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RHEOLOGY AND THE PRINTING INDUSTRY—II

by E. W. J. Mardles

The printer, as the artist, is interested in new effects, obtainable with the new colours, materials and processes new being made available. The ink formulator with a combination of skills, talents and experience, rare in industry, has to choose paper and ink (pigments, dyes and vehicle) to reproduce in print, say, a delicate water colour or colourful oil painting, bearing in mind the economics and the rapid drying times demanded in modern production.

It has been said that the ink maker holds the key to progress, for if a new printing process is invented it will fail if a suitable ink cannot be made to give the required printing quality; here rheology has a wide and important scope. The ink must flow adequately, distribute in the press properly while possessing "body," "tack" and "length," and a modicum of thixotropy and be without the faults of "picking," "misting" and "slinging"; the ink film must be laid evenly without smear, mottle or ghosts on a surface without undue dullness in tone. Apart from investigations on the rheology of bulk material little is known apparently on the behaviour of ink films up to twenty microns in thickness prevalent in the printing press. In a paper published in Japan, 1963, the effect of rheological properties of ink on printing smoothness was investigated by Ichikawa, Sato and Ito who state they were unable to observe any clear relationship between a measurement they term "ink covering resistance," which characterises the printing smoothness, and the rheological measurements they made, although regularities were noted with some series of inks.

Volarowitsch in his rheological work with printing inks, 1936, cited by Houwink in the 2nd Report on viscosity and plasticity, Amsterdam, page 230, used the Shvedov-Bingham equation to examine his experimental findings but found it difficult to measure the yield values. This difficulty of the reality of yield values has been discussed by numerous rheologists; Henry Green, 1949, pointed out that all rheo-consistency curves bend towards the origin and how much by plug flow and slippage, seepage, etc., has not yet been settled. The argument began in 1923, J.O.C.C.A., 6 33, when de Waele and also Mardles proposed a power law relation between shear stress and shear rate to describe experimental findings, Mardles including a definite yield value in his equation as measured by a Stormer viscometer. Henry Green considered that rheology is a network of

conflicting ideas which are so evenly distributed among rheologists that no particular school or group predominates; in the Soviet bloc the early equations of Bingham, Shvedov and Buckingham (1921) are in vogue and paper published in Russian, 1963, on the flow of coal and clay suspensions indicate the inadequacy of these equations at low shear rates. Latypov and Filatov, 1963, used approximations of the Buckingham equation which can be reduced to the Darcy-Weisbach formula. Similarly, Gutkin studying the flow of a viscoplastic system on a rotating disc derived a formula based on the Shvedov-Bingham equation and proposed to solve it by the method of successive approximations. For the purpose of increasing the stability of printing inks and minimising pigment settlement the ink vehicle is usually thickened or "gelled" by the addition of metal soaps, resins, gums, polymers, tallow, etc., so that visco-elastic effects arise. Pilpil, 1963, states that £1m. worth of metal soaps are manufactured yearly and it is claimed that processed magnesium montmorillonite will maintain the viscosity of an ink over a wide range of temperature.

Walters and Waters, 1963, consider that although much is known about the general behaviour of visco-elastic systems yet there is a dearth of experimental techniques available to determine the liquid parameters and proposed a rotating sphere rheometer. Rivlin found that a visco-elastic system cannot be distinguished from an inelastic one by means of steady state expressions in which flow is laminar.

Tanner, *Rh.Acta*, 1963, considers that although the general theory of visco-elastic flow now appears to be well established and he quotes the work of Oldroyd and Bland (*Theory of linear visco-elasticity*, Oxford, 1960), yet few applications to the interpretation of experimental results have yet been made and furthermore not enough theoretical results have been worked out fully to test the rheo-equations of state, which appear to fail for liquids of high viscosity ratings.

Crook, 1963, has discussed, on the basis of the theory of Grubin (Moscow), developments in the elasto-hydrodynamics of oils under conditions both of pure rolling and of rolling with sliding. He found film thickness is directly proportional to the square root of the product of viscosity, the temperature of the surfaces and their mean peripheral speed. The effective viscosity of the liquid when within the pressure zone as deduced from friction measurements, indicated a "destructive dynamic behaviour" which can be described tentatively in terms of visco-elasticity. The elastic property of silicone oils has been examined by Hutton, *Nature*, November 16th, 1963.

He postulates that under high shear rate when the total elastic energy contained in the sheared sample of liquid exceeds a critical value the liquid will fracture.

It has been known for many years that printing inks and other

pigmented systems will fragment in a rotary viscometer at high speeds and the phenomenon is probably the same as that known to the printer as ink sling or spit. Miller and Myers have described the spitting of ink from roller coatings as being due "to the drying out of a shear-thickening material at higher rates of shear, like wet beach sand when trodden on; the ink may lose adhesion to the roller and fly off." They continue, "this may involve a major reformulation of the ink and change of clothing of the operator as the dry material regains its fluidity and penetrative ability."

Some outstanding problems in ink rheology require the better understanding of the behaviour of pigmented systems, especially both at higher rates of shear when shear hardening occurs with eventual fragmentation and at low rates of shear when shear thinning occurs.

Can thixotropy and dilatancy be explained as "hydrodynamic," being manifestations of changes in particle positioning and freedom of movement?

At the conference held by the Institute of Physics and Physical Society on the Liquid State (September 1963), Everett showed a film of the motion-in-a-plane of an array of cork balls agitated by a stream of air when it could be seen that there was a co-operative motion in lines and rings. Bernal and King also described experimental studies of random close-packed arrays of steel balls which often show long-ordered lines of particles. By means of computers, calculations of the pressure and rate of approach to equilibrium of systems of simple molecules have been made using equations of motion for a small assembly. This work gave an impetus to the study of simple molecules and the past two years have seen the development of at least two sets of integral equations and one of them can be solved for a system of hard spheres. J. C. Williams, *New Scientist*, December 12th, 1963, has used a new optical technique of studying the positionings of powders in motion and the segregation of different-size particles during vibration and pouring. Several investigators have recently reported that the flow of suspensions is not homogenous but movement is by rotating plugs or colonies of varying sizes. It is possible that with inks in rotary viscometers small portions rotate as described by Reiner in his book *Deformation, Strain and Flow*, 2nd Ed. 1960, for liquid elements defined by vortices? These rotations are of the nature of rigid body rotation and the vortices can occur in simple shear. Reiner states that rotation, connected with simple shear, the teapot effect, is not a mathematical abstraction but a physical reality. Hoffmann and Baronet, 1964, *Nature*, March 31st, have described single stable vortex motion of definite location when a cone rotates in a Newtonian liquid. They measured the thrust on the cone at different speeds for both Newtonian and non-Newtonian liquids. Fragmentation of an ink into tiny pellets may be the outcome of this vortex motion at high speeds.

Zettlemoyer and Myers have stated that the "length" of a printing ink is apparently the rheological property of most importance in the distribution of ink in the printing press and they define it as the Bingham plastic viscosity divided by dynamic yield value; a "short" ink has a high yield value and the quotient tends to zero. This arbitrary measurement of ink "length," although a guide to what may happen in the rotary press, *e.g.*, if the ink is too "short" the ink will not follow the rollers properly and poor or uneven distribution may result and if too "long" picking of the paper surface or misting of the ink may occur, yet the measurement has not been found to correlate with ink transfer or printing quality. A difficulty is that the measurement is dependent on the instrument and method of measurement and wide variations are possible as shown recently by de Waele. Houwink described several kinds of yield values while Goodeve and Whitfield state that their constant θ , the coefficient of thixotropy, is not a yield value, as a yield value of a thixotropic material should decrease on stirring. Views have been expressed in the literature that no difference exists between yield value and thixotropy, a situation not yet clarified and there is no reason why yield value cannot exist without thixotropy.

It is known that the yield value of a suspension of a finely divided solid is a function of the viscosity of the suspending media; in glycerol or long oil varnishes of high viscosity a suspension of fine sand has Newtonian properties whereas the same concentration suspensions in water or raw linseed oil exhibit both thixotropy and dilatancy with high yield values. Again, with the same concentration of sand in liquids of different chemical composition but of the same viscosity, made possible by varying the temperature, wide differences in rheological behaviour may be observed. It has been found that the Einstein coefficient, 2.5, of the well-known Einstein equation describing the effect of particle addition on the viscosity can vary from 2 to 10 with the same powder in different liquids or different powders in the same liquid.

Precise information on the wetting properties of liquids and the effect on the rheological parameters of suspensions is lacking and the required combination of wetting and rheological properties of inks has not been delineated sufficiently to permit formulation of an ink to be made strictly on a rheological basis. If printing ink solvents are chosen haphazardly only a few inks will transfer well on the roller system of a press. New chemical solvents are continually being advertised as being highly suitable for inks, with good "solvent release," *i.e.*, of quick drying time. Oosterveld, 1963, stated that 2-nitropropane, as an ink solvent, used up to about 25% of total volatile matter, confers important improvement on photogravure and flexographic inks. According to several authors 2-nitropropane is a powerful wetting agent for hydrophylic pigment surfaces and according to Kitchener, *Endeavour*, September, 1963, this phenomenon of

wetting and "solvation" remains one of the classical unsolved problems of physical chemistry and new experimental data are required.

Dr. R. F. Bowles, 1950, suggested that for gravure printing, inks should be dilatant and should stiffen under the roller action; gravure or intaglio printing uses a roller with a design engraved into the plate, thus all the ink is held in depressions below the roller surface and is literally pulled out by the substrate.

Multicolour printing is accomplished by passing the web through several colour stations in a press, with little time for ink drying between stations. Usually light colours are printed first followed by darker. In common use the sequence is yellow, red, blue and black; the yellow film, still wet, should pull the red ink from the roller or "trap" it. According to Henry Green the capacity of trapping at high printing speeds is measured by Bingham's plastic viscosity but Bowles has doubted this identification of plastic viscosity with the property of an ink known as tack and a discussion on the subject took place at the Smithfield research laboratories of PATRA just after the founding of our Society. Since then the research staff of PATRA has shown that the phenomenon of tack is highly complex, and as yet not well understood, involving cavitation, surface tensions, liquid cohesion in the breaking of liquid threads, adhesion, etc. The breaking of ink threads can occur in several ways depending on speed and variety of ink; if the threads break into fragments instead of at a single point with snap-back of the broken thread into the ink film, then misting can occur.

Tack has been defined as the pull resistance during the splitting of the ink film and is a complex function of the time and pressure in the nip of the press. In the printing trade a measure of the resistance in terms of instrument readings is made by the tackmeter (Inkometer, Reed) which, although giving little insight into the rheology of the process, yet can grade inks in order of tack. This has been found useful in colour printing when inks of increasing tack are required in sequence.

The phenomena involved in film splitting are as yet little-known especially that of cavitation, its onset and progress.

Some progress is now being made in bubble counts and increase in size, using transparent models of a press and observing with high-speed photography the splitting film as it emerges from the nip. P. Eisenberg, 1963, in reviewing the subject of cavitation indicated that it is a complex and many-faceted process and as yet little understood. It is thought to begin in the presence of minute gas or vapour nuclei; however the source of these nuclei and just why they exist are still unresolved questions. Once a nucleus starts growing into a full-fledged bubble, the resulting flows may become very complicated. In one mode, the bubble may retain its identity through several cycles

of tentative collapse and rebound, and final collapse produces high pressures in the nearby liquid. The bubbles in the ink film on emergence from the roller nip act as centres of dilation until they coalesce and leave an accumulation of filaments. The higher the ink viscosity the lower is the velocity at which cavitation sets in.

The insight into the complex nature of film splitting is undoubtedly a step forward in establishing the rheological theory of tack but little is known clearly of how the rheological parameters of the bulk ink correlate with tack, the problem being complicated by the heterogeneous nature of the inks and their widely differing formulations. The presence of moisture, inclusions of air, variations in temperature and pressure distribution, add to the problem. Tackmeters for high-speed inks have now been developed and it is possible to grade inks according to their degree of tack, the resistance being recorded by special devices other than by the original Reed inkometer torque. The printer is now able to purchase a range of tack graded inks in numbered sequence, standardised by "most modern equipment" from soft letterpress to stiff hand-proofing black, so that as advertised he can check the results of his own efforts of subjective testing with a rubbed-down blob of ink and flick of the forefinger.

In lithographic printing tacky inks necessitate the use of papers with high pick strength and a complex ink distribution system to improve the flow. Now new printing plates requiring less damping and improved damping systems have made possible the use of inks of lower tack.

The application of adhesives and polymer coatings in the printing and paper trades requires special equipment and speeds to obviate uneven coatings and stringing or cottoning. New materials are continually being tried out in the formulation of adhesives as with inks, e.g., it was recently stated that high-speed labelling machines require changed properties of gum dextrans which are now replaced by pyrodextrans (starch roasted at 230° to 275°F.).

Again, polydiene and polyturpene resins are said to confer beneficial properties to polyethylene.

A section of Severs' book, *Rheology of polymers*, Reinhold, 1963, is devoted to the application of polymer solutions and compositions. The two principal methods of application involve: (a) coating by means of a knife, either floating or fixed and the web of the substrate is continuously passed under the knife. With the fixed knife there is a "back-up" under the web. (b) roller application, either by a forward roller (like a two-roller wringer) or more usually by a reverse roller. In the forward roller method, when the speed of the web is the same as the roller, ridges in the emergent film are formed and disappear only if the rheological properties are right—as with freshly painted enamel coatings showing brush markings. In the reverse roller coating machine the roller rotates in a reverse direction to the

movement of the web. Viscous coatings can be applied in this way without corrugations and less solvent is required. Severs next describes the application of polymer solutions containing dyes and pigments used in the printing press for plastics, metal foil, etc., by the letterpress printing method, developed by Gutenberg, in which a raised inked surface, usually in the form of a forward-moving roller with raised pattern or inscription, is pressed on the web.

No explanation has yet been given for the formation of the tiresome corrugations in the film of adhesive or polymer coating emerging from the nip of the forward-moving roller applicator, described by Mill for printing-ink films, at the Exeter University conference; can it be due to turbulence, vortex motion, surface tension effects in thin film formation, compressional waves or a combination of these? A general theory of the flow of thickened suspensions over a range of shear rates can be established only when more definite information is available on the internal relative motions of the individual particles, their rotations, positionings and general freedom of movement.

Ruth Weltmann in *Rheology Theory*, 1960, vol. 3, chap. 6, has given descriptive equations relating the plastic viscosity and dynamic yield value of suspensions with pigment concentration—the constants of the equation being functions of particle shape and surface. Kluitenberg, 1963, in a paper on the thermodynamics of viscosity and plasticity, has derived a general rheological equation from which well-known equations of flow can be derived. He gives explicit expressions for free energy, internal energy and entropy. For plastic media with memory, a rheological equation holds which may be considered as a generalisation of the Poynting-Thomas equation.

Rheology of Paints—Principles and Difficulties

A one-day symposium, organised jointly by the British Society of Rheology and the Paint Research Association, was held at the Paint Research Station, Teddington, on April 29th, 1964.

The support for this meeting was extremely gratifying and indicated how live were the topics discussed. Unfortunately, a number of people had to be disappointed as accommodation available made it necessary to limit the attendance to 200 registered delegates.

The meeting was notable in several ways. It was the first meeting devoted entirely to paints, printing inks, etc. that had been held for many years by the Society and it was also the first joint venture of the collaborating bodies. Moreover, it was also an experiment with a concentrated “reporting” type of meeting as some twenty pre-arranged contributions were presented, besides general discussions,

in the few hours available. Clearly, such a meeting had to be fairly strictly timed and our best thanks go to all the contributors who so ably presented the salient features of their papers in their allotted times. Timing, incidentally, was assisted by use of an electric "lecture prompter" for the loan of which we are indebted to the Council of the Institution of Chemical Engineers.

Some of the summaries of the main contributions have already appeared in Rheology Abstracts and the remainder will appear in the next issue. It is now hoped to publish the transactions of the symposium in full.

Rheology Course at Slough College

The Secretary, as representative of the Society, was present as a guest of the College at a one-day course entitled "Viscosity and its Measurement" held on April 16th, 1964, at Slough College, William Street, Slough, Bucks. Unfortunately, we were not notified of this meeting in time to announce it in the last issue of the Bulletin.

The course was organised by Dr. J. F. Richardson and Mr. J. W. Sellars of Slough College and there was an attendance of about a hundred. The programme was as follows: General review of recent techniques for viscosity measurement (Dr. H. G. Jerrard of Southampton University); Techniques for the measurement of viscoelastic behaviour under alternating shear stress (Prof. J. Lamb of Glasgow University); Rheological classification (Dr. G. W. Scott-Blair of the National Institute for Research in Dairying); Viscosity of oils (Mr. C. E. Carpenter of the Admiralty Oil Laboratory); Rheology of paints (Mr. T. R. Bullett of the Paint Research Station).

Future meetings of the Society

As was mentioned in the last Bulletin, the dates for the Autumn meeting are September 28th to 30th and the subjects are "Rheology in Education" and "Rheogoniometry." Our guests at the annual dinner will be Sir James Cook, F.R.S., Vice-Chancellor of the University of Exeter, and Lady Cook, Professor G. K. T. Conn and Mrs. Conn. Any member wishing to make a particular contribution to the educational discussion should contact Dr. J. H. C. Vernon, 15 Long Deacon Road, Chingford, London, E.4.

The Committee is trying to arrange a conference for April 1965 at Nottingham University and a topic being considered is "Flow Properties of Powders."

Has powder rheology been too much neglected in the U.K.? We well recall T. C. Daniels on apparent viscosity measurement of a fluidised bed at the Swansea Conference in 1957 ("Rheology of Disperse Systems" Ed. C. C. Mill, Pergamon 1959) and that one of

our members, Dr. Barbara Neumann, contributed a chapter on powders to "Flow Properties of Disperse Systems" (Ed. J. J. Hermans, Amsterdam, 1953). There would appear to have been some interesting developments that might find applications in the fields of powder metallurgy and granular plastics, *e.g.*, Jenike's work (Inst. Chem. E. 3rd Congress of the European Federation of Chemical Engineering 1962, paper 1026: University of Utah Bulletins 95, 96, 108) and of course a considerable amount on fluidisation. Is it time that these matters were reviewed from the rheological standpoint?

Would any member who can either contribute a formal paper at the proposed Nottingham conference or who has any special thoughts on powder rheology generally, please get in touch with the Secretary or with Dr. R. L. Whitmore of the Department of Mining Engineering, University Park, Nottingham.

Other meetings

The Acoustics group of the Institute of Physics is arranging a symposium on "Sonic investigations on internal damping in solids" to be held in London on August 5th to 7th. For further details write to the Institute, 47 Belgrave Square, London, S.W.1.

The Institute of Physics and the Physical Society is also organising a conference on many-body problems in physics and chemistry at Manchester on September 22nd to 24th. There will be sessions on polymers and liquids.

On October 7th and 8th the Institution of Mechanical Engineers is holding a symposium entitled "Plastics and the mechanical engineer." Write to the Institute at 1 Birdcage Walk, London, S.W.1.

Further afield is the venue of the Second Australasian Conference on Hydraulics and Fluid Mechanics. This will be held at the University of Auckland, December 6th to 12th, 1965. Papers on all aspects of fluid mechanics and hydraulics are invited. The address of the Conference convenor is: c/o University of Auckland, School of Engineering, Ardmore College Post Office, Auckland, New Zealand.

Rheology in Agriculture

Dr. A. C. W. Davies of the National Institute of Agricultural Engineering, is interested in the rheological properties of wheat and barley grains, peas and beans, apples, pears, potatoes, etc. Will any member who is also interested in these products, or who may have techniques which could be used on them get in touch with Dr. Davies. His address is: Harvesting and Handling Dept., National Institute of Agricultural Engineering, Wrest Park, Silsoe, Bedford.

Address wanted

Can anyone inform the membership secretary of the present address of Mr. A. R. Payne, please ?

Postgraduate Courses in Rheology

Details are now available of the courses in the Physics Department, Battersea College of Technology, commencing on October 5th, 1964. The duration of the course leading to the postgraduate diploma of the College (D.C.T.(Batt.)) will be one year full-time or at least two years part-time, but individual lecture courses may be taken by students who do not wish to register for the examination.

Lecture courses so far announced are as follows:

- I. "Mathematical Theory of Stress and Deformation" by R. Tearse, M.Sc., and E. G. Lawrence, M.Sc. Wednesdays, 10 a.m.-12.15 p.m. until March 1965.
- II. "Measuring Techniques and Analysis of Observations" by R. W. Whorlow, B.Sc., A.R.C.S., A.INST.P. Fridays, 2.45-5.00 p.m. until March 1965.
- III. "Rheology of Solid Polymers" by M. Braden, PH.D., A.INST.P., A.I.R.I., A.P.I. Wednesdays, 6.30-8.30 p.m. until December 9th, 1964.
- IV. "Rheology of Metals." Wednesdays, 6.30-8.30 p.m. commencing January 13th, 1965.

Full-time applications should be sent to the Head of the Physics Department. Further details and enrolment forms for part-time courses may be obtained from the Secretary (Rheology Courses), Battersea College of Technology, London, S.W.11.

Miscellaneous news in brief

The Exploratory Committee on Rheological Research has now almost completed its allotted task and will report to the Executive Committee in June.

Dr. J. H. C. Vernon now represents the Society on the working party for materials, science and technology, set up by the Institution of Chemical Engineers.

Professor Raymond R. Myers of the Department of Chemistry, Lehigh University, Bethlehem, Pa., and Editor of the (American) Society of Rheology, will be in Britain during June and hopes to visit British Nylon Spinners, the Paint Research Station and Glasgow University.