

POLYMER COLLOID GROUP NEWSLETTER

Vol. 5 No. 1

15 September 1975

I am sorry to say that contributions from only half the members reached me by the deadline for this issue. If I do hear from Ottewill, Pochlein~~X~~ Saunders~~X~~, Stannett, ~~Wagstaff~~, Vanderhoff~~X~~ Wallace, and Yelisiyeva in the next few weeks, I can bring out a Supplementary Issue in December. Will both contributors, defaulters, and newly elected members make a note of the deadline for Volume 5, Issue 2 now? If need be, go out and buy yourself a 1976 diary instead of waiting in the hope that some one will give you one for Christmas!

Both Nomura and Piirma have agreed to join the Group but I think they may be excused from contributing to this issue. I had a contribution in hand from Ed Collins raising questions about the analysis of Higher Order Tyndall Spectra but since he couldn't abbreviate the eight pages of data, he is sending his contribution out directly from Avon Lake. Osmond's contribution is even longer but he was judicious enough to delay sending it until the last minute by which time it was clear that the 8 members noted above were not going to take up their 24 pages!

Although Irv Krieger has had to resort to the use of double-spacing to pad out his contribution, his student seems to have made a lot of progress with the preparation of the azo-sulphonate initiator. Gardon has addressed letters on this topic to Rhone-Poulenc both to New York and to Paris but hasn't had any reply yet. The Litt-Waite route from propane sultone may be the best proposition.

Spring Newsletter The deadline for the second (as distinct from any supplementary) issue of the year will be Monday 26th April 1976 in my office. Will members therefore despatch their contributions (up to 3 pages - single spaced) before the Easter holiday.

Annual Meeting Friday/Saturday 18/19 June 1976 at Lehigh University, Bethlehem, Pennsylvania preceeding the 50th National Colloid Symposium at San Juan, Puerto Rico 21-25 June 1976. Will members let Gary Pochlein know their intentions as to attendance as soon as possible.

A.S.D.

Polymer Colloid Group
Membership List - 1975

North American Circulation

1. Dr E.A.Collins, B.F.Goodrich Chemical Co. Technical Center, P.O. Box 122, Avon Lake, Ohio 44012, U.S.A.
2. Dr R.M.Fitch, Department of Chemistry, University of Connecticut, Storrs, Connecticut 06268, U.S.A.
3. Dr J.L.Gardon, M & T Chemicals Inc., 26701 Telegraph Road, Southfield Michigan 48076, U.S.A.
4. Dr I.M.Krieger, Olin Building, Case-Western Reserve University, Cleveland, Ohio 44106, U.S.A.
5. Dr S.G.Mason, Department of Chemistry, McGill University, P.O.Box 6070, Montreal 101, Quebec, Canada.
6. Dr I. Piirma, Institute of Polymer Science, The University of Akron, Akron, Ohio 44325, U.S.A.
7. Dr G. Poehlein, Department of Chemical Engineering, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.
8. Dr A.A.Robertson, Pulp and Paper Building, Department of Chemistry, McGill University, P.O. Box 6070, Montreal 101, Quebec, Canada.
9. Dr F.L.Saunders, DIG Physical Research, Building 1712, Dow Chemical USA, Midland, Michigan 48640, U.S.A.
10. Dr V.T.Stannett, Department of Chemical Engineering, Box 5035, North Carolina State University, Raleigh, North Carolina 27607, U.S.A.
11. Dr J.W.Vandernoff, Center for Surface and Coatings Research, Lehigh University, Bethlehem, Pennsylvania 18015, U.S.A.
12. Dr T.P.Wallace, Department of Chemistry, Rochester Institute of Technology, Rochester, N.Y. 14623, U.S.A.
13. (Associate Member) Dr D.J.Williams, Foster Grant Co. Inc., 289 North Main Street, Leominster, Massachusetts 01453, U.S.A.

Circulation to the Rest of the World

- ✓ 14. Dr D.C.Blackley, National College of Rubber Technology, Northern Polytechnic, Holloway, London N7 8DB, England.
- ✓ 15. Dr A.S.Dunn, Department of Chemistry, UMIST, P.O. Box 88, Manchester M60 1QD, England.
- ✓ 16. Dr D.H.Mapper, Department of Physical Chemistry, The University of Sydney, Sydney, New South Wales 2006, Australia.
- ✓ 17. Dr M. Nomura, Department of Industrial Chemistry, Fukui National University, Fukui, Japan.
- ✓ 18. Dr R.H.Ottewill, School of Chemistry, University of Bristol, Bristol BS8 1TS, England.
- ✓ 19. Dr J. Ugelstad, Department of Industrial Chemistry, Norwegian Institute of Technology, 7034 Trondheim-NTH, Norway.
PWS Osmond Research & Development Dept.
- ✓ 20. Dr ~~F. Waite~~, I.C.I.Ltd. Paints Division, Wexham Road, Slough, Bucks. SL2 5PS
Dr J. A. Wetton
- ✓ 21. Dr V.I.Yeliseyeva, Institute of Physical Chemistry, Academy of Sciences of the U.S.S.R., Leninsky Prospekt 31, 117312 Moscow, U.S.S.R.

RELATIONSHIP BETWEEN PARAMETERS OF POWER-LAW FLOW EQUATION FOR RUBBER LATICES

D. C. Blackley, National College of Rubber Technology, The Polytechnic of North London, Holloway, London, N7 8DB.

INTRODUCTION

In recent years, we have become very interested in the flow properties of rubber latices whose viscosities have been increased by the operation of factors which are usually assumed to cause some destabilisation of the latex as a colloid system. Our investigations have fallen under two main headings:

(1) Those concerned with blends of concentrated soap-stabilised non-carboxylated SER latices and ammonia-preserved centrifuged natural rubber latices (1-5). The principal interest here is the observation that a rise in viscosity occurs when the blend is first prepared, but that, on maturing over a period of a few hours, the viscosity falls to the level which would be expected if the latices merely mixed with no interaction occurring between the particles. The extent of the initial viscosity rise depends very much upon the composition of the blend, being greatest when the volume fraction of natural rubber in the contained polymer is in the region of 60-70%.

(2) Those concerned with the gradual thickening which occurs when ammonia-preserved natural rubber latex is compounded with zinc oxide and ammonium salts are also present (4-7). This problem is of considerable industrial interest, since zinc oxide is frequently added to natural rubber latex as a compounding ingredient, and ammonium salts are either added deliberately, or are present anyway through interaction between the ammonia preservative and various acidic substances in the latex.

In common with many other workers in the field of flow properties of materials, we have found that our data for shear stress (T) as a function of shear rate ($\dot{\gamma}$) over several decades of shear rate can often be accurately represented by a simple power-law relationship, which we write in the form $T^N = \eta' \dot{\gamma}$. In this equation, N is an index whose value indicates the degree to which the flow properties deviate from those of a Newtonian fluid (for which $N = 1$), and η' is a measure of the apparent Newtonian viscosity under conditions of given shear rate. (Note that η' is primed to emphasise that it is not a viscosity in the usual sense, nor are its units Poise, except in the special case when $N = 1$.)

Hitherto, the parameters N and η' of the power-law flow equation have been regarded as independent parameters. However, in our work we have frequently noticed that the changes in N as some variable (e.g., time of maturation) is varied seem to follow those of η' , in that high values of the one seem to be associated with high values of the other. The purpose of this contribution is to report that, having taken a random selection of pairs of values of N and η' , we find that there is indeed a strong correlation between the two in that $\log \eta'$ seems to vary linearly with N . However, the precise nature of the relationship between the two depends upon the mechanism by which the change in flow properties was brought about.

RESULTS

Figure 1 summarises the data which first drew attention to the existence of the correlation. This graph gives a random selection of pairs of values for $\log_{10} \eta'$ (η' in cgs units) and N obtained from the programme on the flow properties of blends of SER and IR latices. The viscometer used was the Hoake Rotovisko with a bob and cup arrangement. Shear stress as a function of shear rate was obtained from the raw experimental data using the procedure of Krieger, March and Bird (3,8). The relationship between $\log_{10} \eta'$ and N is clearly linear if one excludes certain points for latices having $N = 1$. The latter are, of course, Newtonian in behaviour, and this implies that for such fluids η' and N are independent parameters. For those latices whose flow behaviour is markedly non-Newtonian, the relationship

between η' and N can be represented by the equation

$$\log_{10} \eta' = 2.85(N - 1)$$

Figure 2 gives a few pairs of results for $\log_{10} \eta'$ and N selected at random from the programme on zinc oxide thickening. Again a concentric cylinder viscometer was used, but in this case the instrument was the Sprecht Rheomet 15. The same computational procedure was used for obtaining shear stress as a function of shear rate. Although the data in this case cover a rather smaller range of values of η' , and N , Figure 2 shows that again the relationship between $\log_{10} \eta'$ and N is linear, and also the slope is approximately the same as that for the results summarised in Figure 1. However, the intercept is different. For a given value of N , η' is approximately two orders of magnitude lower than in the case of the previous results.

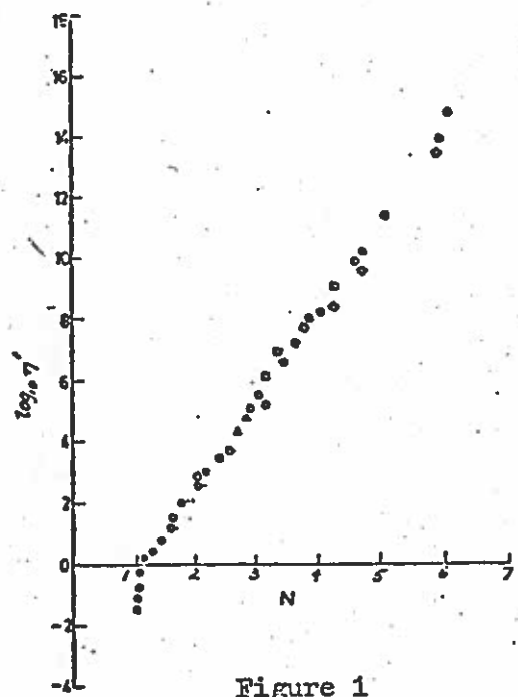


Figure 1

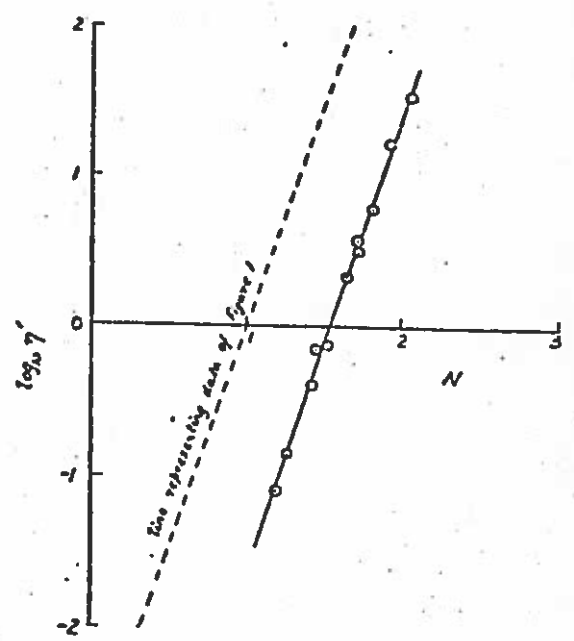


Figure 2

DISCUSSION

The power-law flow equation as given above can be re-written in the form $F/G = \eta' / F^{N-1}$. Since F/G is equal to η , the apparent Newtonian viscosity when the shear stress and shear rate are respectively F and G , this equation shows that:

- (1) η' can be interpreted as the apparent Newtonian viscosity under conditions of shearing such that $F = 1$; and
- (2) the fluid is shear-thickening, Newtonian, or shear-thinning according as $N < 1$, $N = 1$, or $N > 1$.

Scott Blair (10) has given a very simple mechanistic interpretation of the significance of N for disperse systems. Non-Newtonian behaviour is assumed to arise essentially from a superposition of two effects:

- (a) The application of a shear stress is assumed to encourage the breakdown of "linkages" between particles, i.e., to induce de-flocculation.
- (b) The presence of the shear rate which inevitably accompanies the application of a shear stress then discourages re-flocculation of the particles produced by de-flocculation of agglomerates under the influence of the shear stress.

Thus, whereas the shear stress increases the concentration of de-flocculated particles, which situation would otherwise be expected to lead in turn to an increase in the rate of re-flocculation, the shear rate discourages re-flocculation.

Scott Blair assumes very simple kinetics for the effect of shear stress and shear rate upon the number of linkages, n , namely $dn/dF = -a/F$ and $dn/dG = -b/G$, where a and b are constants. Elimination of dn followed by integration readily gives a power-law relationship between F and G with $N = a/b$. Thus N is interpreted as the ratio of two quantities, one of which characterises the ease with which the system de-flocculates under the influence of the applied shear stress, and the other of which characterises the reluctance to re-flocculate because of the prevailing shear rate.

The correlations we have observed suggest that N increases linearly with $\log \eta'$ and that the precise relationship depends upon the mechanism by which the instability to which the viscosity variation is attributed was induced. For the data to which Figure 1 refers, the destabilising mechanism is believed to be transfer of adsorbed stabilisers from one latex to the other; for the second set of data, the destabilising mechanism is believed to be adsorption of zinc ammine ions at the rubber-particle interface, with possible chemical reaction between adsorbed cations and soap ions.

Thus our observations indicate that N varies linearly with the logarithm of the apparent Newtonian viscosity at unit shear stress. If the Scott Blair interpretation of N is accepted, then the implication is that the ratio of the parameters characterising stress-induced de-flocculation and shear-prevented re-flocculation increases with $\log \eta'$. That N should increase with η' is understandable in a general way, since a higher η' implies a higher shear stress at a given shear rate, and therefore a higher rate of de-flocculation at any given rate of re-flocculation. However, the precise significance of the logarithmic relationship is not clear at present, and is being given further consideration. That the observed relationship between N and η' depends upon the manner by which the stability of the latex was reduced is also understandable, since the mode of destabilisation would be expected to affect the nature of the linkages to be broken. It will be interesting to see whether the slope of the $\log \eta'$ vs. N relationship is generally independent of the mode of destabilisation, and also to what extent the relationships observed for rubber latices apply to other disperse systems.

REFERENCES

1. D. C. Blackley and R. S. Charnock, J. of I.R.I., 1973, 7, 60
2. D. C. Blackley and R. S. Charnock, J. of I.R.I., 1973, 7, 113
3. D. C. Blackley and R. S. Charnock, J. of I.R.I., 1973, 7, 151
4. C. M. Lau, B.Sc. Project Thesis, N.C.R.T., 1972
5. C. K. Thong, B.Sc. Project Thesis, N.C.R.T., 1973
6. B. A. Ahmad Zamani, B.Sc. Project Thesis, N.C.R.T., 1973
7. S. H. Goh, B.Sc. Project Thesis, N.C.R.T., 1974
8. I. M. Krieger and S. H. Maron, J. appl. Phys., 1952, 23, 147
9. I. M. Krieger and H. Elrod, J. appl. Phys., 1955, 24, 134
10. G. W. Scott Blair, Rheological Acta, 1965, 4, 55

Does the Smith-Ewart Theory account adequately for the effect of changing the emulsifier?

Mr W. Al-Shahib, a graduate of the University of Baghdad, has been working on this problem here for the past year and is now submitting an M.Sc. Thesis. I showed some of the results he has obtained in the course of my lecture at the Trondheim A.S.I. I hope that we shall be able to prepare a definitive publication on this topic within the next few months.

B.D. Peppard (Ph.D. Thesis Iowa State (1974) University Microfilms 74-15,446 Supervisor: W.H. Abraham) has recently confirmed the occurrence of the oligomeric precipitation mechanism of latex particle formation can occur even with styrene if the latex is sufficiently dilute leading to the formation of new particles below the c.m.c. of the surfactant in seeded polymerisations. Nevertheless the classical assumption of the micellar mechanism for latex particle formation is generally believed to be valid for styrene. The results which Dr N. Sutterlin (Rohm, Darmstadt) tend to confirm this: he showed that there was a rapid increase in the number of latex particles formed as the emulsifier concentration was increased through its c.m.c. with styrene but that this effect diminished as the water solubility of the monomer increased. C.P. Roe (Ind. Eng. Chem. 60 (1968) 20) obtained similar results and additional evidence indicating that the micellar initiation hypothesis of Harkins should be discounted and that it was possible to derive the Smith-Ewart equations (which have by several independent schools to be quite precisely applicable in the case of styrene) without reference to this assumption the critical factor being rather the strength of the adsorption of the surfactant on the latex particles. Since the concentration of surfactant molecules in molecular solution is practically constant above its c.m.c. the concentration of adsorbed surfactant (and hence the stability of the latex particles) must also be constant. However as the surfactant concentration is increased beyond its c.m.c. the total amount of surfactant available increases so that a greater total area of latex surface can be stabilised. This results in a greater number of latex particles provided the surface charge density (or steric barrier in the case of a non-ionic) provided by the constant adsorbed concentration is large enough to prevent particle coalescence. If it is not addition of salt may increase the concentration of adsorbed surfactant enough to stabilise the particles despite the simultaneous effect of increasing ionic strength decreasing barrier heights by decreasing Coulombic repulsion. Such an effect would account for the early observation of W.B. Reynolds (quoted by Fryling in Whitby ed. 'Synthetic Rubber' Ch.8) that soaps which have an insufficiently long alkyl chain to be effective in emulsion polymerisation may be used if salt is added: the effect was originally attributed to lowering of the c.m.c. but has not been investigated quantitatively. It looks as though we need a lot more information about the adsorption isotherms of surfactants on latex particles at various ionic strengths although Ron Ottewill said at Trondheim that he had more information of this kind not yet published.

Anyway, Roe still obtains

$$N \propto (p/\mu)^{0.4} (a_s)^{0.6}$$

and a_s the interfacial area occupied by unit amount of soap at the time when particle generation ceases is the only factor variations in the constitution of the surfactant used can be taken into account: it is generally taken as the area occupied in a supposedly saturated monolayer at the point where micellisation begins in solution as determined by the soap titration method. However Dr T.R. Parson pointed out at Trondheim that he had found (J. Coll. Interface Sci. (1968)) that latex particle surfaces are not, in fact, generally saturated with surfactant at this point. The values of a_s vary only from 41.4 for C_{12} to 23.4 $\text{\AA}^2/\text{molecule}$ for C_{18} in the sodium alkyl carboxylate series. This variation seems insufficient and in the wrong sense to account for the observed effect of variation of the alkyl chain length in a homologous series of surfactants on the rate of emulsion polymerisations. Several publications

(Carr, Kolthoff, Meehan, & Williams (1950) for SBR, Hopff & Falka for vinyl chloride, Ivanova & Yurzhenko (1960) and Ryabova, Beresnev, & Smirnov (1972) for styrene) find the rate of emulsion polymerisation increases with the alkyl chain length of the emulsifier both when equal weights and equimolar amounts of emulsifier are used. This is because of an increase of the number of latex particles formed since it was found in the last investigation cited that the rate per particle is independent of the emulsifier used. However the equation and the values of a_s cited above indicate that the number of particles formed would be expected to decrease with increase of alkyl chain length when equimolar concentrations are used which seems implausible! Curiously no attempt to investigate this point experimentally has previously been reported. This is most probably because the alkyl carboxylic acids are the only homologous series of surfactants available commercially in high purity. Other series have to be synthesised from the alcohols: there are several reports of their colloidal properties (e.g. c.m.c. etc.).

Initially surprising difficulty was encountered in trying to determine conversion-time curves gravimetrically with persulphate initiation because of irreproducible induction periods. Use of azodiisobutyronitrile initiation overcame this difficulty but at the expense of inability to calculate expected rates quantitatively since no theory for oil-soluble initiators is yet available. The origin of the difficulty was only discovered at a late stage: although the monomer had been carefully deoxygenated, the water phase had not been! So the reaction studied was actually the styrene-oxygen copolymerisation! However its rate was found to increase with alkyl chain-length for n-alkyl sulphates and n-alkyl sulphonates as well as n-alkyl carboxylates.

When persulphate initiation was used in a thoroughly deoxygenated system the observed rate with sodium dodecyl sulphate emulsifier was in good accord with his observations on this system and the expected rate calculated from his equations. However SDS is a surfactant with a relatively high c.m.c. of 0.011 M which is not negligible in comparison with the total concentration used 0.0232 M. B.M.E. van der Hoff pointed out some years ago that if, as assumed by Smith & Ewart and by Gardon, latex particles are formed exclusively from micelles, then the soap concentration to be used in the equations should be the concentration of micellar soap found by subtracting the critical micelle concentration from the total concentration. The difference is negligible only for surfactants with low c.m.c. such as potassium stearate or potassium palmitate. It was found that in the oxygen retarded experiments the concentration of the lower homologues used was actually below their c.m.c. (the observed rates, though low, were nevertheless significantly higher than in a blank experiment using a high stirring speed but no emulsifier). Accordingly in the new series of experiments concentrations of emulsifiers were chosen to give equal concentrations of micellar soap, 0.012 M. Rather to our surprise we found that all the soaps appeared to give the same rate of polymerisation in Interval II under these conditions and to give the same size (and hence number) of latex particles. However this tentative conclusion may have to be revised. The lower homologues may actually give higher rates. We had already noticed that the results were sensitive to the purity of the emulsifier different rates being observed with samples of 'pure' stearic acid of different origin. Spectrographic and polarographic analysis of the two samples of decanoic acid used showed that the sample giving the same rate as the higher carboxylates was actually the less pure sample containing traces of heavy metals e.g. Mn which, surprisingly, seem to be retarding rather than accelerating the reaction. We hope to try the experiment of adding similar amounts of the impurities identified to the purer sample to see if the retarding effect can be reproduced.

It may happen, as suggested by Ottewill, that the amounts of the different soaps adsorbed on the latex particles are equal at the point where their critical micelle concentrations are attained in solution although this does not seem to be in accord with the determinations of a_s by soap titration. If, as suggested by Gardon, particles are initiated from micelles and the critical factor is the total surface area presented by the micelles, this would be expected to vary for different members of the homologous series at equal micellar concentrations because the micelle sizes vary.

Emulsion Polymerisation of Styrene at 60°C using EqualMicellar Concentrations of Alkyl Potassium Carboxylates

Initiator Potassium persulphate 0.2% on water phase = $7.46 \times 10^{-6} \text{ mol cm}^{-3}$
 Micellar soap concentration 0.012 mol dm⁻³ *Ionic strength* $2.24 \times 10^{-2} \text{ mol dm}^{-3}$

Acid	Alkyl chain length	c.m.c. mol dm ⁻³	Conc. mol dm ⁻³	Rate %/min	10 ⁵ B/s ⁻¹		10 ⁻¹⁶ N/cm ⁻³	
					Obs.	Calc	Obs.	Calc.
Octanoic	C ₈	0.39	0.4020	1.73	8.80	-	0.263	-
Decanoic(A)	C ₁₀	0.10	0.1120	2.10	10.6	-	0.247	-
" (B)	"	"	"	1.77	9.0	-	0.267	-
Lauric	C ₁₂	0.025	0.0370	2.46	12.5	8.60	0.304	0.122
Myristic	C ₁₄	0.0065	0.0185	1.74	8.85	7.62	0.234	0.108
Palmitic	C ₁₆	0.0017	0.0137	1.73	8.80	6.38	0.234	0.090
Stearic	C ₁₈	0.00044	0.01244	1.75	8.90	6.03	0.234	0.085
Behenic	C ₂₂	0.000028	0.0120	1.73	8.80	-	0.219	-

May be ~ 10% low because of ionic strength.

The names of the acids are those favoured in the current B.D.H. catalogue. Purity better than 99% by G.L.C. (or acidimetry for lauric, stearic, and behenic) All B.D.H. products except Palmitic which was from Fluka, and Decanoic (B) from Price's Ltd (Bromborough) 99% acidimetric; this sample contains traces of heavy metals absent in sample (A).

c.m.c. calculated from $\log(\text{c.m.c./mol dm}^{-3}) = 1.96 - 0.296n$ given by Gerrens in the 'Polymer Handbook' 1st (1966) Edn.

Values of B and N were calculated using Gardon's equations where values of a_s were available, using the concentration of micellar soap not the total surfactant concentration as used by Gardon himself.

Repeatability of experiments

Persulphate initiation with potassium behenate (with a slight excess of alkali) at 60°C.

Weight in 212 cm ³ water		Rate %/min	10 ⁵ B/s ⁻¹	Diameter D _w /nm	10 ⁻¹⁵ N/cm ⁻³
Persulphate	Behenic acid				
0.414 g	6.8116 g	5.83	28.75	63.36	2.20
0.414 g	6.8116 g	5.65	29.66	55.99	3.19
0.424 g	0.8685 g	1.73	8.80	63.47	2.19 (as above)

Variation of the emulsifier concentration seems to make a large difference to the Interval II rate but none to the final particle size (measured at 100 % conversion).

Particle sizes were measured by the Light Scattering technique of Burnett, Lehrle, Overall, & Peaker (J. Polym. Sci. 29 (1958) 417)

Polymer Colloids Newsletter

News from UConn by R. M. Fitch

Lately we've been working in two areas, (1) kinetics of polymerization and of particle nucleation - coagulation - radical capture by a combination of time dependent light scattering and laser interferometry. From the former we have found that primary particles coagulate at rates approaching the Smoluchowski limit when they are uncharged. In the presence of sodium lauryl sulfate the coagulation rate is greatly retarded. These primary particles were formed as a result of the u.v.-induced initiation of MMA in aqueous solution by acetyl radicals. We conclude that coagulation of primary particles may be extremely rapid and an important factor in determining N from the very beginning of a polymerization, when ionic end-groups and/or emulsifier are present in amounts insufficient to stabilize. In other words, in the equation $dN/dt = R_i - R_c - R_f$, the last term, the rate of coagulation, may be positive almost from time zero. This work was done by postdoctoral fellow Richmond Watson last year.

(2) Chemistry at the interface. We are looking at polymer colloids as possible chemical reagents, heterogeneous catalysts, drug-release agents, etc. Our results to date are summarized by Mssrs. Gajria and McCarvill below:

C. Gajria:

Polymethyl methacrylate latexes have been prepared at room temperature using a persulfate-bisulfite - iron redox system. Two types of ionic end-groups are supposedly obtained, $-SO_3^-$ and $-SO_4^-$, which migrate to the polymer/water interface and are measured by conductometric titration of the ion-exchanged latex. Both $-SO_3^-H^+$ and $-SO_4^-H^+$ are titrated as strong acid groups but the presence of weak acid groups has also been observed. These are thought to arise from the hydrolysis of the methacrylate ester of the MMA monomer. Presence of the $-COOH$ groups has been confirmed by titrating the latex in a 1:1 isopropanol: water mixture, according to the procedure recommended by Dave Bassett.

For our conductometric titrations we have used $Ba(OH)_2$ which gives approximately 30% higher weak acid content as compared to titrations of the latex with $NaOH$. This higher weak acid value is obtained in titration with both $Ba(OH)_2$ and $NaOH$ when the latex is diluted in the $i-PrOH$ - water mixture.

Surface charge density calculations for one of the latexes show that surface area per charged end-group is nominally $\sim 10 \text{ \AA}^2$. This would seem to indicate that the PMMA particles do not have a hard surface as envisioned for polystyrene latex particles, but a gel-like, filamentations surface.

We have observed an increase in the weak acid content with time for the ion-exchanged, very high surface charge density latex. No such increase was seen with a latex of much lower surface charge density. We attribute the increase in weak acid content to hydrolysis of the methacrylate ester in the surface polymer chains.

The hydrolysis of the surface ester groups is probably catalyzed by neighboring $-SO_3^-H^+$ and $-SO_4^-H^+$. Kinetic data at 75°C and 90°C , show that the self-catalyzed interfacial hydrolysis follows an apparent zero-order rate with an activation energy of ~ 14 kcal. Surprisingly, even at 90°C very little hydrolysis of the $-SO_4^-H^+$ groups to $-OH$ and yielding H_2SO_4 is observed.

W. McCarvill:

During the preparation of small particle size polystyrene latices it was observed that upon treatment of the raw latex with large amounts of mixed bed ion exchange resin the latex flocculated. Numerous exchanges of the latex with small amounts of ion exchange resin was also unsatisfactory in that the solids content decreased due to adsorption of particles on the exchange resin. Since conventional dialysis requires very long times, a continuous hollow fiber device was used to remove most of the salts and emulsifier from the latex in 24 hrs. This was followed by a single treatment with a relatively small amount of ion exchange resin. Polystyrene latices of about 500 Å diameter particle size, stabilized by surface sulfate acid groups, and about 10% solids were successfully purified by this method. It appears that hollow fiber dialysis alone cannot purify the latex as well as the combination of dialysis and ion exchange. After five days of continuous dialysis a sample of latex exhibited much higher conductance than that of another sample which had been ion-exchanged after 24 hours dialysis. The effluent water from the dialysis of the 5-day run had the same conductance as the entry water. The treatment involved dialysis against H₂O, then HCl and finally water again to ensure that the surface groups were in the hydrogen form.

The surface acid groups of a polystyrene latex particles initiated by Potassium persulfate/sodium bisulfite/iron appear to be hydrolyzable confirming observations of others. To circumvent this latices are being prepared using the redox couple sodium bisulfite/ferric nitrate yielding non-hydrolysable (hopefully) surface sulfonic acid groups. A solution of ferric nitrate is metered into a reaction vessel containing water, monomer, emulsifier and sodium bisulfite. Purification by the dialysis/ion exchange method results in a stable, iron-free latex.

Finally, I should like to report that we have found a convenient source of large quantities of an ionizable monomer, sulfomethyl styrene. Dow recently announced availability of chloromethyl styrene (mixed m- and p- isomers). From it we have made in 62% yield the sodium salt of sulfomethyl styrene by an easy synthesis, directions for which I shall happily send on request. For those who want small samples ($\leq 20g$), we can send you some.

Three new people have joined our group: K. Prakash will be working on the synthesis and characterization of latices containing novel chemically reactive groups at the interface; Bob Traut will attempt the synthesis of model colloids based on PTFE and study particle-surface interactions; Kalyan Chakraborty will be applying laser interferometry to obtain the kinetics and absolute rate constants of polymerizing systems under non-steady-state conditions.

J. GARDON

Dr. John Gardon, in cooperation with Dr. Rebecca Spearot of the University of Detroit, started a new project on thixotropy and non-linear viscoelasticity. Many latex-based systems are thixotropic, that is their viscosity decreases with increasing rate of shear and increasing time of shearing.

In the past, study of such systems was subject to an "uncertainty principle" in that only one shear field was used both for measurement and for imparting changes in structure. Now the measuring shear field and the structure-destroying shear field are separated.

A rotary viscometer is used, with the spindle rotating and with the cup conventionally stationary. In the new work the cup can be oscillated in the vertical direction. Thus the measuring shear field, imparted by the rotating spindle, is horizontal and the structure-destroying shear field is vertical.

Latex-based paints and drilling muds were first studied. At a given spindle velocity, the viscosity decreased with increasing amplitude or frequency of the cup oscillations. (Alternately, at given oscillations or with a stationary cup the viscosity decreased with increasing spindle velocity). It is significant that for a Newtonian liquid such as glycerol, vertical oscillations do not influence the measured viscosity (and, of course, the spindle velocity has no effect either).

We are now switching to well defined model systems, improve our apparatus and try to develop mathematical interpretations. Also, time effects are being studied.

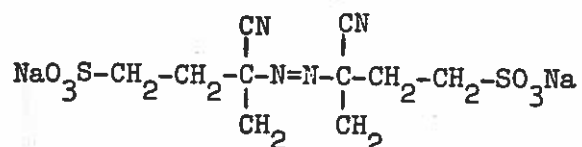
Polymer Colloid Newsletter Contribution

September 15, 1975

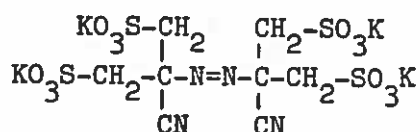
I. M. Krieger

Very little progress to report since the last Newsletter. There has been a turnover in personnel, change in direction, and much soul-searching.

Emulsion polymerization studies: M. S. Juang completed his study of emulsifier-free polymerizations incorporating ionic comonomer. This work is embodied in his Ph.D. Thesis, and in a paper submitted to the Journal of Polymer Science (preprint sent to all corresponding members). The polymerization studies have been picked up by L.-J. Liu, who will focus on the problem of incorporating desired chemically bound groups at the particle surface. He has carried out the synthesis of



according to the Rhone-Poulenc patent (U.S. #3,161,630). Yield was low and, although he obtained positive NMR identification of the last intermediate, he has not yet been able to confirm the identity of the product. It decomposes in solution to give N_2 , initiates emulsion polymerization of styrene, and gives a stable uniform latex containing only strong acid surface groups. A sample will be sent out for elemental analysis. Mr. Liu is also attempting synthesis of a tetrafunctional analog:



and will proceed with the synthesis of a difunctional analog starting with propane sultone, as suggested by M. Litt and by F. Waite.

A set of standardized recipes has been developed for uniform polystyrene latices, using a mixture of ionic and nonionic surfactants. These were tested by a student inexperienced in polymerization. Recipes for stirred reactors (round-bottom flasks or resin kettles) proved reliably reproducible, but recipes for bottle polymerizers gave large amounts of coagulum, and required modification to incorporate more surfactant. The latest recipes will be tested further before dissemination.

Rheology: M. Eguiluz completed his work on the second electroviscous effect in 1974. It has been submitted to Transactions of the Society of Rheology for the Eirich commemorative issue, and can be found in the NATO Preprints. No rheological work is currently active.

Light scattering: C. Havens is starting work on laser light scattering from dilute suspensions and free films. Professor J. A. Mann, Jr., is collaborating in directing this work, and has made his autocorrelator and his photon counting spectrometer available.

Cooperative Program: At the Group meeting in Trondheim, the CWRU contingent agreed to prepare a sample of emulsifier-free latex for distribution to eight laboratories. Because of the low polymer content ($\sim 10\%$) of emulsifier-free recipes, and the limited size (4ℓ) of available reactors, Mr. Liu will have to prepare and blend two batches in order to provide sufficient polymer. He is currently comparing several batches, and hopes to meet the October 1 deadline.



DEPARTMENT OF CHEMISTRY
OTTO MAASS CHEMISTRY BUILDING (514) 392-4467

McGILL UNIVERSITY

S.G. MASON and A.A. ROBERTSON

Contribution to Polymer Newsletter September 1975.

The following are reports of recent developments in research projects related to polymer colloids.

Polystyrene latexes have been synthesized in a surfactant-free system by a method based on that of Kotera et al. (Kolloid-Z.u.Z. Polymere 239, 677 (1970) but in which the polymerization rates and yields have been improved by the addition of an alcohol (methanol) to the reactants. The effects of varying the methanol content and other process variables on the polymerization and on the properties of the latex have been reported in a preprint, circulated to the group, of a paper "Experiments with Soap-Free Polymerization of Styrene in the Presence of Alcohols" (J. Appl. Polymer.Sci., in press).

Dr. Per Stenius, while a guest at our laboratories, has been looking at the mechanism and kinetics of this system.

The progress of the reaction has been followed as a function of temperature, monomer concentration, methanol content, initiator concentration and ionic strength by (a) measuring the styrene content by amperometric titration, (b) measuring the turbidity of the solution and (c) measuring the final size and charge of the latex particles by electron microscopy and conductometric titration respectively.

Conditions were chosen to ensure initiation in completely homogeneous solution. The appearance of latex particles is shown by the increase in turbidity and is accompanied by a substantial increase in the rate of polymerization. Hence, it would seem that the coagulation of oligomers into latex particles is accompanied by a transfer of the main site of the polymerization into these particles. The particle radius increases linearly with time, indicating that the rate of adsorption of monomers into the particles is diffusion controlled. The rates of polymerization before and after the point of coagulation are easily reproducible, but the point at which coagulation takes place is very sensitive to initial conditions. It appears that the solution becomes supersaturated with oligomers that, on coagulation, form colloiddally stabilized particles. The reason for the increased polymerization rate in methanol/water mixtures probably is a consequence of the increased solubility of the monomer which increases the rate of diffusion to the particle surfaces. At the same time, continuous initiation appears to be necessary, since for lower $K_2S_2O_8$

concentrations the reaction stops at low conversions. This may be due to competitive reactions between the persulfate radical and the methanol.

Mr. Mohamed Labib has undertaken work to follow up the applicability of mass transport electrophoresis to the characterization and investigation of latexes. In the course of this work, the usefulness of an Amicon TCF 10 Diafiltration apparatus has been demonstrated for the purification, equilibration or concentration of latexes with considerable savings of time over conventional procedures.

The stability of cationic latexes and their interaction with fibre surfaces is the subject of an active project involving Mr. Mitsuo Inoue and Dr. B. Alince. Some of the aspects of the work were presented at Trondheim and a report is being prepared for publication.

Microrheology of Colloidal Dispersions (E.B. Vadas, H.L. Goldsmith and S.G. Mason)

Work has been completed and is being written up for submission as a Ph.D thesis to McGill University. The following is the proposed abstract.

"An experimental apparatus, the hydraulically driven microtube, was designed and built to permit tracking the movements and interactions of individual colloidal particles and aggregates in Poiseuille flow through capillary tubes from 400-100 μ radius. The operation of the device was tested using dilute aqueous suspensions of 2 μ diameter latex spheres and biconcave 8 μ diameter human red cells in plasma, particles subject to Brownian diffusion and electrostatic and van der Waals forces.

The perturbation of the shear-induced motions of doublets of 1 μ and 2 μ diameter rigid spheres by rotary Brownian diffusion was studied in detail. The effect of rotational Brownian motion on the distribution of the orientation of the axis of revolution was experimentally determined and shown to agree with theoretical predictions.

Finally a study was made of concentrated transparent O/W emulsions containing 50 to 70% dispersed phase. Marked blunting of the velocity profiles was observed at all flow rates, the extent of blunting being dependent on dispersed phase concentration and flow rate. The radial dispersion of tracer particles was measured along with distributions of the particles across the flow tube as a function of downstream position."

Interaction of Colloidal Particles in Shear Flow (T.G.M. van de Ven and S.G. Mason)

The theoretical and experimental work has now been completed and is being written up for submission as a Ph.D. thesis to McGill University. The following is the proposed abstract.

"The theory describing the behavior of two equal-sized spheres in shear flow of low Reynolds numbers has been extended to take into account interaction forces between the spheres. Depending on the nature of the interaction forces, two kinds of doublets can be formed in a flowing suspension: two spheres constituting a doublet can either touch or orbit each other at a small distance. From the period of rotation of non-touching (secondary) doublets it is possible to determine the equilibrium distance between the spheres.

The existence of both types of doublets in monodisperse suspensions of polystyrene latex spheres was confirmed experimentally, although secondary doublets behaved somewhat differently from the predictions, making the determination of the equilibrium distance rather difficult. The discrepancies are most likely due to inhomogeneities in the distribution of surface electrical charges on the spheres.

The theory of secondary doublets in shear flow was extended to linear aggregates. It is predicted that a linear array of non-touching spheres will stretch and shorten periodically as it rotates in shear flow. Observations of linear aggregates of polystyrene latex spheres confirm this. Observations of aggregates show that they are either flexible or rigid depending on the ionic strength of the medium. Flexible aggregates are believed to consist of non-touching spheres and rigid aggregates of touching ones.

Using a two-sphere model we have developed a theory for orthokinetic coagulation in dilute suspensions. It is found that the capture efficiency in such suspensions depends on the shear rate G and on the nature of the particles and the suspending fluid (e.g. the particle size, surface potential, Hamaker constant, ionic strength, viscosity, retardation wavelength, dielectric constant).

We have also calculated the capture frequency in systems in which the effects of Brownian motion dominate those of shear. It is found that the usual assumption of additivity of ortho- and perikinetic collision rates is incorrect; the increase in the capture frequency due to shear is proportional to G^2 and to the perikinetic capture efficiency.

These findings have a number of important implications in the stability, flocculation and coagulation of colloidal sols."

Polymer Colloids at Sydney University

D.H.Napper

1. Emulsion Polymerization Kinetics We have (we think) solved the the set of differential equations that govern seeded emulsion polymerizations allowing both for first order free radical exit from the particles and for bimolecular termination. No resort was made to the stationary state assumption. We argue that such a solution is superior to the steady-state analysis on two accounts: first, it describes both the steady-state and the approach to the steady-state (i.e., it describes in principle the whole of a seeded kinetic run); second, it circumvents a logical inconsistency that we maintain appears when one attempts to solve the Smith-Ewart equations containing an exit term, with the aid of the steady-state assumption. The new solution brings the Smith-Ewart cases I and II together under the same theoretical umbrella.

2. Stability of Emulsions We have spent some time showing that sterically stabilized emulsions exhibit the same incipient flocculation behaviour as do latex particles, provided one takes due precautions. This enables one to transfer many of the ideas developed for latexes to the discussion of emulsion stability.

3. Elastic Steric Stabilization We have recently developed an analytic expression for the elastic contribution to steric stabilization in the compressional domain. It is difficult to test this expression experimentally because the accompanying mixing term is usually large. However in a polymer melt, the latter term is near zero and stability arises primarily from the elastic term. The theory predicts good stability for large particles with PEO of M.W.1540 and 6000 as stabilizers in liquid PEO of the same (or different) MW but the onset of instability with PEO 600 . Experimental results that support these conclusions have been obtained.

THE SHEAR-THICKENING EFFECT IN CONCENTRATED DISPERSIONS

Introduction

The fact that many concentrated particulate dispersions exhibit an abrupt increase in resistance to flow with increasing rate of shear has been known for many years; equally, the effect has long been assumed to be associated with the phenomenon of "dilatancy". Dilatancy was first described by Reynolds (Ref 1) as the increase in volume which must occur in reasonably closely packed beds of particles if large-scale displacement of the particles relative to one another is to take place.

Although a number of papers, both experimental and theoretical, have appeared on shear-thickening (Ref 2, 3, 4, 5, 6) no fully satisfactory quantitative theory of the phenomenon appears yet to exist. In part, this may be associated with the inadequacies of the experimental materials examined. For example, in dispersions of corn starch in water, the particles are not spherical, nor mono-disperse, nor is the colloidal stability perfect or its mechanism fully understood.

Some years ago, Wagstaff et al carried out for ICI Paints Division an elaborate series of rheological measurements on a range of well characterised non-aqueous polymer colloids. A brief selection of their results and a discussion of general pattern into which they fell, has recently been published (Ref 7). With the exception of the finest particle sizes (in which the volume occupied by the steric stabilising sheath is substantial compared to that of the particle core) all of the specimens showed pronounced shear-thickening, although the abruptness and shear rate at which occurred depended upon particle size and phase volume.

Last year, a visiting worker (Dr Charles Chaffey) attempted a re-analysis of the Wagstaff results. Although he had considerable success in fitting equations to Wagstaff's curves, (and indeed this work is to be published) the equations were at least in part empirical and some of the fundamental mathematical parameters could not therefore easily be identified with any specific physical process. In the course of many group discussions on the progress of Dr Chaffey's work, it became clear to us that the concept of an "apparent mean viscosity", in the way it is usually conceived, is probably an illegitimate concept when applied to the flow of highly concentrated particulate dispersions (Cf Ref 3). In many cases, the degree of particle packing is so high and yet, at moderate shear rates, the resistance to flow (in appropriate viscometers) is so extraordinarily low that the flow of the material must involve ordering on a scale which is very large compared to the size of an individual particle. i.e. in the flowing system the bulk of the particles must exist in rods or sheets, at concentrations very close indeed to critical packing, and undergo negligible relative displacement, while the whole of the relative motion between these effectively "solid" masses of particles and the rigid walls of the apparatus is accommodated in one or more relatively thin layers of mobile pure continuous phase (or very dilute dispersion).

However, the problem now arises, as to why such a stable organised structure, once established, should not persist - at least to shear rates very much higher than those at which the abrupt onset of shear thickening (which we identify with the dilatant jamming effects due to the breakdown of this organised behaviour) actually occurs. However, it is important to realise that the results of Wagstaff et al were obtained on a Weissenberg Rheogoniometer and therefore do not present a continuous sweep of increasing shear rate on a given sample; on the contrary, each point constitutes an individual experiment in which a sample "at rest" was accelerated (during which time presumably, the appropriate organisation occurred) up to the recorded shear rate. Now the Weissenberg Rheogoniometer is deliberately designed so that the time to accelerate the plates is short and nearly constant irrespective of the ultimate shear rate; i.e. the rate of acceleration (which is of course inversely related to the time available for the achievement of an ordered structure) is directly related to the ultimate shear rate to which the specimen is to be exposed. The horrid possibility thus appeared, that all of the shear thickening which had been observed was associated with instrumental artifacts! Fortunately, a representative (approximately one micro-metre particle diameter, homo-polymer methylmethacrylate particle core) dispersion used by Wagstaff had survived. Arrangements were therefore made to examine the behaviour of this material on a borrowed Ferranti-Shirley viscometer, using programmed increases in shear rate. The results (which it is hoped to publish in due course in the ordinary literature) were rather more complex than anticipated, but clearly indicated that certain features-notably the conditions under which shear-thickening occurred for a given specimen - were indeed dependent upon the characteristics of the measuring instrument.

As an alternative to the problems of working with a borrowed instrument, it was realised that the variables of starting transient time-constant, shear rate, absolute rotational speed, etc. could be disentangled while still using the Weissenberg Rheogoniometer by appropriate modification of the geometry of the plates. Initially, this was limited to changing diameter and cone angle, but later, despite the theoretical objections, it was found particularly useful to move to a parallel plate geometry and vary the rotational speed and the gap width. The results obtained, which comprise the body of this contribution, contain some surprising, and we believe important, features.

Acknowledgements

The experimental work described below was carried out by T A Strivens and directly supervised by F A Waite. The author wishes to thank both of these for permission to submit this preliminary account of their work to the Polymer Colloid Group Newsletter.

Summary

The rheological characteristics of a single sample of a well characterised non aqueous polymer colloid have been studied. Results are presented for a Weissenberg Rheogoniometer using both cone and plate and parallel plate platten geometries.

The variables studied have been:-

- 1 Concentration of the polymer colloid
- 2 Cone angle and plate size
- 3 Gap width (for parallel plate geometry)
- 4 Rotational speed

Conclusions

- 1 The results are not independent of instrument geometry unless all dimensions (including gap width) are very large compared to the size of an individual dispersed particle. It thus follows that all results on highly concentrated particulate dispersions obtained using cone and plate geometry are in error!
- 2 Even with appropriate instrument geometries, concentrated polymer colloids do show a sharp transition from low resistance, apparently Newtonian-like flow to a highly resistant, solid-like character. Although the point of this transition does depend on the characteristics of the instrument, particularly the time-constant of its starting-transients.
- 3 This transition may most plausibly be associated with the failure to achieve (or the break-up of) a highly organised laminar flow pattern to give a random, dilatantly jammed mass of particles.
- 4 The transition from the stable, low resistance flow pattern is associated not with a specific value of shear rate, initial transient time constant (although this must be short enough, relative to the shear rate and the "intrinsic" time constants for diffusion of particles in the sample to initiate the transition,) rotational speed, rheometer geometry, nor even dispersions concentration, but for a given sample of dispersion, is defined uniquely by a critical shear stress.
- 5 The analysis of the full Wagstaff results, in the light of Conclusion 4 above, suggests that the critical shear stress for the transition does, however, depend upon the particle size.
- 6 There is evidence to suggest the provisional correlation of the actual value of this critical shear stress for any given system with the point at which the associated interparticle hydrodynamic stresses provide interparticle compressive forces which exceed the collapse strength of the interparticle stabilising barriers, so that the particles are no longer able to move (with low friction) past one another into "close-packed" arrays.

RESULTS AND DISCUSSION

Preparation of Sample

Methyl methacrylate was polymerised at 80°C with azobisisobutyronitrile initiator in an aliphatic dispersion medium of hexane and a high boiling hydrocarbon fraction (B.Pt. 230-250°C), using a 1% w/w on a monomer of poly 12-hydroxystearic acid stabiliser (M.Wt.1600). A two-stage seed and feed process was used. (Ref. 8).

At completion of polymerisation, the hexane was stripped off under vacuum to give a high solids dispersion.

Characteristics of Dispersion Sample

As prepared, the material was a viscous dilatant liquid at room temperature, showing characteristic solid-type fracture when pushed hard or quickly with a spatula; such fractures filled up slowly by liquid flow.

Solids of the sample were determined as 70% w/w. Electron microscopy showed remarkably even sized spherical particles. Measurement of pictures showed a mean particle diameter of 1.0×10^{-6} metre with coefficient of variance = 6.6%.

Preparation of Dispersion Samples for Rheological Measurements

As prepared, the sample was not very convenient for rheological measurement. A series of diluted samples, covering the solids range 60-70% w/w (corresponding approximately to a polymer core phase volume fraction of 0.50-0.60), was prepared, yielding a range of apparent viscosities from a few tenths to a few hundred poises. Dilutions were carried out by weight and the sample bottles rolled for six hours to homogenise the samples before sampling for rheological measurement.

Rheological Measurements

These were made in steady continuous shear using the Weissenberg Rheogoniometer, equipped with a cone and plate or parallel plate pair of plattens. The diameter and cone angle or gap widths of these were varied. Temperature control was effected by maintaining the room temperature at $25.0 \pm 0.5^\circ\text{C}$.

As previous work by Dr I Wagstaff had shown that normal force measurements were difficult to obtain due to erratic behaviour with these samples, a solid lower platten assembly was used in the Rheogoniometer measurements. Care was taken to ensure that the plattens were mounted exactly as specified for accurate work in the instrument handbook.

Previous Work

This work has been presented briefly as part of a book (Ref 7). Concentrated polymethyl methacrylate dispersions of different particle sizes were prepared as above. The significant features of their rheological behaviour may be seen in Fig 6.2 and 6.3 of Ref 7). As shear rate is increased, the apparent viscosity decreases (shear thinning), then passes through a minimum, before increasing more or less steeply (shear thickening). In some cases, abrupt rises in viscosity of several orders of magnitude occurred at a particular shear rate.

At constant phase volume, reducing the particle size increased the shear thinning and viscosity minima values. On the other hand, shear thickening was more pronounced with coarser particles (2.02×10^{-6} metre diameter), whilst the shear thinning effects were smaller and the viscosity minimum value lower than for fine particle dispersion (1.1×10^{-7} metre diameter). Reduction of the solid phase volume led to reduction of shear thinning and a shift of shear thickening to higher shear rates. The effects were most noticeable with essentially monodisperse systems, broad distribution of particle size or deliberate blending tended to flatten out the characteristic curves obtained.

Shear thinning effects were distinctive in that equilibrium viscosity values were obtained almost instantaneously at all shear rates. If the phase volume was calculated to include not only the polymer core, but also the phase volume of the stabiliser sheath, then the occurrence of shear thinning was noted only when this total phase volume was similar or greater than that corresponding to random close-packing (Ref 7). No detectable hysteresis occurred in the shear-thinning (i.e. the system is not thixotropic). These results were reanalysed in the light of our own results with one of these dispersion samples and theoretical work by Dr C Chaffey (Ref 9).

Effect of Change in Cone and Plate Dimensions on Rheological Measurements

Measurements were made using the one micron particle diameter dispersion at solids concentrations of 60%, 65% and 67.5% w/w with plate diameters varying from 2.5 to 7.5 cm and cone angles of $\frac{1}{4}^{\circ}$ to 4° . The results are presented in Fig 1-3.

The essential features of the earlier work of Wagstaff and Waters are reproduced as described above. However, rather wide differences in behaviour were observed, when the cone and plate parameters were changed. However, with one cone and plate system, successive samples gave reasonable reproducibility of rheological behaviour, even when the instrument sensitivity was changed by using a torsion bar with a different torsion constant (c.f. Fig 3).

It was noticeable that the "breakaway" in viscosity values was not correlatable with any particular values of shear rate or angular velocity of the cone. However, when shear stress was plotted against shear rate, instead of apparent viscosity, a correlation becomes obvious, namely, most of the curves approximated to Newtonian behaviour (45° slope on double logarithmic plate) with the onset of viscosity breakaway occurring in a narrow band of shear stress values (Fig 4).

In the Weissenberg Rheogoniometer, the mechanical structure of the instrument is such that measurements can only be made at discrete shear rate values. Further, the sample has to be at rest for at least one minute, whilst the gear box settings are changed to alter the shear rate value for the next measurement. The provision of an electromechanical clutch between the motor drive and the driven platten ensures that shear of the sample stops and starts very rapidly (within 10^{-2} second according to the instrument manufacturers), consequently, the acceleration the sample receives is variable but always a function of the shear rate value chosen, for a particular pair of plattens.

Measurements with Ferranti-Shirley viscometers allow the acceleration rate to be controlled independently of the shear rate value, but by equipping the Weissenberg Rheogoniometer with parallel plates, it is possible to maintain the acceleration of the lower plate constant, whilst varying the shear rate by systematic variation of the gap width. Whilst the parallel plate geometry is not amenable to exact rheological analysis in the steady shear rate regime (for discussion of this point see Walters Ref 10), it does allow wider variation of shear rate, using the same plattens, than the corresponding diameter cone and plate system, merely by varying the gap width setting between the plates.

Variation of Gap Width. Rheogoniometer with Parallel Plates

Markovitz (Ref 11) has published an analysis of the steady shear rate regime when applied to parallel plate geometry, and we have used this to calculate shear stresses and shear rates (see below).

Six gap widths were chosen ranging from 0.5 thou to 50 thou and the 65% solids dispersion sample was measured at each of these gap widths over an angular velocity range of 0.025 to 1.25 radian sec^{-1} . At the narrowest gap setting, the gap width corresponds to only 12 times the particle diameter, whilst at the widest gap setting, the gap width corresponds to 1200 times the particle diameter. Further, at the widest gap setting, clear visual observation could be made of changes in the liquid flow pattern. The data obtained is presented in Fig 6. It will be seen that the data for 10, 25 and 50 thou gap settings are exactly coincident, whilst if the gap width is narrowed beyond this range, the stress-strain rate plots move progressively along the x axis (i.e. to lower viscosity values). The plots all have a 45° slope and breakaway more or less abruptly at the same critical shear stress value as was obtained for the cone and plate data. The breakaway is more abrupt and to a line of steeper slope the wider the gap setting whilst, below the breakaway point, exact straight lines of 45° slope were obtained (c.f. cone and plate data over same shear rate range, below).

However, as will be seen from the figure, a Newtonian standard oil tested at two gap settings shows coincident data lying on an exact straight line of 45° slope over the whole range of shear rates tested. Further, the corresponding viscosity value is within 5% of the calibration figure for the oil.

Clear evidence of a change in liquid flow regime at the breakaway point was obtained with the widest gap setting. At the shear rate setting of 98 sec^{-1} , when platten rotation commenced, the torsion head deflection was in excess of the maximum measurable, and the liquid at the edge of the plattens formed into pockets and twists and projecting lumps. After about thirty seconds, the liquid edge became smooth and this corresponded to the attainment of a steady measurable torsion head deflection. At the next highest shear rate setting (155 sec^{-1}), the same behaviour was observed, but although the drive was maintained for up to three minutes, no reversion to smooth flow occurred.

Re-examination of Cone and Plate Data Weissenberg Rheogoniometer

Fresh diluted samples of dispersion were prepared and examined in more detail, using the same cone and plate pairs as before, and a more sensitive torsion bar to allow the shear rate range covered to be increased. The data is presented in Fig 5.

The results were similar to the previous runs. In contrast to the parallel plate data, shear thinning was observed, and even in one sample, indications of a first Newtonian region at very low shear rates.

Assessment of Critical Shear Stress

The shear stress value corresponding to the onset of a shear stress-strain rate relationship whose slope exceeded unity (on double logarithmic axes), and the appearance of apparent turbulence in the sheared liquid flow, was determined when possible. In some cases, the change was so abrupt that only the last recorded shear stress value in the Newtonian region is given. The results are given in Table I, together with the results from a similar analysis of the earlier data of Wagstaff (Ref. 7, 9).

It should be noted that in all the Weissenberg experiments, although the liquid edge was initially level with the platten edges, before the critical shear stress was attained, the liquid was bulging outwards from the platten edges. As spot checks showed no alteration in the gap setting, it is suspected that the total suspension volume has increased under shear stress (volumetric dilatancy, see below).

TABLE I

Dispersion System : polymethyl methacrylate dispersed with poly 12-hydroxystearic acid in high boiling aliphatic hydrocarbon.

1 Effect of particle size and solids (Wagstaff data)

Cone Angle 0.5° Gap Setting 0.5 thou Diameter 5.0 cm

Particle diameter (10 ⁻⁶ m)	Solids (% w/w)	Critical Shear Stress (dyne cm ⁻²)	Remarks
0.11	61.3	-	Critical shear stress not reached
	56.5	-	
	50.2	-	
0.24	73.8	(450-1000)	Abrupt shear stress rise at next point
	60.5	-	Critical shear stress not reached
	55.0	-	
0.52	64.9	270	Abrupt shear stress rise at next point
	61.9	260	Slope exceeds 45° at this value
	55.8	260	
2.02	56.0	18	"

2 Effect of Cone Angle and Plate Size (Strivens data)

Particle size : 1×10^{-6} m diameter

Gap Setting (thou)	Cone Angle (degree)	Cone Diameter (cm)	Solids (% w/w)	Critical Shear Stress (dyne cm ⁻²)	Remarks
0.55	0.31	2.5	60.0	140	First departure from 45° slope
			60.0	120	
			65.0	110	
			67.5	125	
0.83	0.48	5.0	60.0	140	" Abrupt change at next point
			60.0	120	
			65.0	140	
			67.5	110	
2.75	1.53	7.5	60.0	180	First departure from 45° slope
			60.0	120	
			65.0	140	Abrupt change at next point
			65.0	125	
			67.5	100	
67.5	110	"			
6.96	4.00	7.5	67.5	30	

3 Effect of Gap Width

Particle size : 1×10^{-6} m diameter. Dispersion solids 65.0% w/w
Platten diameter 5.0 cm

Gap Setting (thou)	Critical Shear Stress (dyne cm ⁻²)
0.5	130
1.0	125
5.0	125
10.0	120
25.0	115
50.0	120

DISCUSSION OF RESULTS

Comparison of Cone and Plate and Parallel Plate Data

Below ten thou gap width, the apparent viscosity value of the dispersion falls as the gap width between the parallel plates is decreased. A similar dependence on gap width is to be seen with the cone and plate data, except for the 67.5% solids dispersion, where difficulty in obtaining sufficiently reliable data points may well have obscured the effect. It should be noted that data independent of the gap width value was not obtained until this was some 250 times the average particle diameter for the dispersion. These effects are reminiscent of the wall effects, "sigma phenomenon" etc. commonly observed in capillary viscometry of suspensions. Such effects, and their possible causes, have been reviewed by Goldsmith and Mason (Ref 12). The parallel plate data show at all gap widths an absence of the shear thinning or thickening, which is clearly noticeable in the cone and plate data, prior to the shear stress "breakaway" at the same solids value (c.f. Fig 5 and 8). The shear rate range in both cases is the same. For the parallel plate case, the shear rates quoted are the maximum ones obtaining at the rim of the driven plate, and given by (Ref 11).

$$\dot{\gamma}_r = \frac{\Omega}{l} R$$

Where R is the radius of the plate (or the distance along the radius from the centre) and l is the gap width. This is by contrast to the shear rate independent of radius (for small cone angle α) for the cone and plate system.

$$\dot{\gamma} = \Omega/\alpha$$

is the angular velocity in both cases.

These results must inevitably cast doubt on the validity of any measurements made on dispersion systems, where the sample-filled gaps in the rheological measuring instrument have dimensions less than two orders of magnitude greater than the expected particle size in the dispersion.

Previously Published Work

Freundlich & Roder (Ref. 13) appear to have been the first to have recognised and qualitatively described rheological dilatancy (as opposed to volumetric dilatancy described earlier by Reynolds (Ref. 1)) in the flow behaviour of concentrated suspensions. They also put forward a qualitative explanation; at low shear rate, there is sufficient time for particles to move past each other, but as the shear rate is increased, a certain value of shear rate is reached at which the particles can no longer "make way" for each other and they pile up at the interface with the shearing surface, thus creating considerable resistance to the shearing motion. At points in the

suspension volume remote from the shearing surface, the suspension is stretched and cracks form which fill up with liquid. This behaviour, providing the solids is high enough, resembles solid behaviour, but providing the spheres do not stick together, it lasts only as long as the external force is maintained, and as soon as this is removed, the spheres redistribute themselves more uniformly and the system reverts to a liquid.

Metzner and Whitlock (Ref. 2) were the first to make quantitative measurements. They also reviewed earlier work on dilatancy in suspensions. Reiner (Ref. 3) appears to have been the first to point out the necessity for a close packed high solids suspension to rearrange its particles in layers touching each other before shear flow can occur.

Other experimental results on pigment systems and on dilatant starch suspensions has been published by Fischer (Ref. 4), Green & Griskey (Ref 5) and Morgan (Ref 6).

With the possible exception of Morgan's work on iron oxide pigments stabilised with polymethacrylic acid, all of these papers report results on poorly characterised suspension systems with rather crude rheological apparatus. The first criticism may again be made of recent work by Hoffman (Ref 14) on polyvinyl chloride dispersions in dioctyl phthalate, but he has used more refined rheological measurement techniques. In particular, he has used a most elegant technique to demonstrate not only the presence of the layered two dimensional flow pattern in sheared concentrated suspension suggested by Reiner (Ref 3) and Metzner and Whitlock (Ref 2), but also that the onset of a large shear stress rise and an abrupt viscosity rise at a particular shear rate is identifiable with a breakdown in this pattern. This he has achieved by fitting a Weissenberg Rheogoniometer with a parallel plate system consisting of a lower mirror finish metal platten and an upper polished glass platten. By studying and analysing light diffraction patterns at the same time as making the rheological measurements, it is possible to study shear induced changes in particle order.

Other explanations of the observed rheological behaviour on the basis of phenomena other than dilatancy may be eliminated by the following considerations. Both with cone and plate and parallel plate geometries, Newtonian standard oils (ex Paint Research Institute) give a constant viscosity value over the range of shear values used for the dispersions, thus eliminating the possibility of Reynolds turbulence as a macroscopic phenomena (not, however, on a particle dimension scale). Heating effects may be neglected as a 200 Poise standard oil does not show any fall in shear stress with time at high shear rate. Similarly, centrifugal forces are not high enough (a low viscosity 5 Poise oil is not ejected from the plattens at the highest shear rate used for the suspensions).

We would like to propose the following mechanism to explain our experimental results. In concentrated suspensions, the free volume available to an individual particle is limited and is randomly distributed. For large scale flow of the sample, co-operative movement of many particles into "close-packed" sheets (or other arrays) must occur to generate substantial continuous regions of free volume else-where.

When movement of the lower platten begins at a sufficiently low shear rate value, the time allowed for the bulk of the sample to move unit distance under steady state conditions, is sufficient to enable the particles to move into a spatial configuration appropriate to maintain a steady state under the imposed shear rate. There is no reason to suppose that the steady-state velocity gradient would be linear across the gap width as is the case with Newtonian liquid. As the suspension concentration increases, the freedom of particle movement becomes more restricted and thus more time is required to attain this appropriate spatial configuration. Correspondingly, the shear rate corresponding to the onset of critical phenomena, occurs at a rapidly decreasing value, as the suspension concentration increases close to the close packing concentration. If we take the reciprocal of this critical shear rate value † as being indicative of the time required to attain such spatial configuration, then an interesting pattern emerges, when we consider all the results together.

At 60% solids (corresponding to a total phase volume fraction of 0.534*), the critical shear rate is located at about 250 sec⁻¹ corresponding to a time value of 4×10^{-3} second, which is less than the 10⁻² seconds quoted by the Weissenberg Rheogoniometer manufacturers for the attainment of a given shear rate. The critical shear phenomena are mild, and even when the shear rate is raised to seven times Weissenberg critical shear rate value over a period of two minutes in the Ferranti Shirley, the results closely match the Weissenberg values and no hysteresis is observed.

Once the critical shear rate is exceeded, the spatial organisation does not have time to form, the particles become jammed together and the whole sample acts as a solid. The shear stress increases sharply and the force on individual particles become sufficient to cause the particles to adhere through collapse of the stabiliser barriers. Moreover, if the shear rate is maintained for long enough or the shear stress becomes high enough, the quasi-solid structure fractures. Random aeration of the sample then takes place and the results have no meaning.

The results with the 65% solids show these features nicely. The critical shear rate is 100 sec⁻¹ (corresponding to 10⁻² second) and the total solid phase volume is 0.591 (the value for regular cubic packing of monodisperse spheres is 0.524; this being the "loosest" packing). The critical shear phenomena are .', pronounced, and both hysteresis and "fracture" are observable in the Ferranti-Shirley traces (although the latter only occurs if the Weissenberg critical shear rate is exceeded by nearly two orders of magnitude. Similar comments can be made about the 67.5% solids experiments (total solid phase volume 0.620 and critical shear rate value 10 sec⁻¹, corresponding to critical time of 0.1 second).

* See Appendix at end of report

† We refer to this as a critical shear rate value for simplicity sake, as it has already been shown above, it is associated with the critical phenomena, but very dependent on experimental conditions, which the critical shear stress, corresponding to the onset of critical phenomena, is not.

Summing up, we consider our experiments to be the first report of rheological dilatancy in concentrated suspension systems in which the constituent particles are accurately monodisperse spheres, stabilised by a well-understood mechanism (steric stabilisation, see, for example, Ref 15). We have demonstrated how an apparently mobile liquid suspension can, if it is allowed too short a time to attain a given shear rate value, take some of the characteristics of a solid. It remains only to consider the significance of the critical shear stress value.

Significance of Critical Shear Stress Value

The following argument, although approximate, suggests that the critical shear stress value corresponds to the work done in compressing the steric stabiliser barrier of the particles at one point.

Let the total volume fraction be ϕ , and the number of particles per unit volume n .

Then, for spherical particles of radius r ,

$$\phi = \frac{4}{3} \pi r^3 n \quad (1)$$

For a unit area plane, the number of particles cut by the plane $\sim n^{2/3}$. From (1)

$$n^{2/3} \sim \left(\frac{3\phi}{4\pi} \right)^{2/3} \frac{1}{r^2}$$

If it is now supposed that for any place of unit area, on average, half the particles cut by it have their centres below the plane, and if the plane is parallel to the shear stress direction, the shear stress is forcing half $n^{2/3}$ particles against a further half $n^{2/3}$ particles at a variety of angles. Suppose these angles average 45° . Then

$$\frac{T_m}{T_c} = \cos 45^\circ = \frac{1}{\sqrt{2}}, \quad T \text{ shear stress (dyne cm}^{-2}\text{)} \quad (3)$$

If the measured shear stress T_m corresponds to the critical condition (as is assumed in equ. (3)), then from equ. (2) & (3), the critical force per particle (F_c) is given by

$$F_c = \frac{2}{\sqrt{2}} \left(\frac{4\pi}{3} \right)^{2/3} \left(\frac{\gamma}{\phi^{1/3}} \right)^2 \cdot T_m \quad (4a)$$

$$= 3.675 \left(\frac{\gamma}{\phi^{1/3}} \right)^2 \cdot T_m \quad \text{dyne} \quad (4b)$$

The corresponding work done by compressing the barrier through a distance equivalent to its uncompressed thickness of 130 Å (13 nm)

$$W = 4.778 \times 10^{-6} \left(\frac{\gamma}{\phi^{\frac{1}{3}}} \right)^2 \cdot T_m \text{ erg} \quad (5)$$

Using the data of Table 2 leads to calculated values of critical force per particle and work per particle per point of compression as follows (Table 3)

TABLE 3

Particle (Total) Radius () (cm x 10 ⁻⁵)	Total Disperse Phase Volume (φ)	Average Critical Shear Stress (T _m) (dyne cm ⁻²)	Critical Force per particle (F _c) (dyne x 10 ⁻⁶)	Work Done (W) (erg x 10 ⁻¹²)
1.33	0.541	450 (min)	0.440	0.57
		1000 (max)	0.978	1.27
2.73	0.458	260	1.19	1.55
	0.521	260	1.10	1.43
	0.553	270	1.10	1.42
5.13	0.541	137	2.00	2.61
	0.598	123	1.75	2.28
	0.598	123 *	1.68	2.18
	0.629	115	1.52	1.97
10.1	0.460	18	1.23	1.60

* Parallel plate data

It will be seen that the range of W values between 1.3 and 2.6 x 10⁻¹² erg approaches the range 3.1 to 14.0 x 10⁻¹² erg already published (Ref. 21) for poly 12-hydroxystearic acid. In view of the approximations made in calculating W, the agreement is considered to be satisfactory.

REFERENCES

- 1 Reynolds. Phil. Mag. 1885, 8, 20.
- 2 Metzner and Whitlock. Trans. Soc. Rheology, 1958, 2, 239-54
- 3 Reiner, Deformation and Flow. II K Lewis (London) Ltd 1949 pp. 306-10.
- 4 Fischer. Colloidal Dispersions. Wiley. 1950 pp. 194-205
- 5 Green and Griskey. Trans. Soc. Rheology, 1968, 12, 13-26, 27-38.
- 6 Morgan. Ibid, pp. 511-33.
- 7 Wagstaff and Waters in "Dispersion Polymerisation in Organic Media" ed. Barrett, Wiley 1975 pp. 246-8.
- 8 Barrett and Thompson. Ibid, pp. 234 et seq.
- 9 Chaffey and Wagstaff. To be published.
- 10 Walters. Basic Concepts and Formulae for the Rheogoniometer. Sangamo Controls Limited Bognor Regis 1968.
- 11 Markovitz in "Rheology, Theory and Applications" ed. Eirich. Wiley 1967 Vol IV. pp. 396 et seq.
- 12 Goldsmith and Mason in Ref 6 pp. 150-5, 189, 209-11.
- 13 Freundlich and Roder. Trans. Far. Soc., 1938, 34, 308-16.
- 14 Hoffmann. Ibid, 1972, 16 (1), 155-73.
- 15 Doroszkowski and Lambourne. J Polymer Sci., 1971, C (34), (253-64).