is just the opposite of the treatment to which we subjected the quartz before starting the dilatancy experiments, when we removed any impurities and adsorbed salts which might have been present in the commercial quartz.

The experiments with suspensions of quartz in alcohol-benzene mixtures were carried out with the intention of demonstrating the possibility of gradually changing a false body thixotropic system into a dilatant one, and of finding out by what changes of the $D/\tau$ diagram this process might be accompanied. A similar experiment might have been carried out with quartz and salt solutions but we preferred the quartz-organic liquid suspensions because the quartz can be easily recovered by simply evaporating the organic liquid. In order to eliminate electrolytes from quartz elaborate extraction and washing would have had to be applied. Benzene was chosen as a liquid of low dielectric constant since it is easily soluble in ethyl alcohol.

Some of the curves representing the behaviour of quartz in ethyl-alcohol (96 %) are shown in Fig. 30. Although the curves are not as spectacularly representative for a dilatant system as the curves for quartz-water they show the same characteristic curvature towards the abscissa. In addition it must be noticed that the concentration of solid matter at which these curves have been determined is lower than those of the quartz suspensions in water.

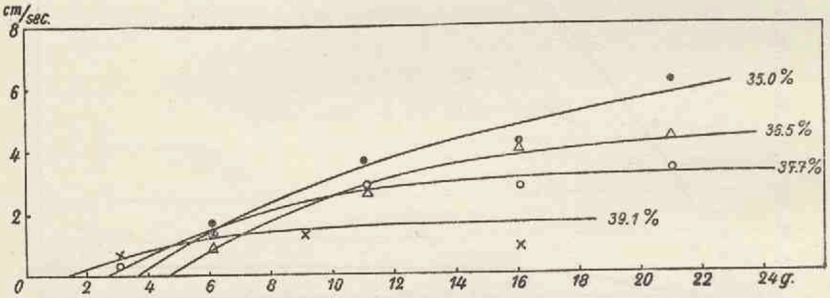

Fig. 30
Speed/weight curves of quartz in ethylalcohol.

In Fig. 31 another example of a dispersion of quartz in ethylalcohol is represented; the same system has been measured with two different spheres (diam. 4 and 8 mm). From this graph it is obvious that a small yield value is present in the systems.

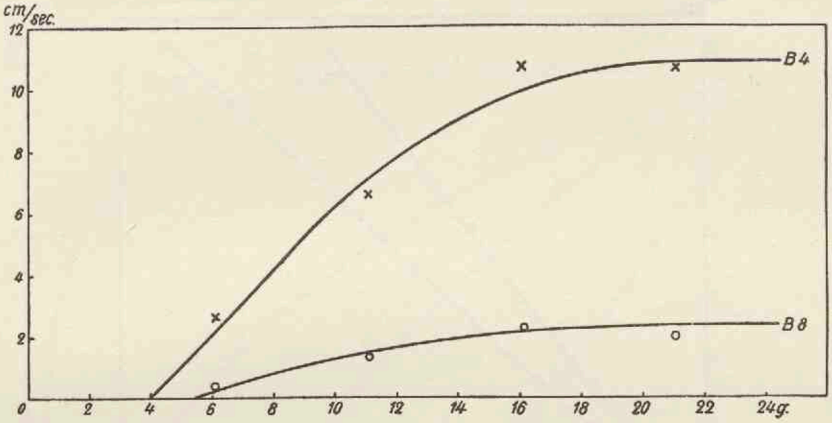

Fig. 31

Speed/weight curves of quartz in ethylalcohol.

Fig. 32 and 33 give curves representing two concentrations of quartz

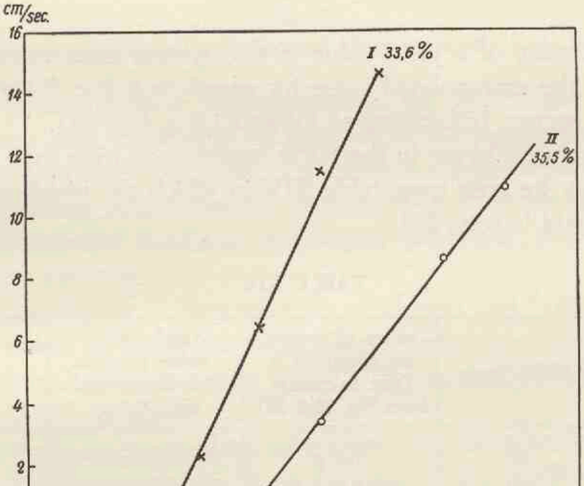

Fig. 32

Speed/weight curves of quartz in 50 % benzene-ethylalcohol.

dispersed in two different mixtures of ethylalcohol and benzene. (a 50 % benzene and a 20 % benzene solution). Curve I of Fig. 32 very clearly shows the presence of a yield value in this system since at forces smaller than those of the extrapolated value for speed = 0 (i.e. 2,1 g) no motion of the sphere occurs. (c.f. points at 1,4 and 1,9 g, Fig. 32).

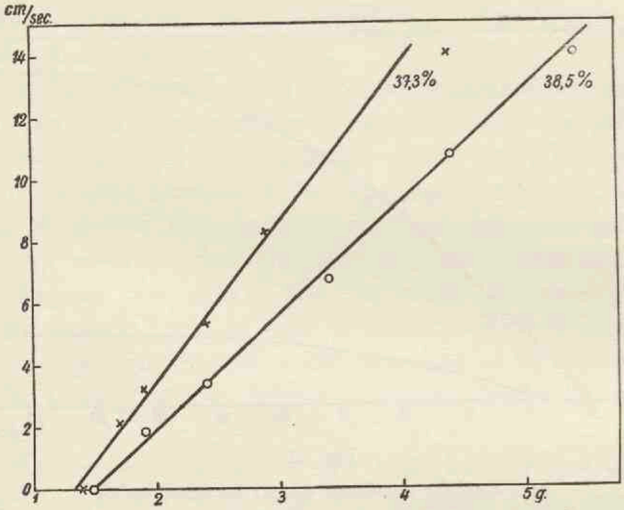

Fig. 33

Speed/weight curves of quartz in 20 % benzene 80 % ethylalcohol.

The yield value is larger in the 50 % benzene solution than in the 20 % solution as may be seen from table XIV in which the yield value pro vol. percent of quartz is recorded.

TABLE XIV

| vol. % of quartz | % benzene | value of weight at speed = 0 (acc. to extrap. from Fig. 32 & 33) | Yield value; (value of prec. col. diminished with 0,6 g) | Yield value pro % of quartz (g) |
|---|---|---|---|---|
| 37,3 | 20 | 1,3 g | 0,7 g | 0,018 |
| 38,5 | 20 | 1,4 „ | 0,8 „ | 0,021 |
| 33,6 | 50 | 2,1 „ | 1,5 „ | 0,045 |
| 35,5 | 50 | 2,7 „ | 2,1 „ | 0,060 |

In addition the value of the yield value as a function of the concentration of the solid phase seems to increase faster in the 50 % solution than in the 20 % solution.

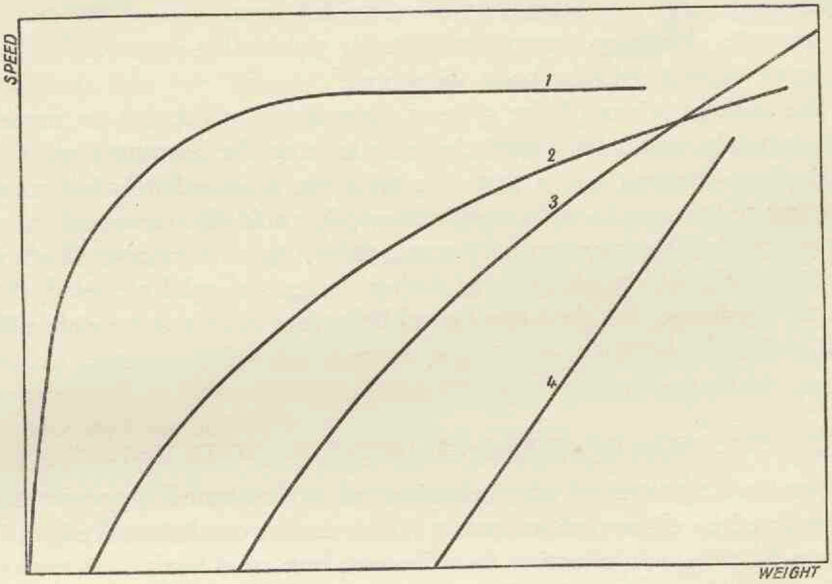

Fig. 34

Schematic curves, illustrating the shift of dilatancy to false-body thixotropy.

Generally speaking these curves confirm the anticipated effect of an increase of the yield value after an increase of the percentage of benzene.

Having adopted the yield value as a criterion for the absence of stability of the particles this means that the dispersion of a certain substance may exhibit dilatant and/or falsebody-thixotropic behaviour, depending on the stability of the particles.

Numerous curves for various mixtures of alcohol and benzene have been determined which all show the same shape while the consistency of the systems increases with increasing content of benzene with the same proportion of solid/liquid phase.

The result may be summed up as follows: 1 - decrease of the stability of the particles always results in an increase of the yield value. 2 - Increase of stability allows the solid phase to be dispersed at a still higher concentration.

Starting from a dilatant system the curves representing the various systems that may result subsequent to a decrease of the stability, are schematically shown in Fig. 34. The curves represent the following systems:

Curve 1: marked dilatancy.
Curve 2: slighter dilatancy; yield value develops.
Curve 3: dilatancy almost disappeared; yield value increases.
Curve 4: marked false-body thixotropy.

The concentrations of the systems decrease from curve 1 to curve 4.

It certainly would have been desirable to keep the concentration of the solid phase constant but in that case the systems immediately fall outside that range of speed-weight relations which could be measured in our apparatus. A dilatant system for instance at least requires circa 42 % of solid matter, while thixotropic systems with a content of solid phase of 42 % are so consistent that their rheological behaviour is of a completely different order of magnitude.

## § 19 - EXTENSION OF LINE OF ARGUMENT TO OTHER SYSTEMS

Our investigations of the behaviour of concentrated suspensions as represented by dispersions of quartz under various conditions drew, in the course of time, our attention to other members of this class of systems. Amongst them came paints. Ever since thixotropy has been "discovered" the ordinary paints, consisting of dispersions of pigments in a viscous vehicle on linseed oil basis, have been recognised as important representatives of the thixotropic systems. In increasing degree thixotropy has been seen to be the essential principle which gives these systems the peculiar qualities which make them suitable in those cases, in which the formation of a film of narrowly defined physical requirements is aimed at.

*Systematic* investigations of the thixotropic properties of paints, however, are so far fairly rare; one of the reasons obviously being that paints are not particularly convenient systems to deal with in testtubes, nor do they show the phenomenon in as striking a way as iron hydroxyde sols, bentonite etc. Thixotropy mainly manifests itself in paints by an increase of viscosity after the system has been stirred and left to stand.

A systematic investigation has been carried out by Pryce Jones[1] by means of his apparatus specially constructed for the purpose. His measuring technique, which registers the recoil of a cylinder, which has been given a certain deflection, as a function of the time elapsed after stirring of the system, reveals the increase of consistency in an obvious

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[1] l.c. page 39.

way, though a rather complicated mathematical treatment would be required to deduce from his measurements a $D/\tau$ relation.

From his measurements he draws the conclusion that there are systems which show a quick increase in consistency upon standing, while others need more time for "setting". So far our observations run closely parallel with the results of his experiments.

While the number of investigations of paint systems on a basis of examination of $D/\tau$ relations is very limited indeed, the amount of experimental facts offered by the paint industry is almost equally difficult to handle owing to its huge dimensions. The difficulty is enhanced by the wild variety of terminology in this field of industry, while the lack of adequate standards of reference for all those properties which are of decisive importance for the systems in their practical application, hardly contribute to a better understanding of those phenomena which are at the basis of these materials.

When we try from this abundance of observations to deduce a picture, capable of explaining at least some of the major phenomena involved, we find that the argument developed in the preceding pages serves us well.

In its most simple form a paint consists of an anorganic pigment dispersed in a vehicle composed of standoil & linseed oil. The standoil forms an essential part of the vehicle since, by leaving it out, a good dispersion will never be obtained. Of course, in actual practice numerous substances are added to the systems to give them all the required properties of a satisfactory paint, but we will ignore these for a moment and focus our attention on the fundamental components, pigment, standoil and linseed oil.

Without the standoil the particles may be dispersed in the linseed oil, with which they form a consistent mass showing a strong tendency to develop a yield value. However, this system will not be anything like a good paint; in order to provide the system with qualities that make it applicable as a coating, standoil has to be added. The standoil exerts on the system what is known as a "dispersing" action; in addition it influences the rheological properties of the system. Obviously the standoil supplies the pigment particles with a stability sufficient to allow the particles to remain in dispersion individually. Consequent on this "stabilisation" of the system its consistency drops, i.e. the viscosity upon stirring decreases. In course of time, however, it may rise again. This increase in stability of the particles, on the other hand, is responsible for the decrease in viscosity which is effected by the addition of standoil.

A simple experiment, reported by Green[1] strikingly illustrates this course of action. When linseed oil is added to lithopone, a consistent mass is obtained, which does not flow after stirring; on addition of a trace of poppy oil, however, the mass becomes quite "fluid" and completely loses its consistency. Now there is nothing special in the choise of the pigment in this experiment since it may be carried out just as well with quartz powder; the poppy oil may be substituted by standoil and in this form the experiment is still as convincing as before. The addition of the highly boiled oil in a minute trace in sufficient to "individualisme" the particles.

Essentially the same phenomenon is described by R. V. Williamson[2] in a paper in which numerous phenomena occurring in various suspensions are mentioned[3]; he described the behaviour of ZnO dispersed in gasoline, which at first exhibits false body behaviour, but becomes perfectly fluid after addition of a few drops of "blown linseed oil". "The dispersion", the author adds "then remains perfectly fluid after shaking but the pigment settles rather rapidly to the bottom of the container", wich, however, is exactly what we should expect in a case like this.

We found that poppy oil influences a suspension of quartz in $CCl_4$ in the same way; two drops of it to a consistent system of 5 g quartz, of particle size $\frac{3}{4}-1\frac{1}{2}\ \mu$, in 18 cc $CCl_4$ turned the system into a perfectly fluid suspension. Apparently the standoil or poppy oil is able to equip the particle with a factor which stabilises them towards the apolair carbon hydroxide dispersion-liquid. Here again we see that an increase of the stability is accompanied by a decrease of the yield value of the system.

The current opinion concerning the rheology of paints has been that the "thixotropic" qualities determine the brushing properties of the system. The decrease of the yield value upon stirring — i.c. brushing — is supposed to allow the system to flow over the substratum, while the yield value, developing as soon as the brushing has ceased is supposed to prevent the "sagging" of the paint film. However, it will be obvious that the yield value must not *immediately* develop, because in that case the brush marks will have no time to disappear; this means that those systems which have been indicated as "false body" are not suitable for an ideal paint. Neither does a system of the $Fe_2O_3$-type represent anything like an ideal paint since the yield value develops too slowly. Apparently a very special yield

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[1] H. Green, Ind. Eng. Chem. **15**, 122 (1923).

[2] R. V. Williamson, J. Phys. Chem., **35**, 354, (1931).

[3] This paper also contains interesting hints at the occurrence of dilatancy.

value/time curve is what is essential for the brushing qualities of a paint. A systematic investigation of these systems by means of an apparatus like the one we constructed might be able to provide data to check this assumption. In this connection c.f. paper by Gamble[1].

Two more classes of systems which must be described in relation to dilatancy are the silica systems described by Bingham[2] and in the second place those systems known as "quick sand".

The former has been refered to on page 63 where the suggestion of Freundlich was reported, according to which these systems should be representatives of dilatancy in a special way. According to Bingham it is possible to prepare systems, consisting of a potassium silicate solution plus silicic acid, which behave as a solid piece under quick mechanical impact, on the other hand continue to flow under however small a pressure.

We found that these systems can be easily reproduced by addition of hydrochloric acid to a potassium silicate solution and heating the system to evaporate a surplus of water. The systems are peculiarly brittle. Upon manipulating them with a spatula small pieces will scatter in al directions. Any small fragment will, however, immediately start to "flow" i.e. round off its angles and tend to become a sphere. Obviously a yield value is not present in these systems. Their resistance to a quick impact, however, is quite remarkable. They share their behaviour with pitch and suchlike bituminous substances. The determinations we made with one of these systems in our apparatus are represented by Fig. 35 which shows the data of Table XV.

TABLE XV

| Weight g | Speed cm/min. |
|---|---|
| 11,0 | 0,014 |
| 21,0 | 0,016 |
| 41,0 | 0,031 |
| 61,0 | 0,048 |
| 81,0 | 0,069 |
| 101,0 | 0,096 |

The perfectly straight course of the curve in this region suggests perfect "Newtonian flow", however paradoxical this may seem at first sight. From this experiment we must draw the conclusion that, although dilatancy *may* occur in systems of more sol than suspension-like character, it is obvious that the size of the constituting particles will have a dominating influence upon the intensity of the phenomenon, in such a way that it is doubtful whether an analogous mechanism is the basis of both forms of appearance. At first sight this hardly seems probable. It rather seems as if a high

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[1] D. L. Gamble, Ind. Eng. Chem. **28**, 1204 (1936).

[2] E. C. Bingham & J. W. Robertson. Kolloid-Z., **47**, 1 (1929).

viscosity per se leads to the behaviour which is exhibited by such systems as bitumen, pitch etc.

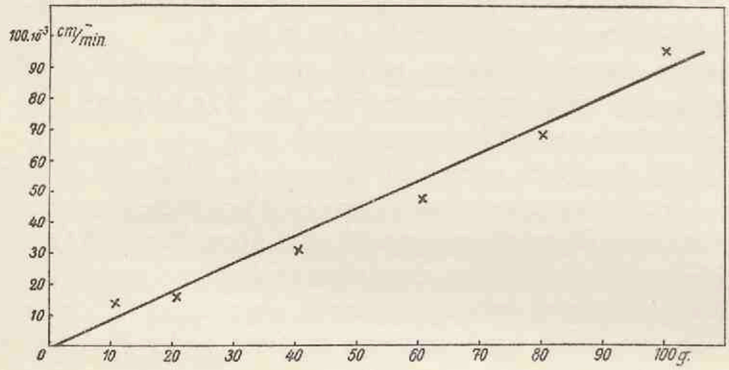

Fig. 35

Speed/weight curve of silica system.

In the second place there are the systems called "quick sand", which, actually were the first to direct attention to dilatancy. In a paper by Freundlich and Juliusburger[1] the authors come to the conclusion that quick sand belongs to the thixotropic systems.

Examination of the samples made it clear that in this case we are dealing with the false body type of thixotropy. Although it may be possible that quick sands show thixotropic behaviour under certain conditions experimental evidence tends to convince us that the typical "quick sand behaviour", i.e. the stiffening under sudden impression and the yielding to prolonged pressure must be due to dilatancy. A dilatant system like quartz-water or rice starch-water, if in sufficient amount present, will doubtlessly provide as treacherous a stretch of "synthetic beach" as the most romantic novelist's pens aim at convincing us to be the case in reality.

A similar view appears to be supported by R. V. Williams and W. Heckert[2] when they describe the behaviour of potato-starch systems — which is virtually dilatancy — under the heading: "Some properties of dispersions of the quick sand type". Sofar we have not personally been able to observe the phenomenon of quick sand in nature.

In connection with these materials a few words may be relevant to point

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[1] H. Freundlich and Juliusburger. Trans. Faraday Soc. **31**, 769 (1935).

[2] R. V. Williams and W. Heckert, Ind. Eng. Chem. 23, 667 (1931).

out those systems in which dilatancy either in one form or another plays a part in systems of practical importance. There is no doubt that the whole branch of engeneering and investigation which deals with sand, stones and water, the constructions of roads, dikes, canals etc. constantly deals with dilatant systems — without calling them by that name.

In quite a different field of investigation a phenomenon occurs which definitely reminds us of the behaviour of dilatant systems, though at first sight there is very little analogy between the systems which show these phenomena most characteristically. We are referring to the investigations concerning the behaviour of muscles carried out by Jordan[1]. What he describes as the "snow-plough-effect", representing a periodic increase and decrease of resistance against deformation of a muscle upon stretching, in such a way that upon slow deformation the muscle exhibits an elongation proportional to the force but an alternating extension movement upon application of higher forces, is completely similar to the phenomenon exhibited by dilatant systems. Although the linking of these two phenomena may at first sight seem hardly more than "just a superficial analogy", considering the wide difference between a quartz suspension and a muscle of Metridium Dianthus, there is one factor which points to the possibility of a somewhat greater similarity between these two classes of systems. It is reported, namely, that the water content of the muscle may have a dominating influence upon the behaviour of the muscle[1]. Within very narrow limits of the water content of the muscle the snow-plough-effect may be exhibited, and disappear upon the slightest transgression of these limits; which is exactly the same behaviour which we have learnt to consider as characteristic for a dilatant system. In how far this analogy may endorse the current opinions concerning the structure of tissues may be left to experts of physiology.

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[1] c.f. First Report on Viscosity and Plasticity. Kon. Acad. Amsterdam.

[2] H. J. Jordan, Naturwissenschaften, **25**, 17 (1937).
also c.f. Dissertatie P. J. Kipp, Utrecht, 1939.

## CHAPTER VII

# SURVEY OF LITERATURE

### § 20 - REVIEW AND DISCUSSION OF CURRENT LITERATURE ON THE PROBLEMS INVOLVED

The literature dealing with thixotropic systems and the measuring of plastic and consistent systems in general, is of such vast dimensions that even the faintest approach to anything like a complete survey might well nigh imply complete "drowning" of the reader — not to mention the preceding state of mind of the reviewer. Almost every author who takes rheology serious will in the course of his paper prove to develop a terminology of his own, followed by a theory and a mathematical treatment of his own, in consequence of which the concert of papers inevitably tends to be of a kaleidoscopic rather than of a coherent character.

When, however, we are going to deal with a few of them in this section, our choice will be guided by an endeavour to see in how far the previously developed point of view can be applied to the results of observations of other investigators, or if it may be of some assistance in explaining hitherto unsolved inconsistencies.

1 - *"Measurement of thixotropy in absolute units"*. Goodeve and Whitfield[1].

The authors give a description of an apparatus for the measuring of thixotropic systems. The apparatus is a modification of the Couette type of viscometer. The two cylinder walls of the Couette apparatus have been replaced by two cone-shaped walls, the outer one of which is rotated by a motor. By simply raising the inner cone the distance between the cones can be modified. Thus the idea is to vary the rate of shear by varying the distance over which shear takes place, while the speed of the outer cone remains constant and the spring which counterbalances the drag imposed

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[1] C. F. Goodeve & G. W. Whitfield, Trans. Faraday Soc. **34**, 511 (1938).

on the inner cone equally remains the same. In this way the inconvenience is avoided of having to change the torsion wire, which rules out an ordinary Couette for application to the type of systems under investigation.

A theoretical derivation is given of a magnitude, called the "coefficient of thixotropy" which is computed from determinations of the force exerted on the inner cylinder as a function of the rate of shear. The derivation starts from the assumption that the viscosity is determined by the equilibrium between a building-up tendency of the system and a breaking-down tendency by the rate of shear. From comparison with Bingham's equation it is learned that the coefficient of thixotropy is similar to the yield value of Bingham. Measurements of suspensions of carbonblack in linseed oil are described. Curves of $\eta$ as a function of $\frac{1}{s}$ i.e. the reciprocal of the rate of shear are reproduced. A different treatment is given for "highly thixotropic" systems. Measurements of these systems are forecasted.

When we try to estimate the experimental method at its intrensic value, we come to the conclusion that there is one condition which is not fulfilled. The determinations are made in such a way that the readings were taken after a number of rotations sufficient to guarantee the inner cone having reached a stationary position. But no account is taken of the fact that the revolutions preceding this stationary position will have interfered with the condition of the system at the very beginning of the determinations. So what is measured is not the properties of the original system when undisturbed, but the properties of the partly destroyed system. Now this will not matter, provided the system is able to restore its initial condition *immediately*, if this is the case then the deduction is perfectly acceptable; i.e. for a falsebody thixotropic system the method may be succesfully applied. When however the condition of immediate restoration is not fulfilled then the evaluations must necessarily lead to erroneous results; i.e. a system of the $Fe_2O_3$ type can not be rightly estimated in this way, owing to the destruction by the measuring method.

In addition, one more objection to the line of approach must be raised. In deducing the rate of shear it is assumed that the shear really reaches from the wall of the outer cone (which has a specified speed) to the wall of the inner cone (which is stationary). This assumption obscures the real difficulty, since the real question is what is the distance over which the shear actually extends. This fact is adequately illustrated in the paper itself by the references to measurements of "highly thixotropic" systems. It seems to us that the primary question to be solved should be the distance over which shear is propagated when a body — or a wall — moves in an infinite amount of system.

2 - *The viscosity of suspensions of rigid particles at different rates of shear.* E. Hatschek & Miss Humphrey[1].

The purpose of these authors was to determine the influence of the dispersion of particles on the viscosity of a Newtonian liquid. They choose dispersions of starch in mixtures of carbontetrachloride and toluene in order to exclude a difference in specific weight between dispersed phase and dispersion medium. The conclusion they arrive at is, that their results do not agree with Einstein's law, but that the viscosity is a function of the rate of shear. In the light of our own results we can perfectly understand these conclusions; we can equally realise that the choise of the system is among the least fitted for checking the law of Einstein, owing to the aggregation-tendency of the particles in this particular system. The conclusions of the authors can thus be summarised: 1 - The viscosity of a suspension is a function of the rate of shear; decrease of the rate of shear results in an increase in the viscosity. 2 - For all rates of shear the increase in viscosity exceeds the increase in concentration of suspended particles. 3 - The same applies to the relative viscosity, the difference becomes less the higher the rate of shear. The experiments lead the authors to the conclusion that there is a strong mutual influence of the particles. Thus their conclusions are perfectly consistent with the results of our observations on the same systems.

3 - *The mechanism of thixotropic gelation.* J. C. Russel and E. Rideal[2].

After an extensive introduction, these authors give a description of the behaviour of quartz suspensions to which $Al_2O_3$ had been added in combination with various amounts of electrolyte. As a result of these experiments, the authors make a distinction between various ranges of thixotropic gelation. The first range lies at low concentration of electrolyte, 50—110 mmol NaCl, where "hydrophobous flocculation" takes place. The second zone ranges from 110—200 mmol where a "gelatinous" flocculation

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[1] E. Hatschek & Miss E. Humphrey, Proc. Phys. Soc. London, **28**, V, 278 (1915).

[2] J. C. Russel & E. Rideal, Proc. Roy, Soc. London **A. 154**, 540 (1935).

occurs, with a distinct optimum at 200 mmol. At concentrations exceeding 200 mmol there is a definite tendency to the formation of irregular flocks which aggregate and settle at random. In this region syneresis is quite definitely present.

An explanation of the experiments is proposed by the introduction of the assumption that suspensoid and hydrophylic components are present, which are influenced by the addition of electrolytes in a different way. The total sum of these influences accounts for the behaviour of the system as a whole. The paper leads to the conclusion that it cannot be precisely stated whether the different properties of the components are due to a difference in chemical composition, or merely to a difference in size of the particles. Concerning this question, it is not difficult to mention a great number of papers which all lead to much this same conclusion. However, it must not be forgotten that it is not only the size of the particles which is determining for its properties, but that it is the sum of the variations of properties as function of the size of the particle that determine its final behaviour. The reason why we have referred to this paper is that the order of magnitude of the additions of electrolytes seems to be of more than occasional relevance. We have observed that with various systems monovalent electrolytes exert their influence at a concentration of about 100 mmol, while complete flocculation is attained at circa 400 mmol/L. This applies to quartz suspensions, and to clay suspensions, as well as to certain dyestuff-solutions like benzopurpurine. This fact may be understood to be another indication that there is a collective factor determining the behaviour of all these systems.

### 4 - *Studies in thixotropy.* Hauser and Reed[1].

In this paper an illuminating description is given concerning the shift of properties of a system as a function of the size of the constituting particles. The particles ranged from 14—87 $\mu$, and their thixotropic properties were investigated by means of mechanically reverted tubes containing the various fractions. From these experiments it is firmly established that a decrease of particle size results in an increase of the "general activity" of the particle. The systems investigated also very obviously show the presence of rheopexy.

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[1] Hauser and Reed, J. Phys. Chem. **41**, 911 (1937).

5 - *Über Viskosität und Plastizität disperser Systeme.* N. N. Kulakoff & Wolarowitsch[1].

A series of highly informing papers has been issued by these authors under the above heading. Various aspects of plastic systems, mostly selected from systems of topical interest from the point of view of a Peat-research Institute are investigated and described. In the paper, mentioned here, a description is given of the results of various methods of viscometry for the examination of peat suspensions. The results clearly demonstrate that measurements like these are seriously liable to be influenced by factors that can not be quantitatively appreciated, owing to which rather divergent results can be attained.

In a paper from the same series a description is given of measurements of suspensions of printing inks by means of an apparatus of the Searle-viscometer type. Incidentally the authors mention a system consisting of naphta soot in hydrocarbon which exhibited a rate of shear/shearing stress curve concave to the stress axis. Since in the opinion of the authors this behaviour was just opposite to the type of curve they were looking for the system was discarded as "inconsistent". It is quite possible, however, that what appeared to be an unusual behaviour may actually have been a case of dilatancy. It seems by no means impossible that naphtha soot should exhibit towards the hydrocarbon dispersion medium a behaviour analogous to that of quartz towards water. The only detail the authors mention is the fact that the naphta soot was of very course particle size, which makes dilatancy even more probable.

6 - *Flow phenomena in liquids and liquid suspensions.* E. G. Richardson[2].

An interesting account is given in this paper of a method of measuring rates of shear by observing the change in resistance brought about in a nickelwire in consequence of the flowing of the system in which it is immersed. It does not need to be emphasised that this is a highly interesting measuring method. The results obtained are in close harmony with experimental evidence obtained with the more usual devices for viscometry. This method certainly deserves close attention for further development and extension to various classes of systems.

[1] N. N. Kulakoff und Wolarowitsch. Kolloid-Z. **80**, 205 (1937).

[2] E. Richardson, Journ. Oil & Col. Chem. Assoc. **21**, 215 (1938).

7 - *Observations of the viscosity of concentrated solutions of cane sugar*. J. Coumou[1].

In this paper experiments are described which lead to the rather startling conclusion that a concentrated cane sugar solution exhibits an increase of viscosity after vigorous stirring. The increase amounts, in the three cases mentioned in the paper, to 18, 6 and 17 % of the viscosity before stirring took place. After 2 hours standing the effect has disappeared and the original viscosity is restored. Provided this effect was not caused by the incorporation of air into the system, it would be a remarkable case and one might be tempted to assume the presence of some mysterious dilatant behaviour. Minute crystals might take the place of particles in the system while the relative high viscosity of the medium might be responsible for the aggregation, caused by the stirring, to be maintained over the period of about one hour. The assumption of the presence of crystals is endorsed by the experimental evidence given in the paper that the viscosity of the system increases during the first 2 hours immediately after the solution has been made — at a temp. of 75° —.

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[1] J. Coumou, Chem. Weekblad, **33**, 542 (1936).

# POSTSCRIPT

Having dealt with the various aspects of dilatant and thixotropic systems, and having gained from our experiments a certain insight into the problems that are involved, we should like to conclude our discussion, with some coordinating remarks aiming at giving a few suggestions concerning the direction in which the investigations might be extended.

The measuring technique which we have described is necessarily still in its infancy, and will need a good deal of development in order to reach such maturity that it should be possible to deduce perfectly reliable magnitudes from the measurements. To reach that goal, first of all the construction of the "car" would need general improvement. A new specimen should be considerably lighter than the one we used. A synthetic plastic would probably be a suitable material for its construction; in addition agate cones should be applied for the axle bearings. It might also be useful to make the apparatus self-registering, the construction of which would offer no difficulties. The measuring method of thixotropic systems might be considerably simplified by the application of broad, shallow containers — in combination with the arrangement of Pict. IV — instead of the glass cuvets we used, which would enable us to make a number of readings by slightly displacing the container each time the sphere has travelled through the system. In this way it will be possible to collect a number of points of the speed/weight curve at one time of rest — at least a practically constant time of rest — without having to refill the container after each determination.

A point which certainly needs closer examination is the question of how far the shear actually reaches in the system at various speeds. By making use of a cuvet provided with walls that can be easily shifted, it should be possible to solve this question quantitatively.

In addition a further investigation of the mathematical evaluation of the measurements should be made in order to be able, not only to compare differences brought about in one system in the semi quantitative way in which we have interpreted our results, but to be also able to compare systems with consistencies of a completely different order of magnitude.

Further development of the measuring technique therefore seems of paramount importance since any further progress of our knowledge in the whole field of rheology virtually depends upon reliable measurements. What is lacking most at the present time is certainly not a collection of fresh suggestions, but far more a simple method for collecting reliable data to enable us to check the numerous suggestions, abundantly launched in the course of years.

And, as far as we can see, it should not be impossible to work out such a technique on the base of the apparatus described in the preceding pages, since the size of the container as well as the size of the sphere can be adapted to any representative of the whole scale of consistencies from 1 poise up to $10^{10}$, while both the container and the sphere can be interchanged in a few seconds time.

# SUMMARY

An investigation has been carried out of the properties of dilatant and thixotropic systems in connection with their rheological behaviour. The aim of the investigation has been, to establish a relation between the shape of the rate of shear/shearing stress curve of the systems and their composition.

A discussion of the way, in which measurements of these systems should be carried out is given, and an apparatus is described which allowed the determination of a magnitude proportional to the rate of shear as a function of the shearing stress.

It is pointed out that the relation between the particles and the dispersion medium is of paramount importance for the behaviour of the system as a whole. Only those systems in which the particles are completely stable show dilatancy; as soon as the mutual attraction of the particles leads to aggregation, a system will develop a yield value and thixotropy results.

It appears to be of some practical value to distinguish between two types of thixotropy: the "false body" type of thixotropy and the "$Fe_2O_3$" type of thixotropy, although the difference between these is a gradual rather than an essential one. The former type is characterised by a momentary increase in consistency after stirring, while the latter systems solidify gradually.

A consequence of the decisive influence exerted by the dispersing liquid is, that the same particles which yield a dilatant system when dispersed in one medium may exhibit thixotropy upon dispersion in another liquid. Quartz particles turned out to present a striking example; with water a dilatant system results, while with apolar liquids perfectly "false body" thixotropic behaviour comes into operation.

A brief survey of the properties of dilatant and thixotropic systems not directly concerning the flow of these systems is given. Attention is drawn to the fact that "unstable" particles, per se, are able to enclose considerable amounts of liquid.

# LITERATURE

A treatment in detail of the subjects under discussion may be found in the following books:

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G. W. Scott Blair; An Introduction to Industrial Rheology. Churchill Ltd. London, 1938.

# INDEX OF AUTHORS

# STELLINGEN

## I

De door Kanamaru c.s. gemeten grootheid „Grenzflächenladungszahl" mag niet als maat voor de $\zeta$-potentiaal der micellen beschouwd worden.

K. Kanamaru und T. Kohno, Kolloid-Z. **79**, 190, 198 (1937),
**87**, 62 (1939).

## II

De door Bergmann op grond zijner experimenten uitgesproken meening, dat de enzymen de richting in welke een reactie verloopt zouden kunnen bepalen, is niet juist.

M. Bergman, Chem. Reviews, **22**, 423 (1938).

## III

Het is in principe mogelijk de moeilijkheden, die optreden bij de structuurbepaling op grond van „von Laue-diagrammen", te ondervangen door de methodiek zoodanig te wijzigen dat de bij iedere reflectie behoorende golflengte berekend kan worden.

## IV

De door Neumann c.s. bepaalde waarden van de vormingswarmte van chroomnitride en mangaannitride zijn te verkiezen boven de door Satoh berekende waarden.

B. Neumann, Kröger und Haebler, Z. anorg. Chem.
**196**, 65 (1931).
S. Satoh, Scient. Papers Inst. phys. & chem. Research, Tokio
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**35**, 158 (1939).

## V

Het is niet gerechtvaardigd een immobilisatie van dispersiemiddel door de disperse phase steeds als solvatatie te interpreteeren.

## VI

De stabiliseerende werking van organische vloeistoffen + electrolyten op amphotere kolloiden kan als opheffing van een inwendig complex worden beschouwd.

Jirgenson, Kolloidchem. Beihefte, **44**, 285, (1936).
L. Theunissen-Van Zijp, Diss. Leiden 1938.

## VII

De bestudeering van het rheologische gedrag van suspensies van anorganische stoffen in organische vloeistoffen biedt de beste mogelijkheid tot verdieping van het inzicht in de eigenschappen van organo-solen.

## VIII

Het is gewenscht dat voor studenten in de Chemie de mogelijkheid geschapen worde om tijdens hun studie met de Industrie in contact te komen.

H. L. RÖDER