~£12 per issue

-7 NOV 1973

International Polymer Colloid Group

Newsletter

Volume 3, No. 1 October 1973

D.J. Williams, Editor

I had my usual difficulties in extracting contributions from the membership, but Bob Fitch has gone to extremes in an attempt to avoid his obligation. His was the last to arrive a few days ago from Trondheim, Norway where he says he is working with John Ugelstad. First Russia and now Norway. Next month it will be the North Pole.

John Gardon was even more clever, however. He worked out a promotion sending him to Detroit where he is too busy with his new duties to contribute. His new title: Director, Research and Development for M & T's Coating and Ink Division. His address: M & T Chemicals Inc., Coatings Research Center, 26701 Telegraph Road, Southfield, Michigan 48076. (Congratulations, John!)

Vivian Stannett has excused himself, figuring he can rest on his recently awarded laurels. He has just received the ACS award in Plastics & Coatings. Congratulations!

I am excusing myself from this issue, but I enclose with this mailing copies of two articles I have just sent off for review.

We look forward to hearing from our newest members next issue.

Finally Bob Fitch has a report on obtaining NATO support for a European meeting. I direct your attention to page F-3.

A. S. Dunn - UMIST, Manchester.

The definitive version of our paper 'On the Question of Enhanced Rates of Initiation in Emulsion Polymerisation Systems' has not yet been submitted for publication because a re-examination of the experimental data showed that the somewhat scattered points are in fact best fitted by the 'best straight line' through them as Tonge had consistently maintained giving the figures which appear in the 'Polymer Preprints' version indicating a slight (ca. 50 %) acceleration in the presence of vinyl acetate monomer of the decomposition of potassium persulphate. The amount of bisulphate ion which could be produced is quite inadequate to produce any appreciable acid catalysed decomposition of the persulphate. It is notable that no previous or subsequent worker has been able to measure rate constants as low as those reported by Kolthoff & Miller for the decomposition of potassium persulphate. However it should be possible to establish this conclusion more soundly by using the Method of Least Squares to fit the data on rates of DPPH consumption and the derived rates of persulphate decomposition and I hope to do these calculations within the next few weeks.

J.M.Lingeois (Liege) presented a paper entitled 'A Kinetic Investigation of the Persulphate Decomposition in Polymerisation Systems' at the IUPAC 1973 Symposium on Macromolecules at Aberdeen. Parallel iodometric and acidimetric determinations of the rate of persulphate decomposition were made in the presence of vinyl chloride: the sulphur content of the polymer was also determined. The results favoured Fronaeus & Ostman's decomposition mechanism

$$S_2O_8^{2-} + H_2O = \cdot SO_4^- + HO\cdot + HSO_4^-$$

whereby only one sulphate end-group is produced for each persulphate molecule decomposed. Recalculation of the result of a similar experiment by Gromov in the presence of styrene (Experientia, 26 (1970) [illegible]) which he claimed disproved Fronaeus & Ostman's mechanism showed that this experiment actually supported it also! Conductivity measurements provided evidence of ion association which explained the differences which have been observed between the decomposition rate of ammonium and potassium persulphates.

Apart from a lecture by John Vanderhoff and a paper by John Ugelstad which the majority of Group members would have heard in June, other papers of interest were given by A.R.Berens (B.F.Goodrich, Brecksville) on 'The Continuous Emulsion Polymerisation of Vinyl Chloride' and D.C.Blackley (National College of Rubber Technology) on 'Blending of Natural and Synthetic Rubber Latices'. There was also an abstract 'Some Aspects of Vinyl Acetate Polymerisation in Emulsion in Presence of Polyvinyl Alcohol' by Gavat, Dimonie, Donescu, Munteanu, and Hagiopol (Bucharest) but none of the authors had been able to attend to present their paper. In the abstract they state that they have found the rate of polymerisation of vinyl acetate in presence of polyvinyl alcohol to be constant for a large part of the course of the reaction, to be proportional to the initial monomer concentration and the square root of the initiator concentration. A decrease of rate (attributed to transfer) and increasing formation of gel is observed as the polyvinyl alcohol concentration is increased: more graft polymer is formed at the lower monomer concentrations.

Berens said that although the continuous emulsion polymerisation of vinyl chloride had been practiced in Germany for 30 years, very little information on the process had been published. Treatments of continuous emulsion polymerisation generally started from the assumption of Smith-Ewart kinetics which were not applicable to vinyl chloride. Batch experiments showed that the rate of polymerisation was proportional to the square root of the initiator concentration and a low power of the number of latex particles in agreement with the results of other workers. Expressions for the instantaneous and steady-state polymer concentrations in continuous seeded reactors had been derived as functions of residence time, seed particle, and initiator concentrations. These indicate that the behaviour of the continuous reactor is highly dependent on residence time. Good agreement is obtained between experimental data on continuous polymerisations and the theretical predictions using rate parameters obtained from batch experiments. The effect of the particle size distribution of the seed latex had been investigated: this affects the reaction rate because large particles grow more quickly than small ones. In unseeded runs evidence of a cycling effect with intermittent particle nucleation was obtained.

Blackley's contribution was concenrned with the sharp increase of viscosity which is observed when 25% SBR latex is blended with 75% natural rubber latex in the manufacture of latex foam acticles. In industrial practice additional soap is added to reduce the viscosity but the reason for the effect remained to be explained. The effect is time dependent and when enough time has elapsed the viscosity of the blend is that expected from additivity of the separate latices. The results are interpreted as being due to differing rates of adsorption and desorption of the soap stabilising the SBR latex and the protein stabilising the natural rubber which results in a temporary agglomeration of the SBR when the latices are mixed initially due to loss of soap.

My own contribution to the Symposium was 'On the Question of Stereospecific Polymerisation in Emulsion using Interfacial Initiation Systems' being a presentation of the results described in the September 1972 Newsletter. Although the n.m.r. spectra we obtained were not good enough to be satisfactory for quantitative resolution, superposition of the spectra was enough to show that there was no significant difference between them. Similarly the small differences in the J values calculated from the infra-red spectra appear to arise more from differences in the precise manner of drawing in the base line than from any significant difference between the spectra of the specimens.

POLYMER COLLOID GROUP NEWSLETTER

R. M. Fitch.

I am enjoying the excitement of living in a new country and the pleasure of working closely with John Ugelstad!

Polymerization in Emulsified Monomer Droplets:

We have started some experiments on the "true" emulsion polymerization of MMA using the now famous Ugelstad mixed emulsifier concept. Initial surface chemical studies were discouraging because with this polar monomer the adsorption of emulsifiers was weak and left much in the aqueous phase. This latter could stabilize primary polymer particles generated in the aqueous medium, which is undesirable. We have found surprisingly that by using very hydrophobic surface active materials, e.g. octadecanol and cetyl (C_{16}) sulfate plus added electrolyte, it is possible to obtain almost quantitative adsorption of emulsifier. And the resulting monomer emulsions are stable, with particle sizes almost entirely below 1 μ dia.
The polymerizations with these systems are just being initiated (pardon the pun!) and it is too early to tell what the results will be.

MMA Latex Polymerization Kinetics.

I have been looking at some old data which T.J. Chen and I took about 5 years ago. We ran a large set of dilatometric experiments at various monomer concentrations all below saturation, and at various initiator concentrations. We were primarily concerned with obtaining the polymerization kinetics during the period of particle formation and proposed that the overall radical concentration was proportional to the total polymer/aqueous solution interfacial area (ACS Polymer Preprints 10, 424 (1969)). This still may be so, but more and better experimental data are required during the first few seconds, a project upon which we are embarked currently in Conn.

But looking at the rest of the data, we now find that the system apparently obeys Smith-Ewart Case 3 very well at 30° even at extremely small particle sizes because of MMA's well known gel effect.
According to Smith-Ewart Case 3, we may calculate the ratio of rate constants:

$$\frac{k_p}{k_t^{\frac{1}{2}}} = \frac{R_p}{\rho^{\frac{1}{2}} v_p^{\frac{1}{2}} \left[M_p\right]}$$

Assuming $\rho = \rho' = R_i$, we obtained the following values for $k_p/k_t^{\frac{1}{2}}$ for four sets of experiments in which only the initial monomer concentration was varied. The experimental ratios are compared at approximately the same M_p-values, since we expected the ratio to be a strong function of monomer concentration, which in turn determines the magnitude of the gel effect:

Approx. $[M_p]$	Exp. No./$[M_o] \cdot 10^2$			
	61/1.73	47/3.45	60/5.18	59/6.77
1.9			4.24	3.94
1.8			4.24	4.02
1.7			4.14	
1.6				
1.5			4.17	4.04
1.4			4.10	
1.3		4.05	3.96	4.03
1.2		4.30		
1.1		4.19	3.84	3.93
1.0		4.04		
0.9		3.90	3.77	3.87
0.8		3.79		
0.7	3.26	3.77	3.33	
0.6	3.72		3.20	
0.5	3.77	3.32		
0.4	3.13	3.08	2.75	
0.3	2.91		2.12	
0.2	2.43	2.60		
0.1	2.02	1.88		

We are obviously past the peak of what would be the maximum in the gel effect in bulk polymerization and are on the descending side. This is of the same order of magnitude and in the same direction as we have found for nonaqueous latex polymerization, as shown in the accompanying figure.

If we use the value of the diffusivity of monomer in polymer determined by Vivian Stannett and his Mitarbeiter under these conditions:

$$D = (8 \pm 5) \times 10^{-13}\ \mathrm{cm^2 s^{-1}}$$

to calculate a diffusion-controlled k_p by Schulz's equation (Z.Phys.Ch. NF 8, 286) we obtain

$k_p \approx 300\ \mathrm{l\ mol^{-1} s^{-1}}$ (slightly lower than the bulk value) and
$k_t \approx 4 \times 10^3\ \mathrm{l\ mol\ s^{-1}}$,

which will give us values of $\bar{n}$ of from ca. 1 to 6, very reasonable. If we use values extrapolated from Gerrens work (Z.Elect.Ch. 67, 751) where he has k_p precipitously descending at these monomer concentrations, we obtain values of $\bar{n}$ that appear ridiculously high, for instance $\bar{n} = 25$ when dia. = 24 nm. We have not yet resolved this disagreement.

NATO and our Next Microsymposium:

NATO will not support a microsymposium of the kind we are planning, tentatively for Bristol in June. They do support Advanced Study Institutes of a somewhat larger scale in which prominent scientists give lectures to advanced "students". They state that "the latest researches of the participants should not dominate". I think it would be desirable for us to hold an ASI in connection with what I hope will be our 1975 international μ-symposium, just as Ron Ottewill has proposed an informal Faraday discussion with the Bristol meeting.

On this basis I wrote a proposal that an Organizing Committee be established and meet in Bristol in June, '74 to plan a NATO/ASI for the following summer (1975); that NATO support the meeting of the Organizing Committee; and that the ASI be held somewhere in Europe. I received a very prompt response from NATO saying that they liked the idea and could contribute about 35 % to 45 % of what I asked for to bring the Organizing Committee to Bristol.

The following have agreed to serve on that committee: Ron Ottewill, Irv Krieger, Sandy Dunn, Don Napper, Vivian Stannett, John Ugelstad and myself.

Although this will only give a limited number only partial support, I hope it will be sufficient to allow us to meet in Bristol in the Spring. In any case, prospects for the following year in still another part of the world are rather promising.

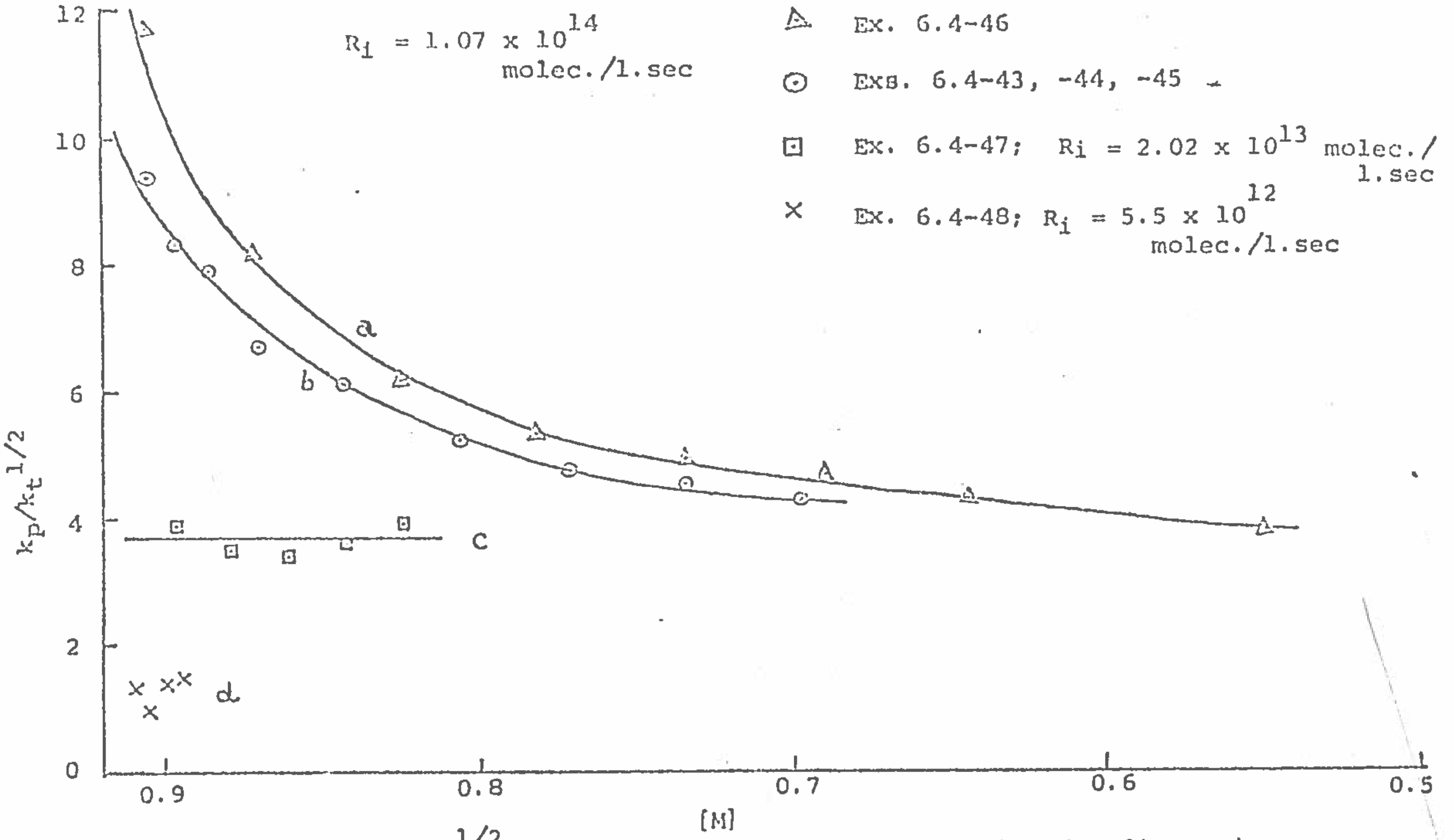

Fig. 56. Plot of $k_p/k_t^{1/2}$ vs residual monomer concentration for dispersion polymerization using PSA stabilizer. Points for Ex. 6.4-48 are crowded because of low conversion.

F4

Polymer Colloid Newsletter

I. M. Krieger

October, 1973

Emulsion Polymerization Studies (M. Juang, R. Seidewand)

Difficulties have been encountered with incorporation of sulfoethyl methacrylate as a comonomer. Polymerizations proceed normally, giving monodisperse latices which, after deionization, apparently show high coverage of strong acid groups. The key symptom of trouble is the fact that the latices are less viscous than are latices with lower surface charge at the same particle size and volume fraction. The reason appears to be that a substantial fraction of the sulfoethyl methacrylate is present as water-soluble polyelectrolyte, which is not removed during ion exchange. Mr. Eguiluz has shown that the polyelectrolyte can be removed by repeated washing of the latex, which is accomplished by cycles of centrifugation, decantation and reconstitution with fresh water. The resulting latices still show higher surface charges than those made without sulfoester, but now show higher viscosities as well. An attempt is underway to purify the latex by adsorption on alumina, as described in a Dow publication. A second route toward achieving high surface charge is substitution of vinyl benzenesulfonic acid which, unfortunately, is not so readily available. Initial experiments show that the polymerization proceeds normally to give uniform latices, but that stability during polymerization is more sentitive to electrolyte content than is the case with sulfoethyl methacrylate.

Electroviscous Effect (M. Eguiluz)

Mr. Eguiluz has completed his study of a single latex at various volume fractions, in which he studies the effect of type of amount of added electrolyte on the non-Newtonian viscosity. As reported previously, the electroviscous effect is a function of the normality of added electrolyte, and is independent of its nature. He also found yield stresses in the partially deionized latices, whose flow behavior was correlatable with the Casson equation. The next projected step in the work, involving variation of latex surface charge, has been held up due to the difficulties described above. Mr. Eguiluz has now prepared usable quantities of polyelectrolyte-free latex whose surface charge is approximately five times that of the latex which he has studied. He will also study the role of particle size in the electroviscous effect.

Order-Disorder Transition (B. Zysman, T. Yang)

Mr. Zysman has attempted to reproduce the work of Hachisu *et al.* (J. Colloid and Interface Sci. 1972-3) on the equilibrium diagram for the order-disorder transition. By adding sodium chloride to deionized latex, followed by centrifuge-accelerated settling, he has achieved a phase separation. Analysis of both phases for chloride content (using silver-silver chloride electrodes in a concentration cell arrangement) he has found a higher chloride ion content in the disordered phase. His measurements appear to correlate well with the requirements of a Donnan-type equilibrium across the phase boundary. Additional studies are in progress with added HCl, which should be simpler to analyze because of the presence of a single cation type.

Mr. Yang is conducting a theoretical analysis of laser Doppler scattering from the ordered phase, using as a model a harmonically bound particle undergoing Brownian movement. His objective is to predict the difference between laser Doppler scattering by a harmonically bound particle and that of a free particle, with the objective of determining lattice force constants. With the collaboration of Dr. Robert Edwards of our Department of Chemical Engineering, an experimental test will be undertaken.

Our group was visited last month by Jim Goodwin, who made several useful suggestions. Among them was the independent measurement of lattice force constant by propagation velocity of shear waves, a method which was originally described by van Olphen, and which has been successfully demonstrated on latex systems at Bristol. We hope to put this method into operation here.

POLYMER COLLOIDS AT SYDNEY UNIVERSITY

D.H.NAPPER

1. It has commonly been assumed, always without proof, that polystyrene latices prepared by emulsion polymerization in the presence of ionic surfactants, are stabilized solely by electrostatic interactions. Hence the popularity of polystyren latices as model electrostatically stabilized colloidal dispersions.

We have been able to show that polystyrene latices prepare at higher temperatures (ca. 70°C), using potassium persulfate or hydrogen peroxide as initiator, may have a highly significant contribution to their stability from non-electrostatic sources. All the circumstantial evidence to-date supports the idea that this contribution originates from the presence of surface carboxylic acids. We reported in this newsletter previously that poly(acrylic acid) behaves as an excellent steric stabilizer, giving rise to latices that are entropically stabilized in water and flocculate on cooling. Polystyrene latices that possess surface carboxylic acid groups behave in a remarkably similar fashion once the electrostatic interactions are removed.

Latices prepared at lower temperatures (ca. 20°C) do not seem to exhibit comparable effects. However since some carboxylic acids are probably formed at all temperatures (even if they cannot be detected by titration), it seems impossible at present to exclude the possibility of some steric stabilization of even the most well-bred (or expensive!) polystyrene latex.

2. We have recently discovered that sterically stabilized latices can be flocculated by bridging flocculation, just as electrostatically stabilized latices can. The surprising thing is that, whereas high molecular weight polyelectrolytes are madatory for bridging flocculation in the electrostatic case, low molecular weight polymers (e.g., 10^4-10^5) happily flocculate sterically stabilized particles at say, 10-20 p.p.m. Thus poly(ethylene oxide) of M_V = 4000 will flocculate the polystyrene latices (described in section 1 above) that contain surface carboxylic groups. The mechanism of action appears to be for the PEO to hydrogen bond to the surface carboxylic acid groups of one particle and subsequently in a Brownian collision, to hydrogen bond to the other particle.

Polymer Colloid Group Newsletter - October 1973

Poehlein

1. Continuous Emulsion Polymerization of MMA.

Our work on continuous emulsion polymerization of vinyl acetate is at a standstill while Richard Greene fulfills a 90-day ROTC commitment with the U.S. Army. Richard hopes to finish his dissertation in early spring.

Another student, Rafael Gonzalez, has started work in the continuous reactor area with MMA. As you may recall, Rich Greene carried out some CSTR (Continuous Stirred-Tank Reactor) runs with MMA and found the reactor unstable and quite prone to cyclic behavior. Mr. Gonzalez has started work with a tubular reactor to determine if the instability can be avoided. A second reason for studying the continuous tube reactor is that such reactors might be desirable for producing continuous seed-streams to feed CSTR trains in commercial plants.

Our first problem was to establish tube flow conditions that might be close to those that would exist in commercial reactors. One would guess that this could be laminar or turbulent flow. While laminar flow is easy to achieve in small tubes, one cannot move into the turbulent region ($N_{Re} = \frac{DV\rho}{\mu} > 2300$) without a very large consumption of materials and quite high velocities. Since we did want to obtain nearly plug flow in some runs it was decided to run the emulsion through the reactor between slugs of N_2 gas. Preliminary experiments in small glass tubing showed considerable mixing between the liquid slugs. since we believed that a major part of this axial mixing occurred because of wall wetting, a change was made to small teflon tubing. Sure enough, the axial mixing was reduced considerably.

We have just completed some preliminary runs in the teflon tube and as usual some problems remain. Conversions beyond about 2.5% have not been achieved even though the same recipe with the same batch residence time yielded 5 to 9% conversion. We have some inhibitor-retarder problems with our water supply (perhaps O_2) which are being corrected. Perhaps the teflon tubing is also a source of inhibition problems. Testing that possibility is next.

2. Drying of Latex Films:

Richard Witmeyer has finished a final draft of his thesis on drying of latex films under stagnant and forced convection conditions. Richard studied the drying of thin films on a flat plate with air velocities of 0 to 4 mph. We were able to predict, within 10 to 20 percent, drying rates during the constant rate period from correlations for heat transfer coefficients for flow over a flat plate. We assumed, for these calculations, that the surface of the drying film was at the wet-bulb temperature of the air.

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CONTRIBUTION TO POLYMER COLLOID GROUP
QUARTERLY NEWSLETTER
SEPTEMBER 1973
A.A. ROBERTSON, DEPARTMENT OF CHEMISTRY, McGILL UNIVERSITY

Studies of the particle interactions in latexes are currently being continued by Mr. Andy Homola. The principal experiments involve the measurement of pressure-volume relationships of a latex confined by a porous membrane. The apparatus is similar to that described in an earlier newsletter by Ron Ottewill except that the volume is controlled and the pressure is measured rather than vice versa. The nature of any transient or rate-dependent behaviour is therefore different but ideally the equilibrium behaviour might be expected to be the same.

The latexes being used are monodisperse (0.5 μm) polystyrene produced by surfactant-free polymerization. The stabilization by functional groups introduced by the polymerization conditions has been looked at, but the main interest is currently the additional effects of selected non-ionic emulsifiers on the pressure-volume relationships. The latexes are both charge stabilized and sterically stabilized and the relative contributions are being investigated by exercising some control over each effect.

Attention is also being paid to the interpretation of the pressure-volume curves which were intended to be indicative of interparticle forces as a function of separation distance. However, hysterisis and time- or rate-dependent behaviour provide complications that demand close consideration of the mechanisms and modes of packing.

EMULSIFICATION WITH MIXED EMULSIFIER SYSTEMS

U-1

by John Ugelstad
Laboratory of Industrial Chemistry
The University of Trondheim, Norway

We have continued our work with mixed emulsifiers.
The following items are under investigation:

1. The effect of fatty alcohols of different chain length.
2. Effectivity of the emulsification with different substrates.
3. Possible methods of determination of the droplet size after emulsification.

In previous papers on emulsification and polymerization of styrene and vinyl chloride with mixtures of cetyl sulphate and cetyl alcohol the following facts were established.

a) To bring about substantial initiation in the monomer droplets it is necessary to bring about such an effective emulsification of the monomer that most of the emulsifier is adsorbed onto the droplets, leaving only a minor part in the aqueous phase.

b) To obtain an effective emulsification of the monomer the ionic emulsifier and the fatty alcohol should be mixed with water at an elevated temperature before addition of the substance to be emulsified.

We have suggested that the rapid emulsification of the monomer takes place by formation of a complex layer at the oil-water interphase, befor any equilibrium distribution of the fatty alcohol between the interior of the droplets and the interface is established. This hypothesis was supported by the fact that the emulsions even with continued stirring at the same rate gradually became poorer. This could be observed by optical microscopy and also by measurements of the amount of cetyl sulphate adsorbed on the droplets as a function of time.

Ad. 1:

We have carried out experiments with different chain length of the fatty alcohol with different monomers and other substrates. A typical example is shown in Fig 2(in the paper sent separately to the members of the polymer group) with emulsification of chlorobenzene. As will be seen an increase in the chain length from tetradecanol to hexadecanol leads to a better emulsification and moreover to a much more stable emulsion.

In the case of octadecanol the maximum cetyl sulphate adsorbed is the same as with hexadecanol, however, the stability of the emulsion is as seen very much improved. This tendency is observed with all subtances investigated up to now. With a monomer like vinyl acetate this tendency is even much more pronounced. With hexadecanol the adsorption of cetyl sulphate is at a maximum only about 50 % at 50 °C, and the stability of the emulsion is relatively very low. With octadecanol the maximum adsorbed is about 80 % and the emulsion much more stable. The results seem to indicate that the destruction of the complex at the interphase by a desorption of the fatty alcohol in the interior of the droplets is much slower with octadecanol than with hexadecanol.

Ad. 2:

Our results on this is up to now rather confusing.

a) We find that with monomers like vinyl acetate and methyl metacrylate the maximum amount of cetyl sulphate adsorbed is considerably lower than with styrene, and at the same time the emulsions are considerably more unstable. This might be explained by a more rapid dissolution of fatty alcohol into the interior of the droplets with these polar monomers. During the emulsification at the constant, rather weak, stirring there is a competition between emulsification and deemulsification. If the rate of the latter is relatively high we might not have time to bring about the optimal dispersion before deemulsification caused by dissolution of the fatty alcohol has seriously reduced the degree of dispersion obtainable. We find, however, that when we emulsify normal alkanes these are also more difficult to emulsify than styrene and give less stable emulsions. We are investigating these effects rather intensively.

Ad. 3:

It would be of very great interest for our quantitative treatment of the emulsification process and for the emulsion polymerization if we could measure the droplet size and the droplet size distribution. Optical microscopy does not show droplets beyond 0.5 μ. Infrared microscopy seems to be difficult because of multiple scattering. We have just started with attemps to measure the droplets by electron microscopy according to a procedure described by Freshwater et al[x]. In this procedure the emulsion

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[x] D.C. Freshwater, M.J. Groves, B. Scarlett: Proc. 25th Cong.Pharm.Sci. 307-31
Butterworth, London 1962.

is dispersed in bovine albamin fraction V and sprayed onto grids coated with Formvar and carbon films. After allowing to dry the grids were placed overnight over 0.5 % osium tetroxyd.
We seem to be able to get fairly good pictures by this methode, however we are far from sure that we measure the correct droplet diameter.

As a conclusion we may say that with proper choice of emulgator systems may be able to bring about effective emulsifications of most monomers. It seems, however, that the most suitable systems and the optimal temperature may be different for different types of monomers. Polymerization experiments with different monomers will be carried out when the process of emulsification has been more thoroughly investigated.

P.S.
A copy of the paper: "Emulsification with mixed emulsifier systems consisting of sodium hexadecyl sulphate and different long chain alcohols" by F.K. Hansen, J. Ugelstad and S. Lange.
Abstract of communications 5th Scandinavian Symposium on Surface Chemistry, Turku/Åbo, Finland, August 21-23 1973 is sent to the members of the polymer group.

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CENTER FOR SURFACE AND COATINGS RESEARCH

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Telephone (215) 691-7000, Ext. 220

October 26, 1973

Dr. David J. Williams
Department of Chemical Engineering
City College of New York
New York, New York 10031

Dear David:

The following is a brief summary of the research areas in which we have been active during the past several months: 1. rate of drying of latex films; 2. characterization of latex particle surfaces; 3. preparation of model microvoid films; 4. electrophoresis; 5. preparation of latexes by emulsification.

Our first student who worked on rate of drying of latex films, Richard Witmeyer, has just received his Master's Degree. For his thesis work, he measured the rate of drying of monodisperse 60:40 styrene-butadiene copolymer latexes in the particle size range 1650-5900A. at air velocities in the range 0-4 mph. Under nominally-quiescent conditions (0 mph), the rate of drying was almost independent of latex particle size and about equal to that of pure water or dilute emulsifier solution (see Figure 1). At the highest air velocity (4 mph), the rate of drying was much greater and also independent of particle size. At intermediate air velocities (2 and 3 mph), however, the rate of drying was strongly dependent on particle size, increasing with increasing size; moreover, the rate observed with the smallest particle size (1650A.) was about the same as that for water, but that for the largest particle size was much greater. At present, we are not able to explain this result and would welcome any suggestions. The correlation suggested by Irvin Krieger at our June meeting, namely, between particle size and Reynolds number, did not hold when the values were calculated accurately (you recall that an on-the-spot calculation seemed to give promise of a correlation). The calculated rate of drying, based on convective heat flow and the experimentally measured variation of wet latex area with time, is generally within 20% of the measured rate. We hope to have a written description of this work available within a few months.

We have a student, Wan Chu Wu, working on the characterization of latex particle surfaces using the ion-exchange-and-conductometric-titration technique. The latexes are ion-exchanged to remove adsorbed emulsifier and solute electrolyte and to convert residual surface groups to the acid form, then titrated conductometrically and potentiometrically with sodium hydroxide. The sodium hydroxide is added using a constant-rate-addition burette, and the pH and "conductance" are monitored using a two-channel recorder. The pH measurement is conventional, but the instrument for measuring the "conductance" (actually a parameter proportional to the conductance) is of a new design, originally from Dow but improved by another graduate student, Chuck Cronan. We do not have any new results to report as Wan Chu Wu is still checking his ion-exchange resins, titrating various strong and weak acids in solution, and characterizing monodisperse polystyrene latexes which we have measured before. We expect to have some results within the next few months.

The preparation of model microvoid films is being carried out by postdoctoral research associate Dr. Mohamed S. El-Aasser under the sponsorship of a paint company. Microvoid films are coating films which derive their opacity from tiny bubbles of air instead of pigment. Our objective is to prepare microvoid films containing monodisperse microvoids and measure their optical properties, so as to determine experimentally the optimum size of microvoid for maximum opacity. To do this, we take advantage of the tendency of monodisperse polystyrene latexes to form ordered rhombohedral arrays upon drying. Such polystyrene latex films are microvoid films, with the interstices between the packed spheres forming the microvoid. If the spheres are monodisperse and the order of packing is good, the interstices are also monodisperse. Polystyrene latex films, however, are weak and friable, and ordinarily it is not possible to remove them from the substrate without their cracking or breaking. Therefore, we polymerize a very thin layer (100-300A.) of polyethyl acrylate or poly-n-butyl acrylate on the surface of the monodisperse polystyrene latex particles. Upon drying, these sticky polystyrene particles form opaque, flexible films which are strong enough to be handled. The films are formed in the ultracentrifuge, and the thickness is controlled by the number of latex particles added to the ultracentrifuge tube. Thus far, we have prepared uniform films as thin as 0.4 mils (10μ). The reflectance-wavelength variation of these films is measured over both a black and a white background, and the Kubelka-Munk scattering and absorption coefficients are calculated. Thus far, films have been prepared and measured from polystyrene latexes of 0.234, 0.357, and 0.800μ diameter; other sizes are in various stages of preparation. The opacity of these films is in the same range as that of practical microvoid films (as it should be because the refractive index ratio between polystyrene and air is almost as great as that between titanium dioxide and polymer film), but we have not yet determined the optimum microvoid size definitively.

I am collaborating with Prof. Fortunato J. Micale on the electrophoresis work, which is under the sponsorship of NASA. Our first objective earlier was to analyze the results of the electrophoresis experiment carried out on the Apollo 16 mission. This experiment involved the separation of monodisperse polystyrene latexes of 0.234 and 0.800μ diameter. The apparatus consisted of three parallel electrophoresis cells, containing the 0.234μ size, the 0.800μ size and a mixture of the two sizes. During the outbound trip, one of the astronauts carried out the experiment, recording the results photographically and taping his observations. The electrophoresis experiment used a high voltage gradient and a high electrolyte concentration, conditions which do not give separation on earth because of the density-gradient-driven convection arising from the electrical heating of the sample. At zero gravity, the moving particle profile was bullet-shaped, with the tip reaching almost to the opposite electrode before all of the latex was out of the sample chamber. The reason for this elongated bullet shape was the strong electroosmotic flow. From measurements of electrophoretic mobilities, electroosmotic flow, etc., we found good agreement between the calculated particle profiles and those observed experimentally (see Figure 2). This work has not yet been published, but I hope to have a manuscript describing our efforts within a few months. Also, I can supply a copy of the NASA report of the experiment upon request. Our current work involves: 1. evaluating various cell-wall coatings to reduce the electroosmotic flow; 2. preparing and dyeing (coloring) monodisperse latex particles of density 1.000 g/gm/cc; 3. designing a simplified electrophoresis apparatus.

The preparation of latexes by emulsification is under the sponsorship of the Air Force Materials Laboratory and involves Profs. John A. Manson, Gary W. Poehlein, and Henry Leidheiser, postdoctoral research associates Dr. Mohamed S. El-Aasser and Dr. Joseph D. Hoffman, as well as graduate students Richard Stoisits and Charles Keifer. Our objective is to transfer to aqueous base some of the coating systems currently used for aircraft. Currently, the aircraft are painted with an epoxide-polyamide primer and a polyurethane topcoat. We propose to prepare emulsions of the appropriate prepolymers using the anionic emulsifier-fatty alcohol technique developed by John Ugelstad, Mohamed El-Aasser and myself during John's stay here in 1972. This technique allows the preparation of styrene emulsions with particle sizes as small as 0.2µ (Polymer Letters 11, 503, 1973). We propose to use the same technique to prepare epoxide and polyurethane emulsions, arguing that the emulsions prepared heretofore were of larger particle size, with average sizes in the range of 1µ and larger, and thus were not competitive with latexes prepared by emulsion polymerization, which usually have particle diameters in the range 0.1-0.3µ. The work is just getting started, but we have succeeded in preparing epoxide emulsions of small droplet size using the foregoing technique in combination with ultrasonic irradiation. However, we have not yet found out how to block or pre-react the isocyanate group of the urethane prepolymer preparatory to emulsification (isocyanate groups react readily with water).

I am sending to each member under separate cover the following reprints (which may be slightly different from the manuscripts distributed earlier):

1. "Competitive Growth of Polystyrene Latex Particles: Theory and Experiment," J. Polymer Sci. 11, 447 (1973).

2. "De-Inking --- The Ink Industry's Position," J. W. Vanderhoff, Am. Ink Maker 31(4), 38 (1973) (the only connection with emulsion polymers is that latexes are often used in the new water-based inks now under development).

3. "Separation of Latex Particles According to Size by Continuous Electrophoresis," G. D. McCann, J. W. Vanderhoff, A. Strickler, and T. I. Sacks, Separation & Purification Methods 2(1), 153 (1973).

4. "The Transport of Water Through Latex Films," J. W. Vanderhoff, E. B. Bradford, and W. K. Carrington, J. Polymer Sci., Symp. 41, 155 (1973).

5. "Emulsion Polymerization: Initiation of Polymerization in Monomer Droplets," J. Ugelstad, M. S. El-Aasser, and J. W. Vanderhoff, Polymer Letters 11, 503 (1973).

Also included are preprints of three papers on polymer-modified concrete presented at the ACS meeting in Chicago in August 1973:

1. "A Hypothesis for the Reinforcement of Portland Cement by Latex," J. E. Isenburg and J. W. Vanderhoff.
2. "Polymer-Impregnated Concrete: Rate of Penetration of Monomer," J. W. Vanderhoff, J. D. Hoffman, and J. A. Manson.
3. "Stress-Strain Behavior of Polymer-Impregnated Concrete," J. A. Manson, W. F. Chen, J. W. Vanderhoff, Y.-N. Liu, E. Dahl-Jorgenson, and H. Mehta.

Best regards to you and all members of the Polymer Colloid Group.

Sincerely,

John W. Vanderhoff

JWV/rm

enclosures

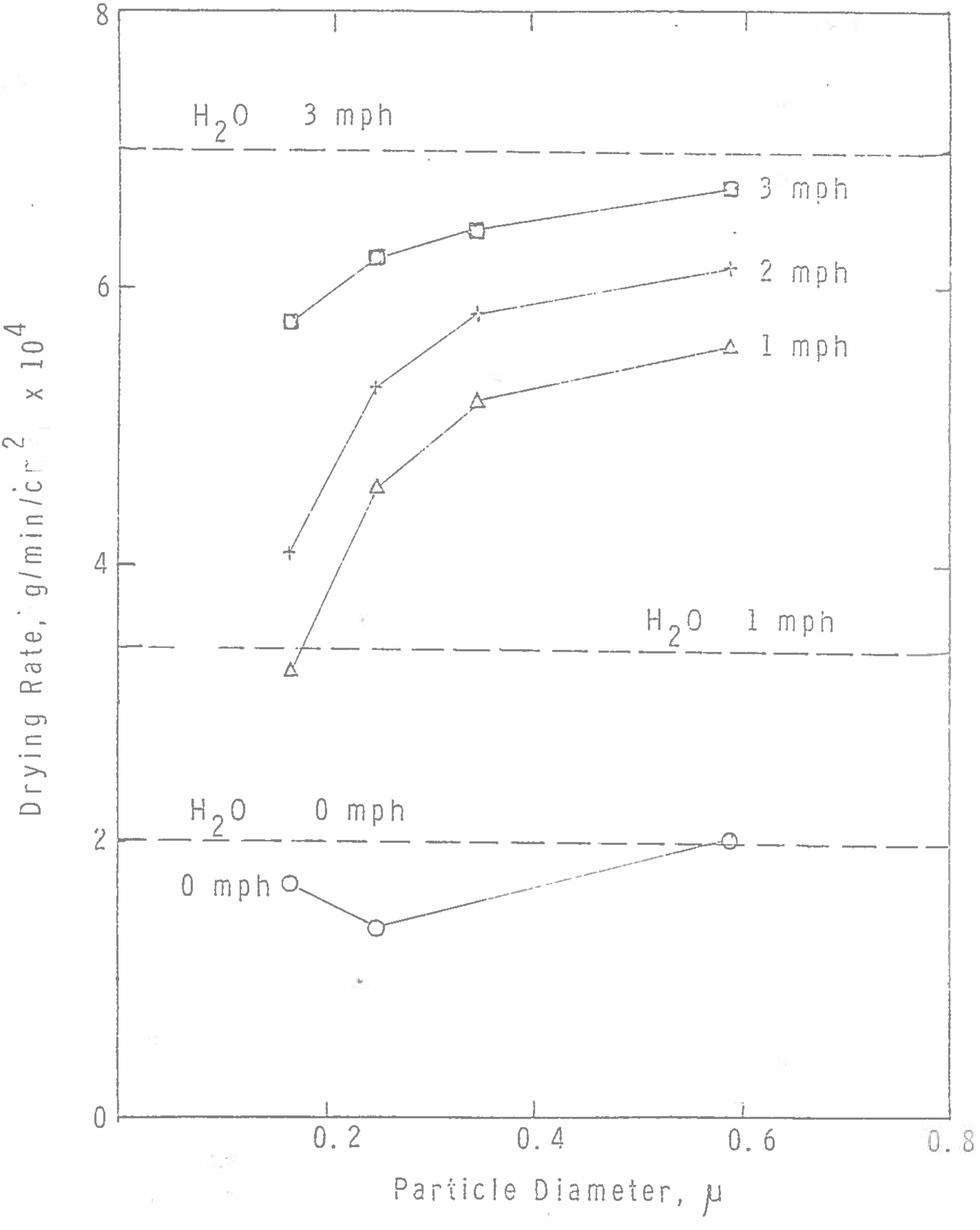

Figure 1. Drying Rate of Monodisperse 60:40 Styrene-Butadiene Copolymer Latexes as a Function of Particle Diameter and Air Velocity.

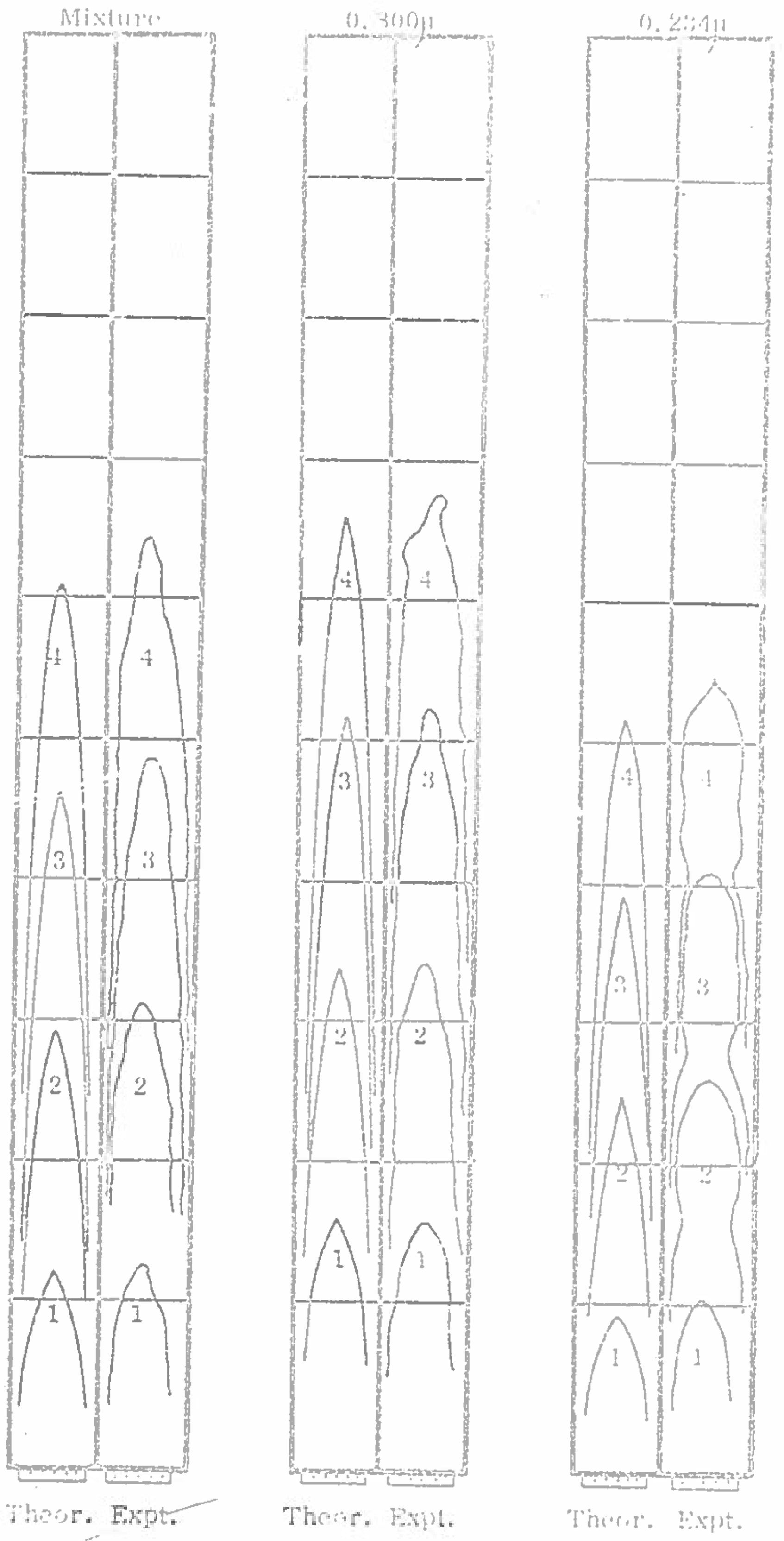

Figure 2. Zero-Gravity Electrophoresis of Monodisperse Polystyrene Latexes: Parabolic Profiles at 1, 2, 3, and 4 Minute Intervals

Size Distribution Analysis of Chemically Mixed Polymer Latex Systems

[illegible]

In the evolution of our development of a combined light scattering - ultracentrifuge technique to determine the size distribution parameters of polymer latex systems, we have successfully analyzed a mixture of polystyrene, PS, polyvinylchloride, PVC, and polyvinylacetate, PVA, latexes. This completes another stage of our program, and we can analyze broad continuous distributions, multimodal distributions, and now mixtures of chemically different latex systems each with its own unique size distribution.

In past reports we have outlined the zonal ultracentrifugation technique which utilizes a density gradient within the rotor and a light scattering technique used to obtain the size distribution parameters. Basically, the technique consists of fractionating the latex system and subsequently performing light scattering studies on a number of fractions. The original size distribution is then obtained from these individual analyses. Using this technique, and the %T vs. fraction number curve from a recording spectrophotometer, which is on line between the rotor and the fraction collection, the data can be converted to a plot of relative frequency vs. diameter.

Stokes law states

$$v = \frac{2}{9} r^2 g \frac{(\rho_p - \rho_m)}{\eta}$$

where v is the sedimentation velocity, r is the radius of the latex sphere, g is the applied centrifugal force, η is the viscosity of the medium, and ρ_p and ρ_m are the densities of the particle and the medium respectively.

The above equation illustrates that separation according to size can be achieved using the density gradient when all particles have the same density (i.e. one chemical component). In contrast to this zonal sedimentation velocity experiment, a separation according to chemically composition (i.e. ρ_D) can be achieved with a mixed latex system (e.g. PVC, PVA, and PS) by a zonal sedimentation equilibrium experiment. This later experiment would be followed by a velocity run for each chemical system obtained. Table I contains the size distribution parameters obtained by light scattering for the latex systems prior to mixing and the results from a fraction of each of the three chemical species isolated.

TABLE I

Latex System	Analysis Before Mixing		Analysis of Fractions	
	Modal Diameter Dm (nm)	Distribution Width σ_0	Dm	σ_0
PS	409	0.05	404	.07
PVA	228	0.14	238	0.13
PVC	419	0.055	424	0.07

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