

25 April 1977

Although contributions from five members were waiting for me on 19th April and the arrival of the reminders in mid-February had stimulated the immediate preparation of three other contributions, reports from 9 academic members are missing. A self-criticism session will be necessary at the Annual Meeting. Unfortunately I can't be there to hear members' excuses because of the exigencies of family holidays. Members at the Annual Meeting might also take the opportunity to remind each other to prepare their contributions for the Autumn issue because it looks as though the deadline should be Monday 3rd October 1977 in Manchester which would mean that members should be getting their reminders just at the time of the meeting!

Members will have received application forms for attendance at this year's special Gordon Research Conference on 'Polymer Colloids' from Chairman Krieger. Gary Poehlein is co-chairman. The Conference will be held at Holderness School, near Plymouth, New Hampshire from Sunday evening 21st August till Friday afternoon 26th August which I can commend from personal experience in 1972. Plymouth N.H. is served by a Continental Trailways bus from Boston but participants without cars usually find it more convenient to take advantage of the special coaches provided for the Gordon Conferences which leave Logan International Airport in Boston at about 3 p.m. on the Sunday and return there the following Friday afternoon. The conference format provides two major lectures in the morning, the afternoon free for recreation (there are tennis courts etc. on the site) and a further major lecture in the early evening. Accommodation and meals can be provided for participants families on the site although those with children under 12 will have to turn to one of the motels in the vicinity. Group members will have to forego recreation on the afternoon of Wednesday 24th August when the Annual Meeting will be held and most will also want to attend another extra item yet to be scheduled when Bob Fitch will give a final report on the co-operative programme on the preparation and characterisation of polymer model colloids which was initiated at Trondheim in 1975. The lecture programmes for all the Gordon Conferences appear in the March 11 issue of Science. The speakers will be G.L.Brown, J.Davidson, R.M.Fitch, J.L.Gardon, A.Klein, S.G.Mason, A.J.McHugh, R.H.Ottewill, A.Rembaum, J.W.Vanderhoff, M.C.Wilkinson, V.I.Yeliseyeva, J.Ugelstad, and K.Barrett. The fees are U.S.\$ 160 for participants and \$ 110 for relatives accompanying them: these include accommodation and meals. Anyone interested who wishes to attend should write for an application form to Dr A.M.Cruickshank, Director: Gordon Research Conferences (until 12 June) Pastore Chemical Laboratory, University of Rhode Island, Kingston, Rhode Island 02881, U.S.A. OR (from 13 June) Colby-Sawyer College, New London, N.H. 03257, U.S.A.

The 8th Annual Lehigh Short Course on 'Advances in Emulsion Polymerization and Latex Technology' will be held from 15-17 June, 1977. The Fee (exclusive of accommodation) is \$400 or \$100 for separate days. Speakers will be E.Allen (Lehigh), G. Biewagen (Sherwin-Williams), G.E.F.Brewer (Consultant) E.A.Collins (B.F.Goodrich), M.El-Aasser (Lehigh), F.Fowkes (Lehigh), A.E.Hamielec (McMaster), W.Heller (ex Wayne State), A.J.McHugh (Lehigh), G.W.Poehlein (Lehigh), F.L.Saunders (Dow), J.W.Vanderhoff (Lehigh), and W.W.White (Uniroyal). Further information from Gary Poehlein.

The 3rd Circular for Macro Dublin 1977 - 17-22 July is now available. It does not contain any list of the contributed papers accepted so far but indicates that it may be possible to accept late offers over a rather wider field than was indicated previously. It seems unlikely that there will be much of special interest to emulsion polymer enthusiasts, however.

David Farmer has completed the provisional programme for the Chemical Society Macromolecular Group Symposium on 'Advances in Emulsion Polymerisation' to be held in London on 27th September 1977. Speakers will be D.C.Blackley, M.J.Garvey (Unilever, Port Sunlight), J.B.Kayes (Pharmacy, Aston) R.H.Ottewill, B.W.Erooks (Loughborough - 2 papers), J. Ugelstad, H. Warson, and myself. Details will appear in 'Chemistry in Britain' and the 'S.C.I. Bulletin (Chemistry & Industry)' in due course.

David Blackley is a member of the committee organising an International Polymer Latex Conference on behalf of the Plastics and Rubber Institute to be held in London in September 1978. Five invited lectures are envisaged and a Call for Papers was issued in February: proposals are wanted by 31 August and complete papers for preprinting by 30 April 1978. Suggested topics include the preparation and properties of latices, latex surface coatings, latex adhesives, latex foam, applications to paper and textiles. It could turn out to be an expensive meeting, however, PRI Conferences usually are! The Annual Meeting might like to consider whether it would be a suitable occasion with which to hold the 1978 Annual Meeting in conjunction although the September date would probably give rise to difficulties arising from the start of the U.S. academic year. Anyway David should be on hand to advise from the U.K. standpoint.

There do not appear to be any further developments as yet on the emulsion polymerisation symposium scheduled for the 1979 Autumn A.C.S. Meeting to be held in Washington September 9-14.

POLICY and ACTIVITIES of the INTERNATIONAL POLYMER COLLOID GROUP

The Group was founded at a meeting held on 27th September 1971 at Lehigh University, Bethlehem, Pennsylvania. The founder members were Bob Fitch, Irv Krieger, Ron Ottewill, Gary Poehlein, John Vanderhoff, and David Williams who subsequently invited others active in research on polymer colloids and emulsion polymerisation to join the group.

The object of the group is to facilitate exchange of information between research groups working in these fields. Membership is by invitation from the Annual Meeting of the Group. Membership is restricted to those active in the field and members are expected to resign when they cease to be active in this field. The Group is international and aims to include at least one member of every research group with a continuing interest in the field. The medium of communication is English since this is understood by all present members.

The Group's object is achieved by (a) circulation to all members of relevant reprints or preprints when available (b) circulation of a Newsletter twice a year and (c) meeting at an annual informal symposium during which the Annual Business Meeting is held: the informal symposium may be preceded or followed or (in alternate years) substituted by a larger, public symposium.

Academic members are obliged to contribute to each issue of the Newsletter and may be expelled by the Annual Meeting if they fail to do so: industrial members are not obliged to contribute to each issue but should contribute whenever possible. Newsletter contributions may be recent research results, progress reports, critiques of previous reports or publications etc. The contents are not to be circulated outside the member's research group or cited without permission until published in the regular literature. Contributions should be typed ready for Xeroxing on A4 (29 x 21 cm) paper, single spaced if practicable, and should not normally exceed 3 pages including any diagrams.

Members are encouraged to bring their graduate students with them to the Informal Symposium and may invite representatives of interested industrial laboratories to attend as guests.

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I. THEORY OF COMPARTMENTALISED FREE-RADICAL POLYMERISATION REACTIONS

My colleague, Dr. D. T. Birtwistle, and myself have recently obtained, and discussed the implications of, an explicit analytic solution to what we tend to refer to here as the "Gilbert-Wapper" problem. This is the problem which Gilbert and Wapper discussed in J. Chem. Soc., Faraday Trans. I, 1974, 70, 591. It concerns the prediction of the variation with time of the populations of particles which contain various numbers of propagating radicals, for the case of a seeded emulsion polymerisation reaction which fulfils the following conditions: (1) radicals enter the reaction loci from a contiguous external phase at a constant rate; (2) the only significant processes which result in loss of radical activity from reaction loci are kinetically of first order with respect to the concentration of radicals in the loci; (3) radicals lost by diffusion from loci to the external phase are not available for re-initiation; (4) the volume of the reaction loci is uniform and does not increase significantly as polymerisation proceeds; (5) no nucleation of new loci takes place; and (6) no reduction in the total number of reaction loci occurs, e.g., through agglomeration.

The general expression which we obtain for n_r , the number of reaction loci per unit volume of reaction system which contain r propagating radicals, is

$$n_r(t) = \frac{N}{r!} \left\{ \frac{\sigma}{k} (1 - e^{-kt}) \right\}^r \exp \left\{ -\frac{\sigma}{k} (1 - e^{-kt}) \right\} \quad \dots\dots (1)$$

where t is the time which has elapsed since the generation of radicals commenced, N is the total number of reaction loci per unit volume, σ is the average rate of entry of radicals into a single locus, and k characterises the rate of loss of radical activity by first-order processes.

We obtained this result by introducing the time-dependent locus-population generating function

$$\Psi(\xi, t) = \sum_{i=0}^{\infty} n_i(t) \xi^i \quad \dots\dots (2)$$

where ξ is an auxiliary variable. Then the set of time-dependent Smith-Ewart recurrence relationships to be solved reduce to the following single partial differential equation in Ψ :

$$\frac{\partial \Psi}{\partial t} = \sigma(\xi - 1)\Psi + k(1 - \xi) \frac{\partial \Psi}{\partial \xi} + \chi(1 - \xi^2) \frac{\partial^2 \Psi}{\partial \xi^2} \quad \dots\dots (3)$$

where $\chi = A_t/v$, A_t being the rate coefficient for bimolecular termination between radicals, and v the volume of the reaction loci. For the model which we have assumed, $\chi = 0$. The simplified differential equation for Ψ , obtained by putting $\chi = 0$ in equation (3), can be solved by the method of separation of variables, to give

$$\Psi(\xi, t) = N \exp \left\{ \frac{\sigma}{k} (\xi - 1) (1 - e^{-kt}) \right\} \quad \dots\dots (4)$$

In arriving at this result, use is made of the boundary condition $\Psi(\xi, 0) = N$, which follows because initially $n_0 = N$. Making use of the fact that

$$n_r = \frac{1}{r!} \left(\frac{\partial^r \Psi}{\partial \xi^r} \right)_{\xi=0} \quad \dots\dots (5)$$

then gives equation (1) above. The total number of radicals in the system at any instant (and hence also $\bar{r}(t)$, the average number of radicals per locus) can be

obtained as

$$\sum_{i=0}^{\infty} i n_i(t) = \left(\frac{\partial \bar{\Psi}}{\partial \xi} \right)_{\xi=1} = N \frac{\sigma}{k} (1 - e^{-kt}) \quad \dots (6)$$

In order to illustrate the numerical consequences of the theory, we have taken the same values of σ and k as did Gilbert and Napper, namely, $\sigma = 1 \times 10^{-5} \text{ sec}^{-1}$ and $k = 5 \times 10^{-4} \text{ sec}^{-1}$, and then calculated (1) the variation of $\bar{\Psi}(\xi, t)$ with ξ for various values of t , (2) $n_r(t)/N$ as a function of t for $r = 0, 1$ and 2 , (3) $\bar{r}(t)$ as a function of t , and (4) the conversion of monomer to polymer, $1(t)$, as a function of t . The results of these calculations are shown in Figs. 1, 2, 3 and 4 respectively. Comparison of our Fig 2 with Fig. 1 of the Gilbert-Napper paper shows that the two theories give almost identical predictions for the chosen values of σ and k .

The advantage of our result compared with that of Gilbert and Napper is that ours is a closed analytic form for $n_r(t)$ whereas their expressions for $n_r(t)$ are rather cumbersome power series in e^{-kt} . Our result is therefore rather more amenable to discussion. The numerical predictions given by the two results are almost identical if (as in the case of the values of σ and k assumed for the purposes of illustration) $\sigma/k \ll 1$. The predicted values of $n_r(\infty)$ are identical.

Amongst the interesting conclusions which emerge from consideration of our result are the following:

- (1) Whilst $n_0(t)$ falls monotonically with increasing t , $n_r(t)$ ($r > 0$) can pass through a maximum if the values of σ and k are such that there is a non-zero integral value of r less than σ/k .
- (2) The $n_r(t)$ form a time-dependent Poisson distribution with respect to the r , the parameter of the distribution at any instant being the average number of radicals per locus at that instant.
- (5) In principle, it is possible to obtain estimates of both σ and k from measurements of $M(t)$ as a function of t over the early stages of a seeded emulsion polymerisation.

The story so far is a happy one. Unfortunately we have now discovered that, at about the same time as we were preparing a note about our result for publication in Chemical Communications prior to the publication of the full paper, a note by Weiss and Dishon was published in J. Chem. Soc., Faraday Trans. I., 1975, 72, 1342, giving the same result as us for $n_r(t)$, it being obtained by using an identical generating function! Our note has been accepted by Chemical Communications, but our full paper will now have to be considerably modified. I am hopeful that something can be salvaged, because Weiss and Dishon do not discuss in any detail the implications of their (and our) result.

II. STABILITY OF SURFACTANT-FREE LATICES PREPARED USING 4,4'-AZOBIS(4-CYANOPENTANOIC ACID) AS INITIATOR

We are endeavouring to prepare reasonably well-characterised carboxylate-stabilised latices of rubbery polymers which we can subsequently use as models for materials such as natural and SB rubber latices. To this end, we have prepared poly n-butyl acrylate latices using 4,4'-azobis(4-cyanopentanoic acid) as initiator, and polymerising at pH 8 in order to minimise the hydrolysis of the monomer and polymer. A typical recipe which works quite well is: water 220g., n-butyl acrylate 40g., initiator 0.8g., and 1M KOH to adjust the pH to 8. It is convenient to carry out polymerisation at 50°C. Conversions of 70-80% are achieved in 3 hours. Similar conversions are obtained by reaction at ambient temperature if the initiator is decomposed photochemically by UV irradiation.

We are rather puzzled by some of the stability characteristics of the latices obtained, and would welcome comments. Latices prepared by a similar recipe but containing 5% of potassium stearate on the monomer coagulate as expected in the range pH 8-9 when dilute acid is added. Coagulation of the surfactant-free latices does not commence until the pH has fallen to about 5.3; coagulation is not complete until

the pH is reduced to about 3.5. At first, we were inclined to attribute the stability of the surfactant-free latices to the presence of polyacrylic acid. The indications are that this is not the explanation; if anything, the addition of polyacrylic acid reduces the stability of the surfactant-free latices. Presumably the stability is due to the presence of combined carboxyl groups derived from the initiator. But the surface concentration of these groups appears to be very low. Assuming a reasonable value for the rate coefficient for the decomposition of the initiator (see III below), I calculate that the minimum value for the surface area per combined carboxyl group is approximately 2600 \AA^2 , i.e., the surface coverage is between 1% and 2% of that expected for a latex fully stabilised by carboxyl groups. We wonder if the enhanced stability is due to the presence of the CN group. Hydrolysis of the latter to CO_2H seems unlikely under the conditions we have employed, but could the presence of the strongly polarised CN group at the particle surface lead to extensive hydration of the particle? The extent of the hydration would presumably not be so dependent upon pH as would that associated with the presence of CO_2^- groups, because, unlike CO_2^- , CN groups do not take part in acid-base equilibria.

Other interesting features of the stability of the surfactant-free latices are as follows:

- (1) The latices coagulate at pH ca. 11.75 when 1M KOH is added.
- (2) The latices appear to be mechanically very unstable. Even attempting to discharge a sample through the orifice of a pipette can induce coagulation. This behaviour is not observed in the case of stearate-stabilised latices, although both types of latex can be easily coagulated by rubbing between the fingers.

III. DECOMPOSITION KINETICS OF SALTS OF 4,4'-AZOBIS(4-CYANO-PENTANOIC ACID) IN AQUEOUS MEDIA

We are also currently investigating the decomposition kinetics of salts of 4,4'-azobis(4-cyanopentanoic acid) in aqueous media, because of their potential usefulness as initiators for the preparation of model carboxylate-stabilised latices. We are pleased to report that the decomposition of the potassium salt seems to be first order over a wide range of conditions, and that the rate coefficient for the decomposition seems to be independent of both ionic strength and pH. We are also determining the rate coefficient for the free acid, but cannot yet say whether it is the same as for the di-anion. An additional variable which remains to be investigated is the nature of the counterion. A reasonable value to take for the decomposition rate coefficient at 50°C appears to be $1.6 \times 10^{-6} \text{ sec.}^{-1}$. The energy of activation for the decomposition is 134 kJ.mol^{-1} ($32.0 \text{ kcal.mol}^{-1}$).

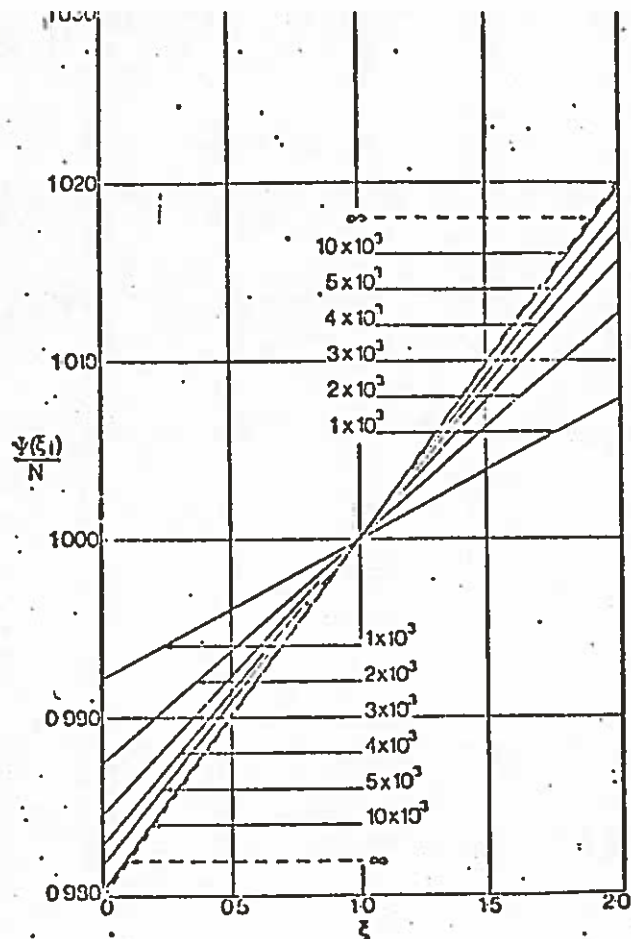


Fig. 1

The numbers appended to the curves give the values of t in seconds.

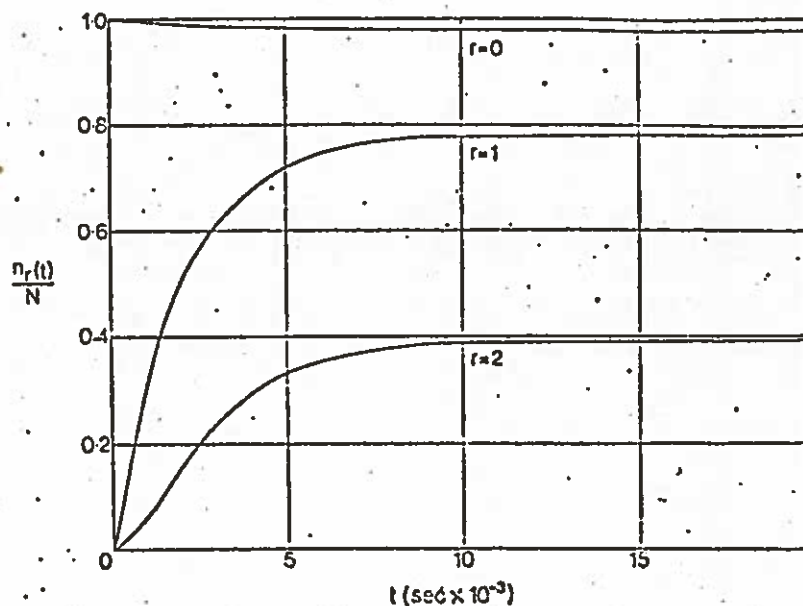


Fig. 2

The ordinates for $r = 0$ are $n_0(t)/N$; those for $r = 1$ are $40n_1(t)/N$; those for $r = 2$ are $2000n_2(t)/N$.

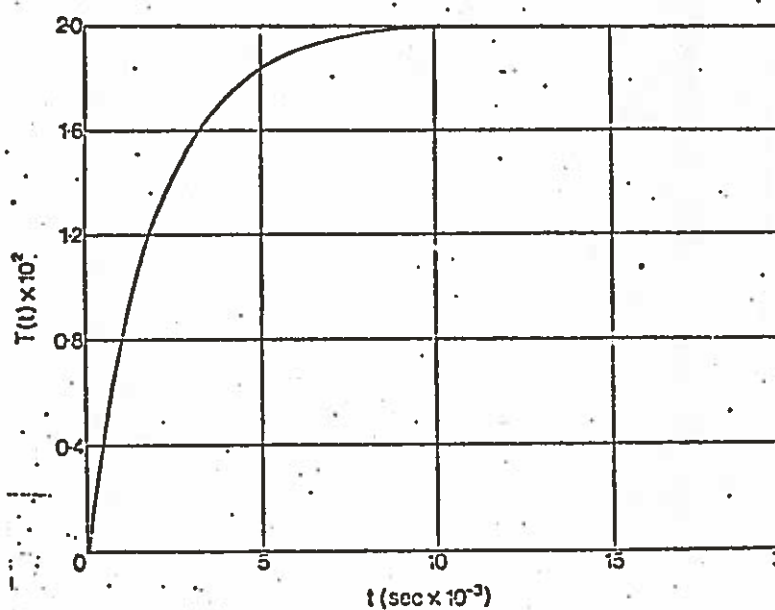
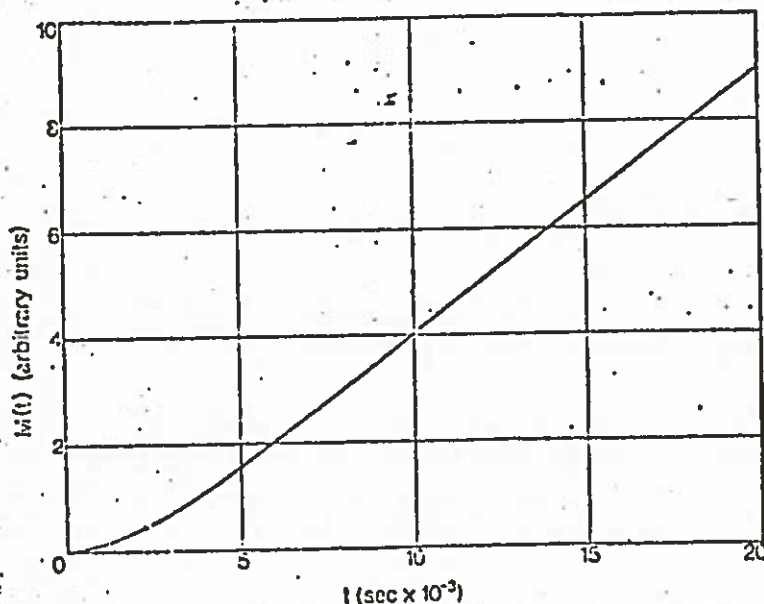


Fig. 3





The November S.C.I. Symposium organised by Henry Warson on 'Control of Particle Size in Polymerisation' was very successful attracting a capacity audience of 120 to the Society's new automated lecture at Belgrave Square: it has even more buttons than the Lehigh theatre! Finn Hansen was prevented from coming because the Trondheim airport was snow-bound but John Ugelstad got through to Oslo by train and was able to fly from there. Dr N. Fischer of Rhone-Poulenc gave a comprehensive review of the methods used in his laboratory to determine the particle size of PVC latices but unfortunately his presentation was too condensed as a result of the very full time-table. The rheology of PVC plastisols is critically dependent on particle size. Ron Ottewill gave an updated report on the Bristol studies of the preparation of surfactant-free polystyrenes emphasising the importance of the ionic strength of the solution. A. Moyles (Vinyl Products) described an improvement to the Joyce-Loeble Diso Centrifuge by addition of a photodensitometer which enables results to be obtained much more rapidly. He noted that commercial latices tend to have multimodal particle size distributions which makes the interpretation of results obtained by direct light scattering procedures difficult. L.S. Golden (Zerolit) discussed suspension polymerisation for producing ion exchange resins. High shear could cause division of large beads: this was undesirable because small beads mixed with large blocked the channels by which a solution should flow through a bed of resin. Dr W.W. Thompson (ICI Paints) said that 80% solids dispersion in organic solvents could be achieved with polymodal particle size distributions. Dr I.G. Carson (Shell) discussed the control of particle size in Ziegler-Natta polymerisations: the shape of the catalyst particles determines the shape of the polymer particles produced. The catalyst particle breaks up during the polymerisation. The particle size of the polymer can therefore be controlled by controlling the size of the catalyst: controlled precipitation can be achieved by carrying out the reaction between titanium tetrachloride and aluminium alkyl at temperatures in the region of -100°C . John Vanderhoff concluded the proceedings with one of his very best presentations reviewing the practice of particle size control in emulsion polymerisation.

Our contribution 'On the Applicability of Gardon's Equations for the Calculation of Particle Size in Emulsion Polymerisation' should be submitted for publication in the British Polymer Journal within the next week. We find good agreement between the calculated particle sizes for polystyrene latices prepared using persulphate and various sodium alkyl sulphate and potassium alkyl carboxylate emulsifiers although the turbidity-average radius measured should be larger than the root-mean-cube radius calculated since the latices are not monodisperse. However the theory is deficient in neglecting the effect of ionic strength on particle size although Gardon's own results show this to be a relevant parameter. Further the order of reaction in emulsifier is not really 0.6: Bartholome, Gerrens et al. 1956 results at a 1:19.5 monomer:water ratio actually correspond to a 0.75 order at low emulsifier concentration which decreases with increase of concentration (cf. Spring 1976 Newsletter). This is probably correlated with a slow change in micelle size with increasing emulsifier concentration (cf. Piirma and Wang's contribution to the 1975 A.C.S. Emulsion Polymerisation). B.W. Barry & G.F.J. Russel (J. Coll. Sci. 40 (1972) 174) show that, at least over a limited range of concentration above the c.m.c., micellar molecular weight M_{mic} varies with the total gegen-ion concentration c_i according to $M_{mic} = \frac{K}{c_i} c_i^c$ where $c = 0.14$ for sodium dodecyl sulphate and $c = 0.22$ for sodium hexadecyl sulphate. This effect together with the increase in the concentration of micellar surfactant owing to the decrease of the c.m.c. may suffice to explain the ionic strength effect although the initial micellar surface area does not appear in Gardon's final equations.

Table I. Calculated and Observed Particle Sizes of Polystyrene Latexes

Alkyl chain length	Micellar surfactant conc. mol/dm ⁻³	(1)	(2)	Calculated		Observed	
		\bar{a}_s/A^2	molecule ⁻¹	r_{rmc}/nm from (1)	r_{rmc}/nm from (2)	r_v/nm	\bar{r}_{ls}/nm
<u>Potassium carboxylates</u>							
C 8	0.0120					29.6	39.6
C 10	"	68	41.4	36.9	40.7	29.7	39.6
C 12	"	66	34.1	37.1	42.3	28.5	35.5
C 14	"	56	25.1	38.3	45.0	31.0	39.6
C 16	"		23.4		45.7	31.0	39.5
C 18	"					31.0	39.5
C 22	"					31.7	39.0

Sodium alkyl sulphates

C 8	"					31.1	37.2
C 10	"	63	52	37.4	39.0	27.9	36.1
"	0.0260			32.1	33.3	27.0	30.7
C 12	0.0120	65	52	37.2	39.0	30.2	39.4
"	0.0510			27.9	29.1	26.2	30.3
C 14	0.0120	61	51	37.7	39.0	28.9	38.9
"	0.058			27.5	28.5	26.2	30.0
C 16	0.012		54		38.7	27.7	37.2
"	0.059				28.1	25.3	28.6
C 18	0.012					30.5	37.0
	0.060					24.2	28.1

Table II Effect of Ionic Strength on Particle Size of Polymethyl Methacrylate Latex (Gardon, 1968)

% in water			Particle size		10 ⁸ r/m	Light scattering
Surfactant	Initiator	Salt	Theory	Electron microscope		
0.256	0.029	0	7.85	6.3		7.9
"	"	0.050	"	7.1		8.7
"	"	0.300	"	8.25		9.9
0.152	0.010	0	9.9	8.65		9.5
"	"	0.050	"	8.75		10.3

The results with sodium alkyl sulphates show that the width of the particle size distribution decreases quite markedly as the emulsifier concentration is increased. This is contrary to what would be expected on the Smith-Ewart hypothesis that particle formation ceases when all the emulsifier has been adsorbed on the surface of latex particles which would indicate that the duration of Interval I (and consequently the breadth of the particle size distribution) would increase with emulsifier concentration as was indeed observed by Gerrens using electron microscopy (Fortschr. Polym. Forsch. 1 (1958) Table 13). The above results, on the contrary, would suggest that the duration of interval I is reduced by increasing the initial surface area of the surfactant micelles. The possible importance of the initial micellar surface area is also indicated by Ryabova et al.'s observation that at a sufficiently high emulsifier concentration micelles persist throughout the reaction although particle formation ceases at an early stage. The explanation is presumably that the probability of an oligomeric sulphate radical entering a latex particle is much higher than that of it entering a micelle (Nomura's 2) presumably because the van der Waals' attractive force between the oligomeric radical and the relatively large latex particle exceeds that between the radical and the monomer molecules solubilised in a micelle. Hence as the latex particles grow they eventually capture all the radicals and particle nucleation ceases. We hope to investigate the contradiction between our results and those of Gerrens further.

W. Al-Shahib & A.S.Dunn 'The Effect of the Homologous Series of Alkyl Sulfate Surfactants in the Emulsion Polymerization of Styrene. Part I. Equal Total Concentrations' has been accepted for publication in J. Polym. Sci. - Polym. Chem. Ed. This shows that equal rates are not observed when equal surfactant concentrations are used but that the variation observed is attributable to variation in the concentration.

28 APR 1977

Dr. A. R. M. Azad has joined our group. He obtained his Ph.D. with John Ugelstad and worked as a Research Manager for Chemanex Ltd. in Sri Lanka for a year prior to coming here in January. He describes his project below:

1. Latex Particle Formation in Suspension Polymerization.

The kinetics and mechanisms of latex particle formation during suspension polymerization of several vinyl monomers are being studied by centrifugation, gravimetry, light scattering and electron microscopy. Experimental variables involve the nature of the stabilizer, rate of initiation, nature and water solubility of vinyl monomers, initiators, chain transfer agents, ionic strength and temperature.

Some other projects currently underway include:

2. Synthesis of Substituted Benzoyl Peroxide Initiators (K. Prakash).

General synthetic pathways towards the synthesis of peroxide initiators bearing chemically functional groups are being explored. The current goal is to make p-sulfo-methyl perbenzoic acid.

3. Kinetics of the Reaction Between HSO_3^- and O_2 (Kevin Healey).

The kinetics of this reaction, catalyzed by Fe(II)/Fe(III) are being followed potentiometrically in the presence and absence of monomer in aqueous solution.

4. Coagulation Kinetics During the Particle Nucleation Stage in Latex Polymerization (Diane Sheldon).

- This is a continuation of the work started with Rich Watson in which we measured the time-dependence of scattered light intensity. Photoinitiation is employed, using a single flash to produce a bunch of particles whose coagulation rate is then determined as a function of initiator type (charged or uncharged), monomer solubility, emulsifier concentration and temperature.

5. Chemical Applications of Laser Interferometry (Tor Henrik Palmgren).

Tor obtained his MS degree from Åbo Akademi under Danielsson and Stenius. He is continuing the work initiated by Deborah Ruszala on non-steady-state polymerization kinetics and the determination of absolute rate constants. This has particular application, we hope, to the growth rate of oligomeric free radicals which ultimately nucleate to form the primary latex particles.

6. Synthesis of Surface Active Monomers (Robert Miller).

As another route to the controlled introduction of chemically functional groups at the particle surface, we are seeking synthetic ways to make monomers which will concentrate at the interface and which will bear the desired functionality. Bob is trying to synthesize substituted, surface active styrenes for this purpose.

7. Chemical Reactions at the Interface (Charles Fifield).

Chip has just joined the group. He hopes to follow up some of the work of McCarvill and Gajria, using physical methods, e.g. nmr, to find out more about the nature of the interface and the interaction of catalytic sites with substrate molecules.

8. Synthesis and Characterization of Model PTFE Colloids (G. Robert Traut).

Bob has completed a literature survey and is ready to start experimental work.



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S.G. Mason and A.A. Robertson

Contribution to the Polymer Colloid Group Newsletter

April 1977.

The recent work of van de Ven and Mason (reported in previous newsletters and now in a series of papers in Colloid and Polymer Sci.) on stabilized and destabilized latex sphere suspensions in dilute electrolytes in shear flow has been extended to systems in which polymers are adsorbed on the particle surface. Detailed studies of the formation and trajectories of permanent doublets of two latex spheres and their period of rotation in the presence and absence of polymers have continued. Further studies of models of polymer-bridged doublets of macroscopic polyethylene spheres linked by elastomer fibers have also been made. A video system for viewing and tape recording the particles has been developed for conveniently measuring the statistical variation in the period of rotation of doublets due to the appreciable rotary Brownian motion of the doublets.

As previously shown both experimentally and theoretically (Arp and Mason) the paths of two colliding rigid spheres in shear flow can be separated into open and closed trajectories, corresponding to separating and permanent doublets respectively. In the absence of Brownian diffusion, interparticle forces and n -body interactions (with $n \geq 3$), it is impossible for the interacting spheres to cross the limiting trajectory within which a permanent doublet exists. However, in the colloidal systems previously studied, interparticle forces and Brownian diffusion have been shown to result in a change of the trajectories of doublets. It is evident that permanent doublets can result from strong van der Waals attraction at high electrolyte concentration as well as from the presence of adsorbed polymer, presumably due to bridging across the sphere surfaces. It is significant that the forces resulting in capture of the spheres appear to be long range, acting across distances as great as $4 \mu\text{m}$. After the formation of such doublets, the spheres were often seen to be visibly separated with the interparticle distance varying continuously during the rotational orbit. From the measured dependence of the period of rotation on the shear rate, it is conjectured that such doublets may be connected by a flexible bridge of dissolved polymer molecules.

To gain further insight into these phenomena, a detailed analysis of the rotation of flexible dumbbells of 3.0 mm diam. spheres joined by an elastomer filament fiber (Lycra, Dupont) was made. It has been observed that the separation distance between sphere centers varied periodically with the connecting fiber exhibiting appreciable bending while the trajectory

of sphere centers executes an approximately elliptical path.

The equivalent ellipsoidal axis ratio of this doublet was then calculated as a function of the orientation of the axis of revolution (i) from the measured separation distance assuming behavior as a rigid dumbbell and (ii) from the measured angular velocity. The observed results can be qualitatively explained by considering the hydrodynamic force acting along the sphere centers and the interparticle force created by the connecting fiber. A calculation of these forces has been made and quite good agreement between measured and calculated angular velocities obtained.

M.E. Labib has had occasion to examine the concentration dependence of the electrophoretic mobility of "emulsifier-free" latexes prepared by recipes adapted from Kotera and Furusawa. Both mass transport electrophoresis and micro-electrophoresis techniques have shown sharply decreasing mobility when the latex is diluted to below $\phi = 10^{-4}$ (typically) with equilibrium dialysate or with isoionic electrolyte solution. The mobility decrease is not observed or is much less marked if the dilution is made with a supernatant obtained by centrifugation of the latex.

The results are consistent with the suggestion, supported by some evidence, that oligomers may be present in the serum and on the latex surface and may be desorbed from the surface by dilution of the serum. The mobility is not decreased by conventional dialysis or ion-exchange procedures that might be expected to have a similar effect. Mobility however was reduced by diafiltration washing or by repeated centrifugation with replacement of serum with isoionic solution. Dr. A.S. Dunn reported in the last newsletter an effect that he attributed to an oligomer concentration in the serum. We would be interested in hearing of any other evidence concerning fugitive stabilizer in emulsifier-free latexes.

The work of A-T. Cao-Thi, reported in previous newsletters, has been completed and an M.Sc. thesis has been written, having the following abstract:

"The rheological properties of aqueous dispersions of hydrolyzed polyacrylonitrile-grafted cellulose (HCPAN) have been investigated. The concentrated suspensions are pseudoplastic and thixotropic. The intrinsic viscosities of the suspended particles have been measured at various electrolyte concentrations, μ , and have been found to increase linearly with $1/\sqrt{\mu}$. The apparent viscosity is reduced by increasing the electrolyte concentration or lowering the pH. The increase in apparent viscosity, η , with concentration, C , at a constant shear rate is initially exponential. The slope of a logarithmic plot of η vs C increases from less than 1 to 4 or 5 at concentrations between 0 and 0.5% but then falls again to near unity at higher concentrations. At the same time the dependence of viscosity on shear rate, $\dot{\gamma}$, increases up to 0.5% but remains

constant above this value, the constant relation being $\eta = k \dot{\gamma}^{-0.66}$. The viscoelastic nature of the suspension is revealed by the development of normal stresses during steady-state or oscillatory shear. Steady-state and dynamic shear moduli have been determined as a function of shear rate or frequency respectively.

The experimental results are consistent with the idea that the elementary particle is a cellulose protofibril stabilized in suspension by associated polyelectrolyte (polyacrylamide-polyacrylic acid copolymer). The extension of the chains and the stabilizing effect are controlled by electrolyte concentration or pH. With increasing concentration the viscosity increases rapidly because of the high axis ratio of the rigid particles. At higher concentrations, particle interactions lead to entanglements and network formation. The behavior of the more concentrated suspensions is qualitatively similar to the predicted and experimental behavior of other concentrated polymer solutions that have a gel-like behavior!"

Reporter : D.H.Napper

25 FEB 1977

1. Disjoining Pressures in Polymer Colloids

There is considerable current interest in the measurement of disjoining pressures in concentrated latex dispersions. Theories of colloid stability, however, rarely predict the disjoining pressure explicitly. What is usually obtained from theory is the free energy of interaction between pairs of spheres or flat plates. We have developed methods for transforming free energies into disjoining pressures for systems that display various types of close-packing (e.g., hexagonal close-packing). The formulae assume, of course, pair-wise additivity for the interparticle forces.

The disjoining pressure, P_d , for a hexagonally close-packed latex is related to the sphere potential, V_T , by

$$P_d = -(\partial V_T / \partial d_0) / \sqrt{2} \quad (a + d_0/2)^2$$

where a = sphere radius and d_0 = minimum distance between the surfaces of the particles.

For the special case where the Deryagin approximation transforms a flat plate potential into a sphere potential with reasonable accuracy, the disjoining pressure can be related to the flat potential $V_T(d_0)$ through

$$P_d = (\pi/\sqrt{2}a) V_T(d_0)$$

These formulae can be applied in principle to electrostatically or sterically stabilized systems, subject to the pair-wise additivity proviso. It can be shown that for sterically stabilized particles, interactions are unimportant provided that the barrier layer thickness is less than ca. 15% of the particle radius.

2. The Concentration Dependence of the Interaction Parameter

Theories of steric stabilization usually assume that the Flory-Huggins interaction parameter is concentration independent. Experiments, however, commonly reveal quite the opposite behaviour : the interaction parameter often increases in magnitude with concentration, sometimes doubling in value in going from infinite dilution to pure polymer.

We have developed a perturbation method that permits the concentration dependence of the interaction parameter to be included into the mixing contribution for steric stabilization. This proceeds via a Taylor expansion of the interaction parameters in terms of the polymer volume fraction, v_2 :

$$\chi = \chi_1 + \chi_2 v_2 + \chi_3 v_2^2 + \dots$$

where the χ_i can be evaluated experimentally.

The leading term is, of course, just that obtained for a concentration independent χ . The first-order perturbation term for the free energy of interaction is found by this procedure to be of order \bar{v} , where \bar{v} = average segment density in the interaction zone. Higher terms are also easily calculated by this procedure and are of order \bar{v}^2 or higher. The higher order terms are unlikely to be important for higher molecular weight stabilizers but may be significant for shorter chain lengths, especially if compression of the polymer occurs.

It may be shown that the observed correlation between the θ -point and the critical flocculation point should not be profoundly altered by the concentration dependence of the interaction parameter.

J.W. Goodwin, R.H. Ottewill and D.E. Yates
University of Bristol

Purification of Polymer Latices

25 APR 1977

The development of methods for the preparation of polymer latices containing monodisperse particles, particularly in the absence of surface active agents^{1,2,3,4}, has lead to their widespread use to test current theories of colloidal phenomena⁵. The most commonly used initiator has been potassium persulphate, frequently with styrene as the monomer. After the preparation, a cleaning procedure is required to remove salts, oxidation products and any remaining monomer from the latex^{1,3,4}. Usually the surface of the latex particles is then characterised using the conductometric titration technique^{3,6,7}. A worrying feature of the cleaning and characterisation procedures is that different authors, using similar recipes for the latex preparation, have observed different surface groups. For example, Vanderhoff et al^{6,7} using mixed-bed ion-exchange resins to remove ionic impurities have concluded that only strong acid groups, i.e. sulphate groups arising from initiator fragments, are present on the surface; their conclusion was based on the single end-point observed in the conductometric titration. Other authors^{3,8}, particularly those using dialysis as a cleaning procedure, have detected the presence of weak acid groupings on the surface in addition to the strong-acid groupings. In fact, weak acid groups could be produced by the hydrolysis of surface sulphate groups to hydroxyl groups followed by oxidation to carboxyl groups³.

Thus a very key question has arisen as to which set of results is correct and which cleaning procedure should be used for preference in preparing clean latices for fundamental investigations. In an attempt to answer this question, we have carried out a detailed investigation of different cleaning procedures. The work will be reported in detail in due course but the main conclusions are summarised in this note.

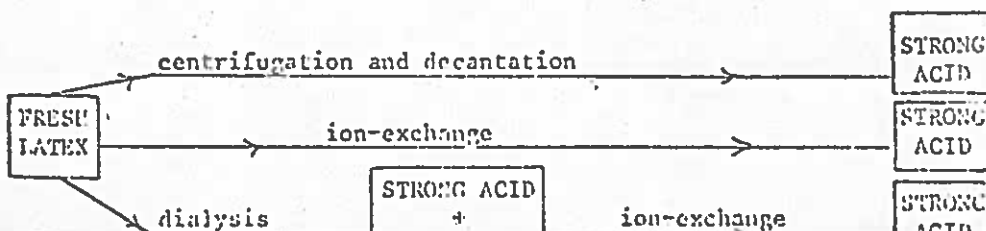
The polystyrene latices were prepared, using potassium persulphate as the initiator, by the procedures previously described⁴ (latex A/70) to give particles with a diameter of ca. 500 nm. Conductometric titration⁶ and microelectrophoresis¹

The initial unpurified latex gave only one end-point when examined by conductometric titration and this was consistent with the presence of only strong acid groups on the particle surface. Moreover, a microelectrophoretic investigation of this material, highly diluted in 5×10^{-2} mol dm⁻³ sodium chloride solution, gave a constant electrophoretic mobility of $-5.0 \mu\text{m cm s}^{-1} \text{ V}^{-1}$ between pH values of 3 and 10, again suggesting only strong acid groups. Moreover, after cleaning the latex by washing with double distilled water, i.e. by centrifuging and decanting several times, the conductometric titration curve was that shown in Figure 1, curve A. This curve is consistent with a strongly acidic surface and no weak acid groups.

Another sample of the latex was cleaned by an extensive dialysis procedure against distilled water with the latex contained in well-boiled bags of Visking dialysis tubing. The conductometric curve obtained after dialysis is given as curve B of Figure 1. The form of the curve strongly suggests the presence of both weak-acid and strong-acid groupings on the latex surface. It is our experience over a large number of samples that dialysis of persulphate initiated latices leads to curves of this form. A series of experiments showed that the weak-acid was also present after dialysis in a rigorously maintained nitrogen atmosphere and that various methods of prewashing the dialysis tubing, i.e. using, 10^{-3} mol dm⁻³ EDTA, 50% ethanol-water, 0.5 mol dm^{-3} sulphuric acid or 10^{-2} mol dm⁻³ sodium hydroxide, had no effect on the conductometric titration curve. It was found, however, that treatment of the dialysed latex by mixed-bed ion-exchange resins did remove the weak-acid groups from the surface and the conductometric curve obtained was indicative of strong-acid groups only.

Treatment of a sample of the original latex with ion-exchange resins by the procedure of Vanderhoff^{6,7} gave a conductometric curve which showed the presence of strong acid groups only.

The experimental procedures used and the results obtained can be summarised as follows:



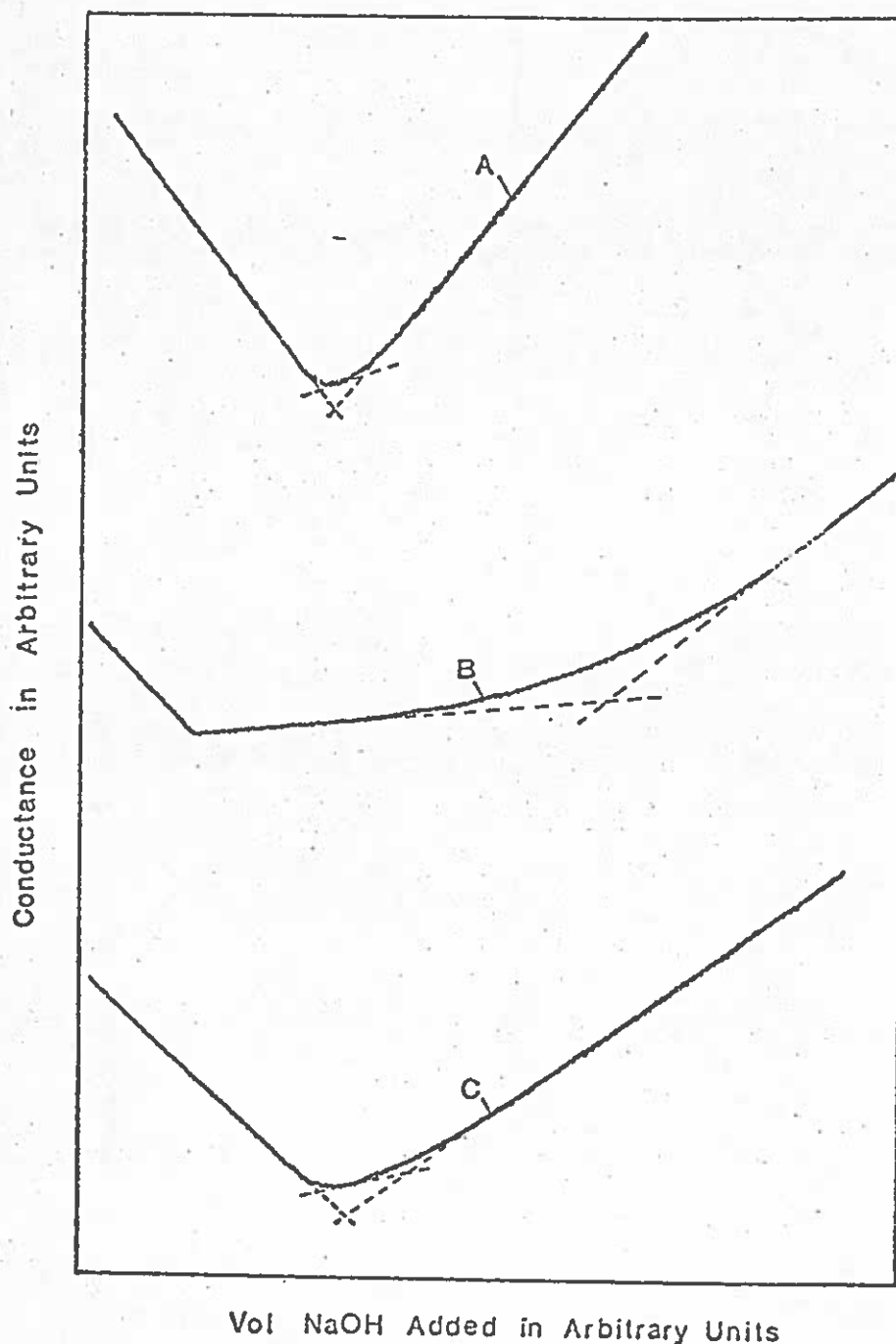


Figure 1: Conductometric titration curves determined in 10^{-3} mol dm $^{-3}$ sodium chloride solution.

- A, after sedimenting several times in distilled water and decanting,
- B, after dialysis ($-\log D_e = 27$) in Visking tubing at initially acid pH,
- C, after dialysis ($-\log D_e = 9$) in Visking tubing at neutral pH.

In view of these results a more extensive analysis of the dialysis procedure was undertaken. Samples were dialysed under normal conditions (starting at ca. pH 2.8) and after bringing to neutral pH. In both cases a periodic analysis was made for weak-acid groupings. The results obtained are given in Figure 2 in the

form of curves of weak-acid content against $-\log D_e$, where D_e was taken as a measure of the extent of dialysis and defined by,

$$D_e = \left[\text{vol. of latex / vol. of dialysate} \right]^x$$

with x = the number of changes of dialysate. It can be observed from these data that in the initially acid samples the amount of weak-acid present increases slowly with time, reaches a maximum at $-\log D_e = 14$ (approx. 14 changes at one change per day) and then decreases slowly. On the other hand when the latex was brought to pH 10 before dialysis and then dialysed at neutral pH, the amount of weak-acid detected was considerably diminished. As can be seen from Figure 1 (curve C) the results obtained conductometrically after dialysis at neutral pH are substantially those of a strong acid.

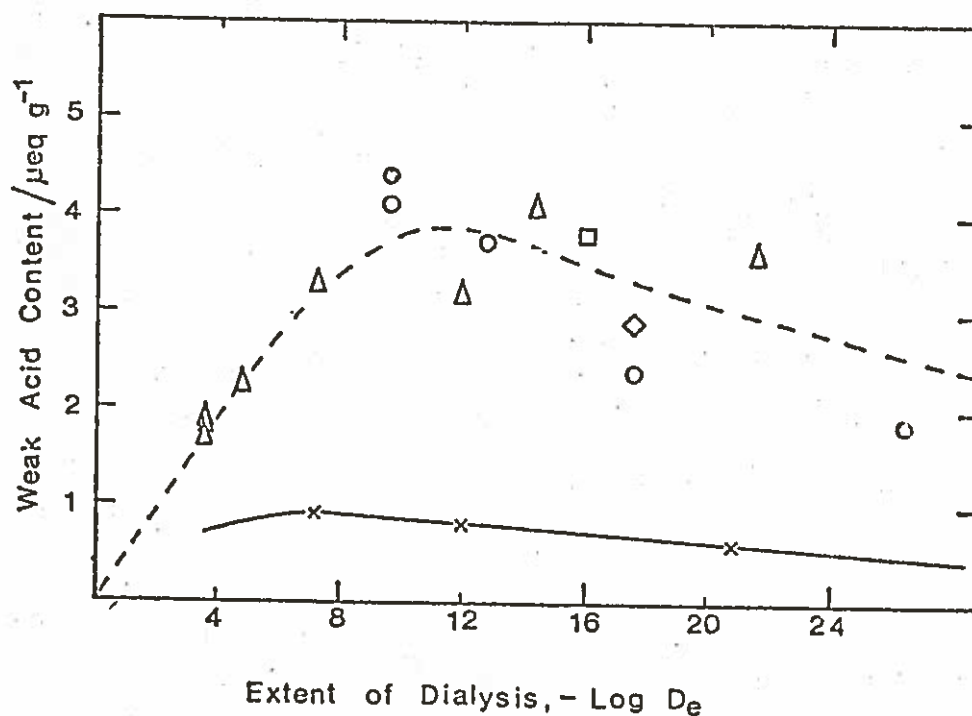


Figure 2: Weak acid content against extent of dialysis, ---, latices initially at acid pH. The symbols refer to different latex preparations. —x—, latices dialysed at neutral pH.

These experiments lead us to the conclusion that the weak-acid residues arise as a consequence of prolonged exposure under acid conditions to Visking dialysis tubing. The most likely explanation is that the cellophane tubing hydrolyses, and perhaps oxidises,

polysaccharides which then adsorb on to the latex particles. It is possible that the monomer, styrene, may play a part in this reaction.

Finally, the question must be posed as to the best method to use for cleaning polymer latices. The usual reason for prolonged dialysis is to remove residual monomer. If this is required, an alternative procedure is to remove the monomer immediately after preparation by steam distillation under reduced pressure. After this a short dialysis using well-boiled dialysis tubing at neutral pH, with rapid changes of dialysate in a 24h period can be used to remove ionic impurities. An alternative viable procedure to remove the latter is to use mixed-bed ion-exchange resins as recommended by Vanderhoff^{6,7}. On a small scale they are very useful to convert the latex into the hydrogen form for conductometric analysis. However, polyelectrolyte impurities from the resins can also introduce a contamination problem and the extent to which this occurs appears to vary with different batches of material; moreover resins are expensive to use on large batches of latex.

References

1. Ottewill, R.H. and Shaw, J.N., *Kolloid Z.u.Z. Polymere*, 1967, 218, 34.
2. Kotera, A., Furusawa, K. and Takeda, Y., *Kolloid Z.u.Z. Polymere*, 1970, 239, 677.
3. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H., *Br. Polymer J.*, 1973, 5, 347.
4. Goodwin, J.W., Hearn, J., Ho, C.C. and Ottewill, R.H. *Colloid and Polymer Sci.*, 1974, 252, 464.
5. Ottewill, R.H., in Colloid Science, (Specialist Periodical Report), The Chemical Society, London, 1973, 1, 191.
6. van den Hul, H.J. and Vanderhoff, J.W., *Br. Polymer J.*, 1970, 2, 121.
7. Vanderhoff, J.W., van den Hul, H.J., Tausk, R.J.M. and Overbeck, J.Th.G., in Clean Surfaces: Their Preparation and Characterization for Interfacial Studies (G. Goldfinger, Ed.) Marcel Dekker, New York, 1970, p.15.

14 FEB 1977

My colleagues & I have been reading the book of the recent meeting of the A.C.S. on aqueous latex preparation. We are comforted to see some resolution of the 'conflict' between the Harkins/Ewart Smith 'Micellar' & the Roe/Fitch 'Precipitation' mechanisms for particle formation. It seems to us that the former appears to operate ABOVE the C.M.C., while the latter takes-over BELOW. However, one point still bothers us & this note is primarily intended to air it.

The original 'Micellar' model implies that not only is particle formation due to the initiation of monomer solubilised in micelles, but also that the initiating species are the PRIMARY ion radicals produced by the decomposition of initiator molecules dissolved in the aqueous phase; no important role is envisaged for solution polymerisation in the continuous phase. This has long seemed to us to be energetically most implausible, as it requires a totally water-soluble anion radical to enter a 'hydrophobic' environment against the strong repulsive field of the anionic surfactant forming the micelle. We have therefore assumed that the initiating species must be the 'Living radical surfactant' which results from solution polymerisation of dissolved monomer by primary radicals. Unlike the primary radicals themselves, such molecules should be able to compete successfully with ordinary surfactant molecules in the continuous exchange which occurs between micelles & the continuous phase.

We have always hesitated to push this view too strongly, because of a lack of experimental justification. However, by chance, some relevant results have recently come to hand.

The orthodox model predicts that, provided that the micelles are swollen with monomer, the concentration of monomer in molecular solution in the aqueous phase is not relevant to the achievement of polymerisation.

Our model on the contrary, predicts that there will be NO polymerisation unless the concentration of molecularly dissolved monomer is high enough to support meaningful solution polymerisation.

Certain monomers - eg. C_{12} to C_{18} methacrylates, tert. butyl styrene, - are much less soluble in water (especially at room temperature) than the monomers usually studied - even including styrene. Attempts to emulsion-polymerise such monomers in conventional systems using persulphate initiators is a total failure, no detectable amounts of polymer being formed.

Addition of minor amounts of highly polar monomers, such as acrylic acid, (the homopolymers of which are water soluble), also gives no LATEX polymerisation, but only the slow production of the water soluble homopolymer.

However, the addition of similar amounts of 'conventional' monomers such as styrene, which have modest solubilities as the monomer but are very insoluble as even low polymers, results in essentially normal latex copolymerisation.

Finally, modification of the aqueous phase with modest amounts of water-miscible organic liquids such as methanol or acetone, to raise the solubility of the main monomer to a similar value to that of 'conventional' monomers in ordinary water, again results in normal latex polymerisation.

While in no way definitive, all of these results support the view that solution polymerisation to form 'surface-active radicals' is the first step in particle formation in aqueous latex polymerisation.

In some ways this view tends to smooth-out the ^{sharp} distinction between the 'Micellar' & 'Precipitation' models. In the former, the main reaction of the 'surfactant-radicals' is interchange with 'ordinary surfactant' molecules in existing micelles; in the latter, they aggregate to form 'self-micelles' from which the latex particles form. Near the C.M.C., where the number of micelles is small (or even zero), but the concentration of 'ordinary surfactant' is significant, we might expect new mixed micelles to be formed from co-aggregation of 'ordinary' & 'radical' surfactants.

POLYMER COLLOIDS NEWSLETTER CONTRIBUTION

from The University of Akron

Submitted by: I. Piirma

Experiments carried out by S. R. Chen

718 APR 57

A. In addition to the results reported in Newsletter Vol. 5, No. 2, we have proceeded to prepare styrene-methyl methacrylate copolymers with MMA concentration varying from zero to hundred (wt. %) in the copolymerization feed. We have found that the saturation molecular area of the sodium dodecyl sulfate (calculated from surface tension measurements) increases with increasing PMMA concentration in the copolymer as shown below.

Wt. % MMA in Monomer Feed of Copolymer	0	25	50	75	100
Saturation Molecular Area of SDS (\AA^2)	47	57	76	112	152

These results again indicate that the surface coverage of surfactant on a latex particle is greatly dependent on the polarity of the polymer. When the affinity between surfactant and the particle surface is not as great as that between surfactant molecules themselves, micelles start to form before the polymer particle surface is completely saturated. Therefore, the molecular area of the surfactant calculated from the titration endpoint shows a higher numerical value when on a polar polymer surface.

B. The effect of an electrolyte in the aqueous phase was also studied using polystyrene latex stabilized by sodium dodecyl sulfate. In the absence of electrolyte the surface area calculated from saturation adsorption had a value of 47\AA^2 , which decreased to 35\AA^2 in the presence of 0.1M sodium chloride. The value of the cmc also dropped drastically. The results are shown below.

[NaCl] (M)	0	0.01	0.03	0.05	0.10
$C_f \times 10^3$ (M)	8.7	6.3	3.1	1.8	1.0
A_s (\AA^2)	47	45	40	37	35

This effect could be visualized as being due to the fact that in the presence of an electrolyte, the intermolecular Coulombic interaction may be critically dampened, allowing the polar groups in the surfactant to come closer together with less energy. The molecular area is thus decreased and the cmc also reduced.

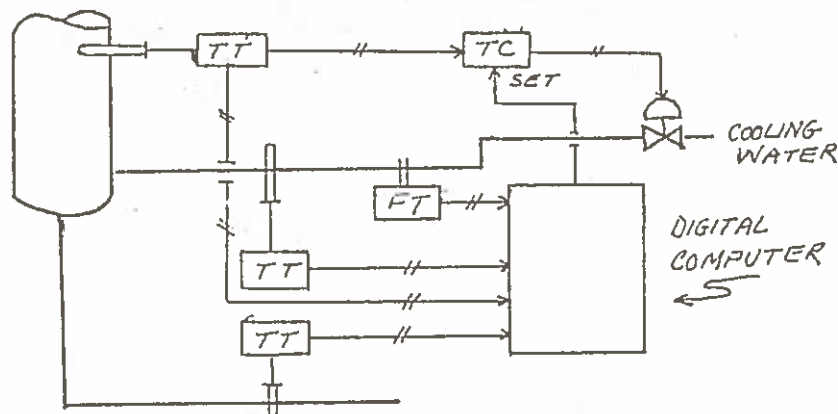
Automatic Control of CSTR Emulsion Polymerization Reactor

The control of continuous emulsion polymerization in a single well stirred reactor (CSTR) has long been a desired industrial process, due to changes in feed streams.

The research program has three objectives. The first is to develop a system for the automatic control of a CSTR for continuous emulsion polymerization. The second is to prepare a mathematical model to simulate the control system given changes in the feed stream's condition. The third is to set up and carry out an experimental program to test the effect of initiator concentration, emulsifier concentration, and mean residence time on steady state conversion of a controlled continuous emulsion polymerization reactor.

The first objective has been accomplished, in a purely preliminary manner, by use of a digital computer control system, which computes the desired variable by the measurement of other, more easily obtainable, variables. In this case we would compute the inlet concentration by measuring: cooling water properties: flow rate, inlet temperature, and outlet temperature; and reactor and feed temperatures. By use of these inlet concentrations a desired theoretical reactor temperature can be calculated. Using this new temperature as a set-point, for the control sequence, it can be compared with the existing reactor temperature to adjust cooling water flow rate. The following illustration, Figure 1, provides a sketchy schematic of the control loop.

Figure 1



Control Loop

The second objective is still in process; a preliminary model for a styrene system with a proportional controller has been obtained. It shows, as is expected, that changes in the inlet feed stream cause small changes in the outlet stream. Further work is being done at present of a proportional-integral (PI) controller. Upon successful completion of this segment, the model will be adapted to methyl methacrylate (MMA).

Equipment for the fulfillment of objective three is in the process of being assembled. The equipment will resemble that shown in Figure 1. Continuous runs of styrene and MMA are planned, with and without controls; the former will verify the model and the latter will determine whether or not this particular scheme is indeed a practical method of reaction control.

NORTH CAROLINA STATE UNIVERSITY AT RALEIGH

SCHOOL OF ENGINEERING

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BOX 5035 ZIP 27607

April 14, 1977

25 APR 1977

Newsletter Contribution

I find myself this time with no students working on emulsion polymerization for the first time for many years. I am, however, writing up the following work of a number of former coworkers.

1. Some colloid chemistry aspects of vinyl acetate emulsion polymerization with Andrew Klein. Those of you attending our Gordon Research Conference will hear Andy report on this work.
2. The radiation-induced emulsion polymerization of styrene with H. Shiota, J. L. Williams and H. Garreau. A summary of this work was presented in a former newsletter.
3. The radiation- and chemically-induced ($K_2S_2O_8$) grafting of styrene to large particle size polybutadiene latex, with K. Yoshida, K. Ishigure and H. Garreau.

I hope to get copies of these manuscripts to you before the next newsletter.


V. T. Stannett

Camille Dreyfus Professor of Chemical Engineering

VTS:ch

Report from The Laboratory of Industrial Chemistry, The University of Trondheim, Norway.

1. Particle formation

F.K. Hansen has continued his work on the theory of particle formation combined with practical work with styrene and vinyl chloride.

It seems that even our last correction to the expression for the rate constant for absorption of radicals was not complete although it was an improvement. If we take into consideration that the concentration of radicals at the outside of the particles has a given value in the evolution of the diffusion of radicals to the surface we obtain the final expression for the absorption constant:

$$kc_j = 4\pi Dw_j r \frac{a_j D_{pj} (X_j \coth X_j - 1)}{EDw_j + W a_j D_{pj} (X_j \coth X_j - 1)}$$

which we may write

$$kc_j = 4\pi r \frac{Dw_j}{W} \frac{a_j D_{pj} (X_j \coth X_j - 1)/E}{Dw_j/W + (X_j \coth X_j - 1)/E}$$

It is different from the expression given in our last correction by the factor E which is an activation parameter given by

$$E = \exp e\psi/k_t$$

where ψ is the actual potential at the Stern layer. Thus E represents an activation energy. It is seen that when $(X_j \coth X_j - 1)/E \ll Dw_j/N$, which involves that the diffusion through the water phase is of no importance for the rate of radical absorption, we obtain:

$$kc_j = 4\pi r a_j D_{pj} (X_j \coth X_j - 1)/E$$

We have as before two different situations to consider.

A $X_j \ll 1$

$$kc_j = v_p a_j k/E$$

B $X_j \gg 1$

$$kc_j = 4\pi r^2 (kD_{pj})^{1/2}/E$$

The incorporation of this term has proven to be of great importance in explaining the experimental results with styrene which now seem to fit well into the picture.

We have two papers in press describing this improved theory.

2. Hindered absorption of radicals

In a recent paper in press we have discussed in some detail the problem of hindered absorption of radicals as discussed by Napper, and also showned by us for the case where one applies a mixed emulsifier system consisting of fatty alcohol and ionic emulsifier. In our review paper in Rubber Chemistry and Technology we discussed the case that all radicals, whether principally stemming from initiator radicals or from monomer radicals desorbed from the particles were hindered in their absorption to the same degree. This is certainly very doubtful. In a recent paper we discuss the situation that the hindrance to absorption is solely restricted to the charged radicals stemming from the initiator radicals while monomer radicals which are formed in the particles and are desorbed reenter the particles unhindered. As it turns out, this treatment which is a non steady treatment, also as a limit gives an alternative and a more general and perhaps a clearer description of the process of desorption and reabsorption with steady state conditions.

I cite from the paper:

Another possibility would be that the hindered absorption of radicals in the particles is limited to the charged radicals stemming from the initiator. Note that this means all charged radicals independent of chain length. Thus we assume that the uncharged radicals stemming from the monomer radicals escaping the particles are all rapidly reabsorbed into the particles without any loss by termination in the aqueous phase. We denote the total rate of absorption of the charged radicals by ρ_{Ai} and furthermore assume that $N \gg N_1 \gg N_2$.

We then have for the N_1 particles:

$$dN_1/dt = (\rho_{Ai}/N)(N_0 - N_1) - 2k_d N_1^2/N + 4k_d N_2 N_0/N \quad (8)$$

The second term on the right side says that if a monomer radical desorbed from a N_1 particle is reabsorbed into a N_1 particle this process of desorption and reabsorption leads to the loss of $2N_1$ particles. If it is reabsorbed into a N_0 particle there is no change in the number of N_1 particles. The third term says that if the desorbed radical from a N_2 particle is reabsorbed

into N_0 particle, this process of desorption and reabsorption leads to the formation of $2N_1$ particles. The rate of this process is $2k_d N_2$, therefore the factor 4. Again if the radical which is desorbed from a N_2 particle is reabsorbed into a N_1 particle, nothing has happened to the number of N_1 particles. One is formed by the desorption, one is destroyed by the reabsorption. Setting $N_0 = N - N_1$ gives:

$$dN_1/dt = \rho_{Ai}(1 - 2N_1/N) - 2k_d N_1^2/N + 4k_d N_2 - 4k_d N_2 N_1/N \quad (9)$$

As $N \gg N_1 \gg N_2$ we have approximately

$$dN_1/dt = \rho_{Ai} - 2k_d N_1^2/N + 4k_d N_2 \quad (10)$$

For N_2 particles we have:

$$dN_2/dt = \rho_{Ai} N_1/N + k_d N_1^2/N - 2k_d N_2 N_0/N - 2(k_t^*/v)N_2 \quad (11)$$

The second term on the right side says that N_2 particles are created if the radical being desorbed from a N_1 particle is absorbed in a N_1 particle. The third term says that N_2 particles are only lost if the radical being desorbed from the N_2 particles is reabsorbed into a N_0 particle. If it is reabsorbed into a N_1 particle, the process of desorption and reabsorption does not change the number of N_2 particles.

Setting $N_0 = N - N_1$ gives:

$$dN_2/dt = \rho_{Ai} N_1/N + k_d N_1^2/N - 2k_d N_2 + 2k_d N_2 N_1/N - 2(k_t^*/v)N_2 \quad (12)$$

As $N_2 \ll N_1$:

$$dN_2/dt = \rho_{Ai} N_1/N + k_d N_1^2/N - 2k_d N_2 - 2(k_t^*/v)N_2 \quad (13)$$

Equation (9) and (12) or (10) and (13) describe a situation where the desorbed monomer radicals are rapidly reabsorbed so that termination of uncharged radicals take place in the particles. Charged radicals, the absorption of which are strongly hindered termination solely in the aqueous phase.

If we have a rapid termination in N_2 particles the treatment is simplified.

In this case we have:

$$dN_1/dt = \rho_{A_i} - 2k_d N_1^2/N \quad (14)$$

which gives for $\bar{n} \sim N_1/N$:

$$\bar{n} = (\rho_{A_i}/2Nk_d)^{1/2} \frac{\exp\{[\rho_{A_i}k_d/N]^{1/2}t\}-1}{\exp\{[\rho_{A_i}k_d/N]^{1/2}t\}+1} \quad (15)$$

We have for the charged radicals in the aqueous phase:

$$dR_{iW}/dt = \rho_i - k_{ai}[R_i]_W - 2k_{tw}^*[R_i]_W^2 \quad (16)$$

where k_{ai} is the absorption constant for the charged radicals. With a sufficiently hindered absorption of the charged radicals we will have that we rapidly build up a steady state of these radicals in the aqueous phase so that

$$[R_i]_W \sim (\rho_i/2k_{tw}^*)^{1/2} \quad (17)$$

Thus the value of ρ_{A_i} is given by: $\rho_{A_i} = k_{ai}(\rho_i/2k_{tw}^*)^{1/2}$

which by insertion in Equation (15) gives:

$$\bar{n} = \left(\frac{k_{ai}}{2Nk_d}\right)^{1/2} \left(\frac{\rho_i}{2k_{tw}^*}\right)^{1/4} \frac{\exp\left\{\left[\frac{8k_{ai}k_d}{N}\left(\frac{\rho_i}{2k_{tw}^*}\right)^{1/2}\right]t\right\}-1}{\exp\left\{\left[\frac{8k_{ai}k_d}{N}\left(\frac{\rho_i}{2k_{tw}^*}\right)^{1/2}\right]t\right\}+1} \quad (18)$$

It follows from Equations (10) and (13) that at steady state $\bar{n} \sim N_1/N$ is given by:

$$\bar{n} = \frac{1}{N} \rho_{A_i}^{1/2} \left(\frac{V_p}{2k_t^*} + \frac{N}{2k_d}\right)^{1/2} \quad (19)$$

With $\rho_{A_i} = \rho_i$, that is if we have such rapid absorption also for the charged radicals that even for those the termination in the aqueous phase may be neglected, Equation (19) is equivalent to the equation previously derived

in a somewhat different way for the steady state situation with unhindered radical absorption. (8)

THE TRONDHEIM COOPERATIVE RESEARCH PROGRAM

26 APR 1977

Contribution from A. Watillon, J. Stone-Masui and J. Delfosse

I. Latex prepared according to the recipe provided by Dr. Homola

- a) Preparation : Special conditions given by Homola have been followed. In our experiment : initial pH = 9.5; final pH = 2.75; solid volume fraction $\varphi = 5.95\%$; conductivity of the prepared latex = $1.34 \cdot 10^{-5} \Omega^{-1} \text{ cm}^{-1}$.
- b) Particle size analysis : method : electron microscopy + Zeiss TGZ3 particle size analyser. Magnification range calibrated with the Dow PS latex LS067A ($D = 1,170 \text{ nm}$). results : number average diameter : 475 nm or 488 nm for two experiments; weight average diameter = 480 nm or 493 nm; standard deviation $\sigma = 0.032$.
- c) Purification : After filtration on glass wool or on a sintered glass filter type G_0 , the latex is purified either by dialysis or by ion-exchange resins.
dialysis : visking tubing boiled in twice distilled water; dialysate changed every 24 h; ratio of dialysate to latex : 20 to 1. About 45 days dialysis.
ion-exchange resins : used in batch procedure. Ratio of wet resin to latex : at least 1 to 2.
Mixed-bed Amberlite MB₁ (8 % DVB) resin is extensively purified just before use by twice distilled water. Dowex (4 % DVB) resins (cationic and anionic) are purified and mixed according to the method of Vanden Hul and Vanderhoff.
- d) Conductometric titrations : on 25 ml (or 30 ml) samples, with NaOH (0.1 or 0.01 M). Solid volume fractions more than 1 %.

Surface groups results : one end point

Method of purification	Experimenter 1		Experimenter 2	
	Solid fraction %	$\mu\text{moles/g}$	Solid fraction %	$\mu\text{moles/g}$
Dialysis	4.92	0.7	6.63	2.1
Amberlite	4.63	11.5	3.94	10.4
Dowex	4.53	8.5	3.89	9.6
		mean = 10.0		mean = 10.0

e) Oxidation of the latex :

Method : 15 % $K_2S_2O_8$ /weight polymer, 10^{-5} M $AgNO_3$, 90°C, 6 hours. Solid volume fraction before oxidation : about 4 %; after oxidation and further purification : about 2.5 %.

Surface groups results : two end points (the first one is rather difficult to determine)

Method of purification	Solid volume fraction %	1st equiv. point (μ moles/g)	2d equiv. point (μ moles/g)	OH groups (μ moles/g)
Amberlite	2.21	1.9	10.8	2.3
Dowex	2.74	1.7 1.7	15.9 14.8	8.1 7.0

II. Latex sent by Prof. Krieger

The first one was bimodal and developed molds.

The second one also developed molds after one week in the lab.

III. Latex sent by Prof. Vanderhoffa) Characterization of the latex (as received)

Solid volume fraction $\varphi = 41.6$ %; conductivity = $2.03 \cdot 10^{-3} \Omega^{-1} \text{ cm}^{-1}$; pH = 8.

b) Particle size analysis : number average diameter : 190 nm; weight average diameter : 191 nm; standard deviation $\sigma = 0.037$ (calibration of the ϵ microscope with Dow PS latex LS-063-4 : D = 557 nm).c) Purification : as before

The visking tubing were boiled in twice distilled water for one hour. This water was changed 5 times. Moreover two kinds of dialysis were performed : one in the presence of the atmosphere and the other in CO_2 -free air.

d) Conductometric titration - Surface groups results

Method of purification	Solid volume fraction %	1st equiv. point (μ moles/g)	2nd equiv. point (μ moles/g)
1st batch.Amb.MB ₁	10.78	8.3	3.7
2nd batch.Amb.MB ₁	8.59	2.3	4.1
3rd batch.Amb.MB ₁	6.32	1.8	4.5
	3.16	1.9	4.0

dialysis (atmos.) 10 days	9.34	2.4	1.5
dialysis (CO ₂ -free) 38 days	8.14	1.8	0.5
3rd batch with Amb.MB ₁ (after oxidation)	1.39	2.9	12.3

- e) Oxidation of the latex : oxidation of the 6 % solid volume fraction latex (after 3d batch) failed. 15 minutes after the beginning of oxidation the latex was completely coagulated. Such a coagulation was not observed with a more diluted sol (~ 3 %). It was not possible to estimate the OH content in this case, because the strong acid content seems larger after oxidation (cf. previous table).

IV. Latex prepared according to the recipe provided by Prof.Vanderhoff (with aerosol MA

- a) Characterization of the latex (after preparation)

Solid volume fraction $\phi = 27.4$ %; conductivity = $2.56 \cdot 10^{-3} \Omega^{-1} \text{cm}^{-1}$; pH = 7.

- b) Particle size analysis : number average diameter : 211 nm; weight average diameter : 212 nm; standard deviation $\sigma = 0.032$ (calibration with Dow PS latex LS-063-A : D = 557 nm).

- c) Purification : cf. section III.

- d) Conductometric titration. Surface groups results

Method of purification	Solid volume fraction %	1st equiv. point ($\mu\text{moles/g}$)	2nd equiv. point ($\mu\text{moles/g}$)
1st batch Amb.MB ₁	9.38	16.3	8.9
2nd batch Amb.MB ₁	6.61	8.9	3.0
3rd batch Amb.MB ₁	5.50 1.10	7.9 8.2	3.8 4.5
dialysis (atmosph) 75 days	8.05	3.1	1.0
dialysis (CO ₂ -free) 38 days	8.49	2.9	0.7
3rd batch with Amb.MB ₁ (after oxidation)	0.98	2.6	12.2

e) Oxidation of the latex : result cf. previous table.

OH content is for this latex 1.7 $\mu\text{mole/g}$ (difficult to determine accurately).