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THE BRITISH SOCIETY OF RHEOLOGY

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Bulletin No. 31

June, 1951

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EDITORIAL

Scarcity of abstracts in this issue does not reflect any change in the Society's policy. The usual number of abstracts has in fact been received, but they are being held over until a later number of the Bulletin in order to make room for the Draft Rules for consideration at the Annual General Meeting in September and the summaries of the papers to be presented at the Exeter Conference. In the jargon of modern science, "an attempt is being made" to get these summaries published in advance of the conference in order to permit more adequate discussion at Exeter. We have a better chance of success herein if the number of abstracts is temporarily curtailed, since many abstracts take long both to set and to correct, and delay the passage of the Bulletin through the press. The remaining abstracts will be published as soon as possible.

The Committee *hopes* that members will study carefully the Draft Rules of the Society and then attend the Annual General Meeting armed with suggestions for their improvement. The Draft Rules are far from perfect and there is plenty of scope here for constructive criticism. Cynics on the Committee *expect* that members, having taken one look at the Draft Rules, will decide that the A.G.M. is, even more than usual, something to be avoided. They will, however, be only too glad if they are proved wrong. A simple constitution and some working rules can no longer be avoided, and we are likely to get better rules if the membership takes an interest in their drafting.

The summaries of the papers to be presented at the Conference need little in the way of comment. Their purpose is to acquaint members with the subject matter of the papers so that the limited time available for discussion may be profitably spent. The programme appears to be interesting and we hope that members will find the Conference as successful, both scientifically and socially, as those run by the British Rheologists' Club in the past.

V. G. W. HARRISON.

CONFERENCE ON THE RHEOLOGY OF FILMS AND SURFACES

A conference has been arranged, jointly with the local branch of the Chemical Society, at the Washington Singer Laboratories of the University College of the South West of England, Exeter, on 27, 28 and 29 September 1951.

The following, and others to be announced later, are presenting papers. Summaries of the papers received up to the time of going to press are given in this Bulletin. H. J. Bezer and R. Schnurmann (Manchester)—Extreme pressure lubricants; E. Eisma (Netherlands)—Yield stress of interfacial films; F. H. Garner and C. W. Nutt (Birmingham)—Cybotactic phenomena at interfaces; M. R. Hopkins (B.I.S.R.A.)—Coating of surfaces; D. W. Jopling (Kodak)—The swelling of colloid layers; E. W. J. Mardles and E. Bielak (R.A.E.)—Flow of liquid films over solids; C. C. Mill (P.A.T.R.A.)—The rheology of printing; B. A. Pethica—Insoluble monolayer penetration; J. H. Schulman and M. Z. Dogan—(Cambridge)—Properties of adsorbed films; K. V. Shooter (Cambridge)—Lubrication; A. de Waele and Mrs. G. L. Lewis (Gestetner Ltd.)—Electrical behaviour of oil-pigmented dispersions.

The conference will open at 2.30 p.m. on Thursday, 27 September, and will close at 12.45 p.m. on Saturday, 29 September.

Members and their guests are asked to inform the Hon. Secretary of their intention to attend the conference, and to make their own hotel arrangements, as early as possible, mentioning the Society's Conference. The following hotels are in order of proximity to the Laboratories: Imperial, Great Western, Windsor, and Rougemont.

LECTURES ON ELASTICITY

A course of twenty-four lectures on Elasticity (with introductory tensor theory) will be given by I. Berenblut, M.Sc., A.R.C.S., A.Inst.P., at the Department of Mathematics and Physics, The Polytechnic, 309 Regent Street, London, W.1., on Wednesday evenings from 7.30 to 9.00, commencing 26 September 1951.

CONGRATULATIONS

Congratulations to Committee member Paul Feltham for award of the degree of M. Sc. for a Thesis on "Theory of Functions of Mathematical Physics and Electromagnetism".

CORRESPONDENCE

National Institute for
Research in Dairying,
Shinfield, Berks.

5 July 1951.

Dear Sir,

I have recently been examining the available information on the changes with temperature in the viscosity of whole milk. Pending the publication of a paper, some of your readers may be helped by knowing that the treatments given to this subject in current text books on dairying subjects need considerable qualification.

Yours faithfully,

C. P. Cox.

Building Research Station,
Garston, Nr. Watford,
Herts.

11 July 1951.

Dear Harrison,

I am, as you know, working on the flow properties of aqueous building pastes, but practical building materials all have their own peculiarities (particle shapes, chemical setting, etc.) which complicate the work excessively in these early stages. Consequently I am looking for a powder which ideally should have the following characteristics :—

- (i) inorganic
- (ii) negligible solubility in water
- (iii) simple particle shape—e.g., spherical, cubic, cylindrical with constant length : diameter ratio
- (iv) obtainability in closely-sized fractions at mean values within the range, say, of 0.1 to 10 microns. Several kilos of each fraction would be desirable, but much smaller quantities would still be very useful.

If you can evoke any helpful replies on this subject, I shall be extremely grateful. I realize that the problem is a difficult one but possibly someone among your wide circle of readers may know of a suitable material.

Yours sincerely,

PETER MASON.

THE BRITISH SOCIETY OF RHEOLOGY

DRAFT RULES

1. NAME.—The Society (formerly known as The British Rheologists' Club) shall be called The British Society of Rheology.

2. OBJECTS.—The objects of the Society shall be the promotion of scientific inquiry and the diffusion of knowledge connected with the advancement of pure and applied rheology, defined as the science of the deformation and flow of matter.

3. MEMBERSHIP.—Any person interested in rheology shall be eligible for membership of the Society. There shall be no corporate members. In order to become a member, an applicant must make a written application in a manner to be approved from time to time by the Committee. A person whose application is supported in writing by a member of the Society and approved by a majority of the members of the Committee shall be enrolled as a member on receipt of the subscription due for the current year.

4. SUBSCRIPTIONS.—An annual subscription of one pound shall be paid by each member. Payment becomes due in advance on the first day of October in each year. If the annual subscription of any member be twelve months in arrear, the Hon. Treasurer shall make application for it, and if it be not paid within one month the name of such person shall be removed from the list of members. Any person who ceases to be a member under this rule may be re-elected to membership by the Committee at any time, on payment of the arrears due from him at the time when his name was removed.

5. THE COMMITTEE.—There shall always be a Committee to manage the business of the Society, which shall consist of a President, an Honorary Treasurer, an Honorary Secretary, an Honorary Editor, not more than three members representing special geographical regions, and four other members. The Committee shall have the management of the funds and affairs of the Society and shall do all such acts as shall appear to them necessary to carry into effect the objects and views of the Society. The Committee shall meet at least four times during the year, and not less than four shall constitute a quorum.

The Committee shall be elected each year at an Annual General Meeting. Any member of the Committee may be re-elected, except that (i) a member shall not normally be eligible to fill the office of President for more than two years successively, or any other single office for more than four years successively, and (ii) a member shall not be eligible to serve on the Committee for more than four years successively without filling an office. In the event of a vacancy occurring during the year in the office of Hon. Treasurer, Hon. Secretary, or Hon. Editor, the Committee shall elect a member of the Society to act until the next General Meeting. The Committee shall elect each year a Chairman from among its own members (excluding the President) who shall deputize for the President in his absence on all occasions.

6. DUTIES OF THE PRESIDENT.—The President shall take the Chair at Annual and Extraordinary General Meetings of the Society, and at meetings of the Committee unless he wishes to the contrary.

7. DUTIES OF THE HON. TREASURER.—The Hon. Treasurer shall receive all sums of money due to the Society, transact all its pecuniary affairs, and keep a regular account of receipts and payments. The Hon. Treasurer's accounts for the twelve months ending on the thirtieth day of June, having been examined and approved by the Hon. Auditor, shall be laid before the Annual General Meeting.

8. DUTIES OF THE HON. SECRETARY.—The Hon. Secretary shall be responsible to the Committee for the general conduct of the Society's correspondence and other

business, except that which relates to finance or to the Society's publications. He shall prepare an agenda for each meeting of the Society or of the Committee, and shall inform every member at least one month in advance of the date of any Ordinary or General Meeting, inviting nominations for any elections on the agenda. He shall take the minutes at all meetings of the Society and at meetings of the Committee, and enter them in a Minute Book. The Hon. Secretary shall have the care of the Society's Library.

9. DUTIES OF THE HON. EDITOR.—The Hon. Editor shall be responsible to the Committee for the Society's publications.

10. GENERAL MEETINGS.—An Annual General Meeting shall be held in each year in the month of September or thereabouts for the purpose of electing the officers and members of the Committee to serve until the next Annual General Meeting, of electing an Honorary Auditor who shall not be a member of the retiring Committee or of the new Committee, and of making or amending the Society's rules. All decisions shall be made by a simple majority of the members voting, except that the making or amendment of a rule shall require a two-thirds majority of the members voting. No change in rules shall be valid unless supported by a number of votes greater than twenty, or 8% of the total membership of the Society, whichever is the less. At the Annual General Meeting the Hon. Secretary shall present a report on the activities of the Society during the year, and the Hon. Treasurer shall report on the financial position of the Society.

At the request of four members of the Committee or of twenty members of the Society, the Hon. Secretary shall call an Extraordinary General Meeting within two months of receiving such request. Such an Extraordinary General Meeting shall have the full authority of an Annual General Meeting.

11. REPRESENTATIVES ON OTHER BODIES.—Representatives of the Society on other bodies, or at conferences of other organizations, shall be elected from among the members of the Society by the Committee.

SUMMARIES OF PAPERS TO BE PRESENTED AT EXETER CONFERENCE, SEPTEMBER 1951

"Extreme-pressure" lubricants and their examination.

H. J. BEZER AND R. SCHNURMANN.

Thermoelectric experiments with "extreme-pressure" lubricants were described in a previous paper. It appeared from these experiments that the function of an "extreme-pressure" lubricant is to reduce the frictional force and that it is therefore desirable to measure the variation of the frictional force or any function of it over an appreciable range of normal loads if one wishes either to examine the mechanism of "extreme-pressure" lubrication or if one wishes to grade "extreme-pressure" lubricants.

A four-ball apparatus of the Boerlage type was built and a method of testing was developed with this instrument so that either the diameter of the wear impression on the three spheres clamped rigidly in the ball cup was measured as a function of the normal load for given testing periods, or the temperature rise of the ball cup was determined as a function of the normal load, or the frictional force was recorded as a function of the normal load. Excellent correlation between the three types of results was obtained by assessing for a given lubricant the so-called transition region, i.e., the region of normal load over which sliding, which is accompanied by the removal of fine particles from the solid surfaces, gives way to tearing. The position on the normal load scale of this transition region varies appreciably for different lubricants and this means that a physically defined method of grading lubricants for definite operating conditions can be applied. It is of interest that below this transition region the temperature rise for a given running period is proportional to the frictional force, both of which show a linear increase with normal load in this region. Therefore in this region and only in this region the coefficient of friction is a defined physical magnitude, whereas this is not the case when appreciable tearing of the frictional elements takes place. There is no evidence for a defined "break-down load" of a lubricant.

The main portion of the mechanical energy dissipated by friction under conditions of "extreme-pressure" lubrication is converted into heat both by deformation of the friction elements and by shearing of the boundary layer of lubricating material. There is a small contribution to the dissipation of energy by the abrasion of particles from the solid friction elements. An energy balance would appear to allow for an appreciable proportion of the order of 10% of the mechanical energy to be available for the separation of electrostatic charges.

Comparison of the Torsion Oscillation and Rotating Disc methods for the measurement of the yield stress of an interfacial film.

E. EISMA.

For the measurement of the rheological behaviour of surface films two essentially different groups of methods can be used. In the one a surface slit is used and the amount of surface material passing through this slit in unit time, the pressure difference between the ends of the slit, etc., are measured. In the second group the resistance exerted by a film on the motion of a disc is determined.

With interfaces it is not yet possible to measure the amount of material passing through the slit and therefore the second group of methods, which includes the torsion oscillation and the rotating disc method, has been applied.

The torsion oscillation method has been applied by several investigators. If a system has purely viscous properties the ratio between two successive amplitudes is a constant. However, the ratio often increases with decreasing amplitude, which is caused by the non-viscous properties of the film. Although R. E. Wilson and E. D. Ries (*Coll. symp. Monograph*, 1923, pp 145-173) suggest that the film might have a yield stress, from their observations they calculate an apparent viscosity. L. Fourt and W. D. Harkins (*J. Phys.*

Chem., 1938, **42**, 897-910) found apparent viscosities increasing with decreasing amplitude, but they could not observe any evidence of rigidity. The same authors described preliminary experiments with a rotating disc apparatus, which has the advantage that the shearing stress during the measurements is constant.

It must be emphasized that the modern trend in three-dimensional rheology also shows a preference to using methods in which the shearing stress applied is constant.

The present investigation was carried out to see whether it is possible to derive a yield stress from torsion oscillations and whether the torsion oscillation or the rotating disc method should be preferred for the measurement of the rheological behaviour of an interfacial film.

As an object for studying this problem, the film between water and a 0.01% solution of dammar resin in xylene was chosen. The measurements were carried out at room temperature about 80 minutes after the formation of the interface. The ratio of two successive oscillations increased strongly with decreasing amplitude.

The differential equation for the torsion oscillation can be derived from the consideration that the loss of total (kinetic plus potential) energy in a short time equals the energy consumed by friction in the same time interval. Previous investigators have assumed that friction was proportional to the velocity, which includes the assumption that the film has purely viscous properties. If this condition does not prevail another assumption should be introduced. There are several possibilities, but on account of the behaviour of the film we introduced the assumption that the film has a yield stress.

To calculate the moment of friction we must further know how far the film follows the movements of the disc. Visual observation shows that only a small part of the film follows these movements. However, the differential equation which takes this into account could be not solved. Therefore the assumption was made that only a very narrow ring of constant breadth of the film follows the movement of the disc.

Based on these assumptions the following equation was derived :

$$a_n = a_0 e^{-np} + \frac{W}{E} \frac{e^p + 1}{e^p - 1} (e^{-np} - 1)$$

where a_n =nth amplitude, n =number of the oscillation, $W=2\pi r^2\tau_0$, r =radius of disc, τ_0 =yield stress, p =a term depending on viscous friction, E =torsion constant of the wire.

W (and therefore τ_0) and p can be calculated from the observations. To check the above equation experiments were carried out with various discs, vessels and torsion wires. In all cases the values of τ_0 varied between 5.3 and 7.5 dynes/cm with a mean value of 6.4 dynes/cm.

No interfacial viscosities were calculated as the differences in viscous damping (p) between experiments with and without film were very inaccurate.

The same film was investigated by the rotating disc method. The torsion of the wire was stepwise increased at different rates until the disc rotated with a constant angular velocity. The yield stress was determined by extrapolation to zero angular velocity. This includes the assumption that only a very narrow ring of the film follows the movement of the disc. We found 6.3 dynes/cm, which is in very good agreement with the torsion oscillation method. No interfacial viscosities could be calculated.

Although it proved to be possible to calculate a yield stress from torsion oscillation measurements, this method has the following disadvantages :

- (1) It is necessary to make an assumption regarding the rheological behaviour of the film.
- (2) During the measurement the shearing stress is not constant.

With the rotating disc method no assumption as to the rheological behaviour of the film need be made and the shearing stress during the measurement is constant.

For the type of material under investigation, characterized by a high yield stress and relatively small viscosity, we prefer the rotating disc method. In the case of purely viscous interfaces the torsion oscillation method might be more advantageous for determining their viscosity.

Cybotactic phenomena at interfaces.

F. H. GARNER AND C. W. NUTT.

Evidence in support of the theory of cybotactic phenomena at interfaces (i.e., molecular orientation into a quasi crystalline structure), will be reviewed and its relation to present knowledge and theories of surface phenomena discussed. Its bearing on rheological and chemical engineering phenomena (e.g., mass transfer across interfaces) will then be considered.

The coating of surfaces.

M. R. HOPKINS.

There are many industrial processes in which the thickness of a liquid coating applied to a solid surface is controlled by means of rollers. The coating of steel sheet with tin by the hot dipping process is an example. The sheet, after passing through a bath of molten tin, emerges through a palm oil bath which is maintained at a temperature above the melting point of tin, and which contains pairs of rollers propelling the sheet through the bath. The members of each pair lie horizontally, parallel to each other, and in contact except when the sheet is interposed on its way out of the bath. One pair is above the other so that the sheet moves vertically. The main function of the rollers is to remove tin from the steel sheet. The final coating thickness depends on the viscosity of molten tin, the radius of the rollers, the speed at which the sheet moves through them and the force per unit length which is applied to the rollers to keep them together. A mathematical investigation based on arguments similar to those used in the theory of lubrication gives the relation between the coating thickness and the relevant variables, for a single pair of rollers. This relation has been tested experimentally by passing a sheet of nickel foil, emerging from a bath of oil, through a pair of polished stainless steel rollers under such conditions that all the quantities of interest could be measured. Experiments with various oils have shown fair agreement with the theoretically predicted results. Some experiments with molten tin have also been carried out.

The rheology of printing.

C. C. MILL.

An attempt is made in this paper to analyse the printing operation as it is affected by the rheology of the printing ink. These remarks are intended to apply to the letterpress and lithographic processes; the photogravure process is fundamentally different and generally simpler rheologically.

Printing ink is distributed by a series of rollers, some of which reciprocate (i.e., move in a direction parallel to their axes), which not only spread the ink in a thin film upon the printing surface, but also break down the structure in the ink by the shearing forces at the lines of contact. The ink is contained in a duct from which it is removed by the intermittent action of a roller and transferred to the main distribution system. In the duct the shearing stress is both discontinuous and small. If the material has too high a yield value it does not feed properly and the condition of "hanging back" occurs. On the distribution rollers the shearing action is still intermittent since it occurs only at the nip between each pair of rollers, but the rate of shear is high. The ink is subject to break-down for a short period in each revolution, but can rebuild its structure during the remainder. Similarly, the application of ink to the printing surface is made under shear and the ink will be in its most fluid condition following the action of the rollers. At this stage it is desirable that the ink should not be too fluid or, alternatively, its structure build-up should be rapid to insure a sharp, clean print.

The major requirements of printing inks can be fairly readily obtained, but there are several more obscure matters which require investigation. It is not easy to estimate the shear rates obtaining at the nip between the rollers, although a number of values have been quoted without an indication of how they were obtained. In some cases the estimate is derived solely from the reciprocating action of the rollers. This uncertainty leaves open the question, "At what shear rate should a printing ink be tested?"

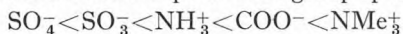
If two rollers rotate in contact, the ink film collects in a series of parallel ridges which are dispersed only if at least one in the system has a reciprocating action. The origin of these ridges is important in other applications too, e.g., varnish coating, tin plating, etc. It is believed that an explanation of the ridging would throw some light on the complex question of "Tack".

On the characteristics of the penetration of insoluble monolayers at different surface phase states.

B. A. PETHICA.

As was shown by Shulman and his collaborators, certain soluble long-chain electrolytes will interact strongly with insoluble monolayers at an air-water interface. The interactions can be followed either by observing the rise in surface pressure at constant surface area, or the increase in area at constant pressure subsequent to the introduction of the soluble component into the monolayer subphase. The present investigation has been concerned with the analysis of constant area penetration. It has been found that the form of the penetration isotherms and the energies of association in penetration depend on the presence of electrolytes in the subphase, on the chain-length of the penetrating molecules, on the specific relations between the polar and ionic groups of reactants of a given chain length, and on the phase state of the insoluble monolayer. In a given phase state, the energy of interaction, as measured by the concentration of the soluble reactant required to obtain an arbitrary interaction surface pressure, depends on the initial state of compression of the insoluble reactant.

In the system chloesterol-dodecyl sodium sulphate, the penetration isotherms (pressure rise—concentration of dodecyl sodium sulphate) are of two types. With the chloesterol initially in the condensed-liquid state, the isotherms are Langmuirian over most of the range. In the vapour-expanded state, the isotherms are sigmoid. Analysis of the pressure changes by the Gibbs Adsorption Isotherm, on the assumption of a constant chemical potential for the insoluble component, indicates that the areas of the penetrating molecule tend to infinity at high chloesterol compression, reach a minimum beyond the condensed state and then tend to the area of the dodecyl sodium sulphate adsorbed at a simple air-water interface, (i.e., at infinite area for the chloesterol). The interaction energy is at a maximum with condensed chloesterol monolayers at low initial pressures. The interaction energy of dodecyl sulphate penetration is increased by the addition of salt to the subphase, but the area of the penetrating molecule is not affected markedly. This shows that the packing of the interacting molecules is primarily a function of the initial state of the insoluble monolayer. Comparison of the Langmuirian isotherms for penetration of liquid-condensed chloesterol with a series of straight chain C_{12} compounds has shown that the polar head group specificity falls off in the order



In all these cases, the interaction is regarded as being akin to physical adsorption. In the case of the interaction of saponin with condensed chloesterol, where a stoichiometric complex is formed, the penetration isotherm shows a transition corresponding to the formation of a two-dimensional solid film. The areas of the saponin show a corresponding change in the transition zone.

A study has been made of the penetration of myristic acid by dodecylamine hydrochloride on dilute hydrochloric acid. Penetrations were carried out at an initial pressure of myristic acid of 1.5 dynes/cm, in the liquid-expanded region. The total pressure variation in this system is only 16 dynes/cm, and the relative scatter of points on the penetration isotherm is therefore greater than in the chloesterol systems studied. With this expanded film the penetraticn isotherm is again approximately Langmuirian in form, with an inflexion at a pressure corresponding to the transition of myristic acid from a liquid-expanded to a liquid-condensed monolayer. Above the transition point, the isotherm is also approximately Langmuirian. The apparent areas of the penetration molecules show a sharp decrease at the transition point, indicating that a closer packing of the amine is possible in the liquid-condensed than in the liquid-expanded film.

Electrical behaviour of oil-pigment dispersions.

A. DE WAELE AND MRS. G. L. LEWIS.

Measurement of thixotropy, as understood by the reversible gel-sol transformation during shear and on subsequent rest, cannot be made by any rheological method. A static method, involving no disturbance of the gelating system, is essential.

It has been claimed that the change in dielectric constant under the conditions of shear and rest bears a relationship to thixotropic change, but our experiments show that :

1. Systems of electrically non-conducting particles in non-conducting (oil) media exhibit little, if any, differences in capacitance under the two conditions named. Furthermore the dielectric constant of the system is very little greater than that of the parent medium.

2. When the particles are electrically conductive, the resulting dispersions exhibit distinct electrical conductivities depending on the state of flocculation of the system at the time and certain other factors.

3. Measurement of dielectric constant of a conductive dispersion involves the great difficulty of resolving the measured impedance into its components of capacitance and conductance.

4. The dielectric constant of dispersions exhibiting conductance increases with the conductivity of the system. It changes, however, very little with the rheological history of the material as compared with changes in conductivity, and the change is of much shorter duration than that observable by rheological means. Dispersions of electrically-conductive pigments in non-conductive oily media suffer a substantial decrease in conductivity during shear. When subsequently left in an undisturbed condition, conductivity rises in accordance with the relationship :

$dC/C \cdot dt = K \cdot t^n$, where C = conductivity at any given moment, t = time counted from arrest of shear, n = a negative value between 1.0 and 1.5, and K = the left-hand term of the equation referred to unit time. The equation can be transformed to furnish a time derivative of more practical significance : $t = C_{\text{inf}}/1000$, or the time taken for the growing conductivity to attain 1/1000th of its final magnitude after infinite rest.

Conductive systems of the types named exhibit a number of electrical anomalies. Thus, they do not obey Ohm's Law, conductance increasing with increase of E.M.F. Their capacitances are also subject to increase with both the value of the applied potential and with the time of application of direct current. They behave, indeed, in many ways as typical semiconductors. However, their electrical behaviour can often be related to their rheological condition. Thus, electrical conductivity at any given stage of rheological history increases with the degree of flocculation of the system and with its concentration. As volume concentration approaches close packing, changes in conductivity with dynamic treatment become less, and in liquid/liquid dispersions where complete close packing is possible, the emulsion suffers no change in conductivity during shear.

Materials exhibiting dilatancy when moderately concentrated, e.g., titanin oxide in liquid paraffin, behave in an anomalous manner electrically when sheared; conductivities increase during shear and rapidly decrease to a constant value on arrest of shear. This effect can be followed at very low concentrations indeed.

Dispersions of polar, oleophilic, electrically conductive pigments in strongly deflocculating media, e.g., carbon black in polymerised linseed oil, may exhibit considerable rigidity and marked thixotropic regain of rigidity extending over several days and yet show neither conductivity nor high dielectric constant. On free dilution with solvent the particles are found to be in permanent colloidal suspension and are hence deflocculated and independent of one another. Under cataphoresis the particles do not separate from the medium, but a more concentrated sol migrates to the anode. Rigidity and thixotropic behaviour are in this case to be attributed, not to any structure of the solid dispersate, but to the close-packed lyosorbed interstitial film of dispersator.

It is interesting to note that dispersions of oleophilic solid powders in oil media carry a negative charge under cataphoresis, hydrophilic particles a positive charge.

The rheology of thin liquid films.

E. MARDLES AND E. BIELAK.

The properties of liquid films of thickness less than about 10μ at solid surfaces appear to differ from those of the liquid in bulk. Hardy, 1921, for example, from his lubrication researches noted that the liquid films behaved as if they possessed rigidity, while earlier Kingsbury, 1903, used the term "intensified viscosity" for oil layers near the metal walls influenced by surface forces, and Devaux, 1913, spoke of the film as an elastic structure. The experiments of Derjaguin, 1939, seem to be a proof of these early views of the relatively large radius of molecular action of surfaces upon neighbouring liquid layers, but the phenomena observed cannot be ascribed to Van de Waal's forces and are not in accord with current theory of hydrodynamics.

A possible explanation of the numerous experimental results including those of Needs, 1940, and Marcelin, 1947, who reported on the plastic character of relatively thick oil films, must be outside hydrodynamic theory and molecular orientation. An explanation of the phenomena, including hydraulic stiction, is suggested based on the fact that thin films tend to rupture below about 10μ thickness and the heterogeneous film of liquid and bubbles or vacuoles assumes a plastic and thixotropic character. From results of film spreading and sliding tests it has been found that the onset of film rupture during the thinning of the film depends on the material of the surface.

The paper gives results of anomalous radial flow of various liquids over and between surfaces and flow through capillaries and includes descriptions of the filigree patterns obtained with dyed liquid films.

It has been found possible to correlate the high friction results, including hydraulic stiction, obtained at low pressures, and the plastic flow of the thin films, especially with liquids of low wettability.

The flow behaviour of liquids over surfaces is a highly complex phenomenon and depends on, besides surface tension forces, the time of displacing adsorbed air and water films by the liquid and its vapour, the character of the adsorbed liquid film, mechanical vibrations, etc. Electro-viscous effects, presence of dust particles, distortion of surfaces and their degree of roughness, are not sufficient to explain discrepancies from hydrodynamic theory.

RHEOLOGY ABSTRACTS

NOTE:—As explained in the Editorial, only a small selection of abstracts is being published this quarter. The remainder are being held over until next issue.

2081. **Report on the principles involved in the determination of absolute viscosity.**

A.S.T.M. COMMITTEE E.1. ON METHODS OF TESTING. *Amer. Soc. Test. Mater., Prepr.*

This report sets out in a valuable manner the principles involved in the following viscometers :—

Bingham Absolute Viscometer.
Ostwald Viscometer.
Triple Capillary Viscometer.
Cannon-Fenske Modified Asphalt Viscometer.
Koppers Capillary Rise Viscometer.
Bingham Plastometer.
Falling Sphere Viscometer.
Hoepler Rolling Ball Viscometer.
Falling Coaxial Cylinder Viscometer.
Garrison Viscometer.
Brookfield Synchro-Lectric Viscometer.
Stormer Viscometer.
Precision-Interchemical Rotational Viscometer.
MacMichael Viscometer.
Open End Rotating Viscometer.
High Consistency Rotational Viscometer.
Electromechanical Transducer.
Torsional Crystal Viscometer.
Parallel Plate Plastometer.

The report concludes with a list of 74 references where further details relating to the principles involved in the determination of absolute viscosity by various types of instruments can be found.

D.C.B.

2082. **Tree growth stresses. 1. Growth stress evaluation.**

J. D. BOYD. *Aust. J. Sci. Res. B*, 1950, 3, 270.

Experimental methods for the determination of natural longitudinal stresses in trees are described and the data are used in the development of a mathematical expression for the stress distribution. Transverse stresses naturally existing within the tree are similarly investigated and the results analysed mathematically. Another significant class of stresses is shown to result directly from the felling or cross-cutting of a tree.

AUTHOR.

2083. **Tree growth stresses. III. The origin of growth stresses.**

J. D. BOYD. *Aust. J. Sci. Res. B*, 1950, 3, 294.

Evidence available indicates that tree growth stresses originate in newly differentiated cells towards the periphery of a tree. It is considered that an origin connected with the structural development of peripheral cells would explain both the longitudinal and lateral distribution of growth stress effects more satisfactorily than other hypotheses suggested. The cause of growth stress development may be explained by the theory that cells tend to shorten in length and simultaneously to increase in cross section during or immediately after differentiation. The resistance of the mature cells throughout the tree to such a shortening could induce the stress effects which occur.

AUTHOR.

2084. The viscosity temperature coefficient of homogenized milk.

J. E. CAFFYN. *J. Dairy Res.* 1951, **18**, 95.

The viscosity (η) of homogenized milk was measured in a capillary viscometer to an accuracy of 1%. Creaming precluded measurements on unhomogenized milk. Plots of $\log \eta$ vs T (absolute temp.) was not linear and appeared to show a change of slope at about 40°C. This is probably due to the melting of crystalline fat particles. At temperatures below 60°C, repeated shearing resulted in a fall in η ; at temperatures above 60°C, η tended to rise. This rise also occurred in fat-free milk and is ascribed to changes in the protein. The initial fall at lower temperatures did not occur in fat-free milk and is due to changes in the fat.

G.W.S.B.

2085. Factors affecting the rheological properties of paints and lacquers.

E. CHADWICK. *Paint, Oil and Colour J.*, 1951, **119** (2744), 1177.

Report of a general lecture dealing with viscosities of polymer solutions and of suspensions.

D.L.T.

2086. Plastic flow of aniline-formaldehyde resins.

L. K. DALTON. *Aust. J. Appl. Sci.* 1951, **2** (1), 132.

The Rossi-Peakes's flow test was used to examine the plastic flow of aniline-formaldehyde resins. It was found that the rate of flow of the resin passed through a minimum as the condensation time during preparation increased. Small changes in the molecular proportion of formaldehyde of the order of 0.05, affected the flow considerably, but the proportion of hydrochloric acid and the concentration of aniline were much less critical. The pH at coagulation had a considerable influence. Furfural assisted the thermosetting of aniline resins as well as improving the initial flow. Hexamine had little influence. Primary and secondary amines, as plasticizers, gave the greatest increase in flow; of those tested benzylaniline is considered the best. The changes in the flow which occurred when conditions of preparation were varied are not readily explained by the structures usually assigned to the aniline-formaldehyde resins.

AUTHOR.

2087. Relaxation processes in the deformation of unfilled synthetic rubbers and the influence of the degree of vulcanization.

B. A. DOGADKIN AND M. M. REZNIKOVSKIĬ. *Kolloidnyi Zh.* 1951, **13**, 11.

A continuation of the authors' earlier work (see especially *ibid.*, 1949, **11**, 314 and 1950, **12**, 102). The relaxation equation used is :—

$$\frac{d(\sigma - E \sim \epsilon)}{dt} = (E'_0 - E \sim) \frac{d\epsilon}{dt} \cdot \frac{\epsilon - E \sim \epsilon}{\tau} \quad \text{where} \quad \begin{cases} \sigma & = \text{stress} \\ \epsilon & = \text{deformation} \\ E \sim & = \text{equilibrium modulus of high elasticity} \\ E'_0 & = \text{initial modulus of high-elasticity} \\ t & = \text{time} \end{cases}$$

Since, for constant strain this reduces to :—

$$-\frac{d\sigma}{dt} = \frac{\sigma - E \sim \epsilon}{\tau}$$

it is clear that τ is a special kind of relaxation time defined to allow for non-relaxing stress.

Another type of relaxation time, τ^* , is defined such that

$$\tau = \tau^* \exp. [-\beta (\sigma - E \sim \epsilon)^2] \quad \text{where} \quad \beta = \frac{\text{Vol. of kinetic element in relaxation}}{2kT(E'_0 - E \sim)}$$

$$\text{and } \tau^* = \tau_0 \exp. \frac{u_0}{kT} \quad \text{where} \quad \begin{cases} u_0 & = \text{energy of activation for structural change} \\ \tau_0 & = \text{initial } \tau \text{ for the material} \\ T & = \text{absolute temp.} \end{cases}$$

Curves are given plotting $\log \tau^*$ vs $1/T$ for varying degrees of vulcanization and different (constant) extensions. Only three temps. were used but the curves are given as linear. (One sample, said to give a non-linear curve, is omitted).

Straight line curves are also given for plots of $\log \tau$ vs $(\sigma - E \sim \epsilon)^2$ for a series of temps. and deformations.

G.W.S.B.

2088. Structural and visco-elastic properties of oil and water suspensions of aluminium oxide.

L. I. EDEL'MAN AND P. A. REBINDER. *Kolloidnyi Zh.* 1951, 13, 64.

Effects of varying concentrations of HCl, NaOH, $AlCl_3$ etc. on shear modulus and viscosity of Al_2O_3 suspensions.

G.W.S.B.

2089. Theory of an apparatus for rheological determinations by the deformation of the material between two annular discs with conical openings.

T. Y. GORAZDOVSKII. *Zhur. Tekh. Fiziki*; 1950, 22 (9), 1107.

Description of a new instrument for measuring flow properties in absolute units, and an analysis of its mode of action. Formulae are given for calculating the viscosity and the shear modulus.

P.M.

2090. The consistency of cheese and of whey cheese.

G. HADLAND. *Tidsskrift for det Norske Landbruk.* Mar.-Apr. 1951.

The sphere indenter designed for cheese at the (British) National Institute for Research in Dairying (see Abstrs. 262, 368, 672, 1306, 1472, 1629, 1630, 1656) has been used on Norwegian cheese and on cheese made from dried whey. The apparatus, renamed the "John Bull Indicator", measures total (Δ_t), recoverable (Δ_e) and non-recoverable (Δ_p) deformations under constant load after arbitrary times. In general, $\Delta_p \propto \Delta_t$. Repeated loading on the same spot increases Δ_e/Δ_t . Δ_t is correlated with total solid content. There are good correlations with subjective judgments of "body" and satisfactory reproducibility. The practical use of this instrument is recommended.

G.W.S.B.

2091. Visco-plastic properties of building pastes.

V. P. LOBANOV. *Kolloidnyi Zh.* 1950, 12 (5) 352.

Yield value and plastic viscosity of lime and cement pastes and mortars are determined using a Volarovitch rotation viscometer. Two cases are considered: one when the speed of rotation is sufficiently high for the shear to be propagated completely across the gap, and one when it is not. The flow constants are used in a Buckingham-Reiner type equation to calculate pumping pressures required for pipe-lines.

P.M.

2094. Application of rheology to some aspects of linoleum manufacture.

S. R. W. MARTIN. *J. Oil Col. Chem. Assoc.* 1951, 34 (369), 97.

A review of four papers dealing with rheological tests on linoleum compositions, viz. extrusion and penetration tests and measurements of flow under constant stress, pointing out their significance and practical application in linoleum manufacturing process control.

D.L.T.

2095. Fluid mechanics and dynamics of transfusion. Rapid replacement on severe blood loss.

D. G. MELROSE AND R. SHACKMAN. *Lancet* 1951, 260 (1), 1144.

The flow of blood and saline solution through standard transfusion equipment was studied using a flow meter and a mercury manometer. For various cannulas the rate of flow was plotted against pressure; bore, length and shape of the cannula orifice. Rates of flow varied up to 700 ml per minute, pressures up to 800 mm Hg. The fluids hardened with increasing rate of flow.

F.A.G.

2096. **An auxiliary method of determining viscosity and thixotropy of clay slips.**

T. SCHUMANN. *Ber. deut. keram. Ges.* 1950, **29**, 369.

Reference is made to several "solid" methods of determining thixotropy. During the war, when the equipment required for those methods was not available, the need arose for the development of a new method that should be as simple and rapid as possible. It was desirable that the new method should indicate the stiffening process in relation to time. The measurements of the degree of stiffening had to take place without too great a destruction of the gel structure in order to prevent liquefaction. Before measuring the stiffening, the fluidity of a clay slip made mainly of a micaceous clay mineral (which had no free Ca ions although there were 10 mg. exchangeable Ca ions per 100 mg. of clay) was determined by dropping a few spots upon a mirror disk placed at an angle of 60° and measuring the distance through which the drops rolled downwards. A test with 3 drops was sufficient, giving no significant deviations, and since so little of the slip was required the same slip could be used for measuring viscosity changes caused by increasing additions of deflocculants. The slip tested consisted of 2,100 g. micaceous clay (pH 4.5), 800 g. H_2O , 4.8 g. NaOH and 4.8 g. humus substance; the s.g. of the slip was 1.600. To this comp. 0-0.5% $CaSO_4 \cdot 2H_2O$ and equivalent amounts of Na oxalate of 0-0.39% were added. The distances covered by rolling drops are tabulated. This method proved to be excellent for the measurement of viscosity; however, it was not possible to determine the progressive stiffening of the slip after a certain period of rest. Therefore the following method was developed eventually for the determination of both viscosity and thixotropy. Tubes are filled with the slip to within 1 cm. of the top; above the tube is a tapless burette on which 1 ml. equals 1 cm. A 25-cm. Al rod (2 mm. dia.) is fixed inside the burette so that it almost touches the slip surface. To begin the test the clamp is removed and the rod allowed to fall by gravity into the slip. The depth reached after different times (in sec.) is read from the burette. To ensure that the rod falls vertically, it is encased in another glass tube with internal dia. 2 mm.

B.C.R.A.

2097. **Investigations of the elastic and plastic deformations of peat.**

V. A. SILIN. *Kolloidnyi Zh.* 1951, **13**, 51.

A simple apparatus for loading small test-pieces of peat and recording deformations is described. Compensation is not made for changes in cross-section. Stress-strain curves show marked hysteresis.

G.W.S.B.

2098. **Fundamental relations in the rheology of visco-elastic systems.**

N. V. TYABIN. *Kolloidnyi Zh.* 1951, **13**, 55.

A tensorial study of stress-strain relations. "Stay-put-edness" ("formosokhranya'emost'") as a most important property of materials, is defined as yield stress $\div$ (density $\times$ g). Data are given for a number of materials: metals, granite, clay, peat, flour doughs, etc.

G.W.S.B.

Definition.

RHEOLOGY is the science of the deformation and flow of matter.

Objects.

The objects for which the Society is established are the advancement and diffusion of a knowledge of rheology pure and applied and for this purpose especially :

- (i) To co-ordinate the activities of Rheologists in the British Isles.
- (ii) To further the appreciation of the importance of rheology in industry.
- (iii) To facilitate the pooling of information with respect to problems and new methods of research.

Membership.

Anyone who is interested in rheology is eligible for membership.

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Each member is required to pay a subscription of £1 per annum.

Activities.

Co-operation with Rheologists overseas has been maintained since the Society started as the British Rheologists' Club in 1940. Meetings, with lectures and discussions, exhibitions and visits to laboratories where rheological methods and equipment are in use, are arranged regularly at various centres in this country.

Conferences were held in Oxford, 1944, at Bedford College, London University, 1946, at Hulme Hall, Manchester, 1947, at Bristol University (Wills Hall), 1949 and at Reading University, 28th to 30th September, 1950. The Society participated in the first International Rheology Conference, The Hague, Holland, September, 1948.

The Officers will be happy to act as a medium for the arrangement of informal contacts between individual members for discussion of urgent technical problems of mutual interest.