POLYMER COLLOIDS GROUP NEWSLETTER

Vol. 16 No. 1

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1986 is a bumper year for Symposia on Polymer Colloids and Emulsion Polymerisation. Mohammed El-Aasser and Irja Piirma organised a two-day Symposium on 'Emulsion Polymerisation and Polymer Emulsions' at the A.C.S. Spring Meeting in New York on behalf of the Division of Polymeric Materials Science and Engineering at which 24 papers were presented: details appear within. Gary Poehlein has organised a One-day Symposium on 'Emulsion Polymers and Polymerisation' at the 60th Colloid and Surface Science Symposium which is to be held 15-18 June 1986 at the Georgia Institute of Technology in Atlanta. 14 papers will be presented and John Vanderhoff will give one of the two Plenary Lectures on 'Emulsion Polymers' on Tuesday 17 June. Details appear in the April 28 issue of 'Chemical & Engineering News'. Registrations ($125, Students $25) to Department of Continuing Education - R, Georgia Institute of Technology, Atlanta, Georgia 30332-0385, U.S.A. Telephone: (404) 894-2400. The Wingspread Advanced Research Workshop on 'Future Directions in Polymer Colloids' will follow a fortnight later: details of the programme appear on a later page: attendance is by invitation only - anyone who wants to go but has not yet arranged to do so should contact Mohammed El-Aasser - Telephone: (215) 861-3598.

This year's 17th Annual Short Course on 'Advances in Emulsion Polymerization and Latex Technology' is scheduled for 2-6 June at Lehigh with Carl Dahlquist (formerly of 3M), Do Ik Lee (Dow), L.C.Rubens (Dow), Ed Schaller (Rohm & Haas), Hans Slooten (Polysar), Jacque Singer (Montefiore Medical Center), and Don Sundberg as Guest Speakers. The European Version in Switzerland is scheduled for 18-22 August. A two-day Workshop on 'Modern Methods of Particle Size Analysis' with Instrument Demonstrations is scheduled for Saturday and Sunday 6/7 September preceeding the A.C.S. Autumn Meeting at Anaheim, California: details from Dr Theodore Provder, Glidden Coatings and Resins,Division of SCM Corporation, 16651 Sprague Road, Strongsville, Ohio 44136.

Two members have new addresses: John Gardon is now Vice President of Research and Development, Akzo Coatings America Inc., 650 Stephenson Highway, Troy, Michigan 48083-1197. Telephone: (313) 589-3660. Ed Collins is Executive Vice-President, Mitech Corporation but has not sent his new address.

I have a note from Professor Lyklema to say he has nothing to report at this time but there are several academic members from whom we have not heard from for some time and, with the honorable exceptions of Dow and the C.N.R.S. Laboratories (are they industrial or academic?), industrial members do not seem to have managed even an occasional contribution recently. This makes for economy in the production of the Newsletter but it may be time for the Annual Business Meeting (for which time will have to be found during the Wingspread Workshop) to make a thorough review of the Membership Roll (or the Rules which oblige academic members to provide at least a brief contribution to every issue and ask industrial members to contribute when they can). Everyone should therefore aim a contribution (short or long but not too long e.g. more than three single-spaced A4 pages) ready for despatch by mid-September. If the Annual Meeting succeeds in appointing a new Editor, notification of the address to which the contributions should be sent will have been received by that time.

A. S. Dunn

Programme for the NATO Advanced Research Workshop on FUTURE DIRECTIONS IN POLYMER COLLOIDS, Wingspread Conference Center, Racine, Wisconsin
30 June - 4 July, 1986

Monday 30 June. Topic I EMULSION COPOLYMERIZATION AND PARTICLE MORPHOLOGY
9.00 Plenary Lecture: J.W.Vanderhoff (Lehigh University)
10.30 D.I.Lee (Dow, Midland) 'Interpenetrating Polymer Network Latexes: Synthesis, Morphology, and Properties'
11.15 J.Guillot (CNRS, Vernaison) 'Simulation of Copolymer Particle Morphology, Characterization Techniques, and Mechanical Properties'
3.00 Panel Discussion I: J.W.Vanderhoff, R.Gilbert (Sydney), H.Kast (BASF, Ludwigshafen), G.W.Poehlein (Atlanta), D.Sundbery (New Hampshire) R.Wessling (Dow, Midland).
7.30. Topic II RHEOLOGY OF LATEX SYSTEMS AND CONCENTRATED DISPERSIONS
Plenary Lecture: I.Krieger (Case-Western, Cleveland)

Tuesday, 1 July
9.00 W.B.Russel (Princeton) 'Microstructure and Rheology: Theoretical Approaches'
9.45 R.Hoffman (Monsanto, Springfield) 'Structure Formation in Flowing Suspension'
11.00 Panel Discussion II: I.Krieger, C.E.Chaffey (Toronto), J.W.Goodwin (Bristol), D.Quemada (Paris), T.G.M.van de Ven (Montreal).
2.00 Topic III POLYMER STABILIZED LATEXES
Plenary Lecturer: B. Vincent (Bristol)
3.45 M.Croucher (Xerox, Ontario) 'Preparation of Sterically-Stabilized Polymer Colloids'
4.30 M.Cohen Stuart (Paris) 'Theories for Disjoining Pressure due to Soluble Polymers'

Wednesday, 2 July
9.00 Panel Discussion III: B.Vincent, T.Corner (International Paint, Gateshead), K.de Kruif (Utrecht), P.Sperry (Rohm & Haas, Spring House), Th. Tairos (ICI Plant Protection, Bracknell)
11.00 Topic IV NEW TECHNIQUES IN CHARACTERIZATION OF POLYMER COLLOIDS
Plenary Lecture: R.H.Ottewill (Bristol)
2.00 T.M.Winnik (Toronto) 'The Characterization of Polymer Colloids by Fluorescence Quenching Techniques'
2.45 R.M.Fitch (S.C.Johnson & Son, Racine) 'A Dielectric Spectroscopy of Model Polystyrene Colloids'
4.00 Panel Discussion IV: R.H.Ottewill, W.A.B.Donners (DSM, Geleen) A.Klein (Lehigh), B.Kronberg (Stockholm), D.G.Rance (ICI, Wilton)
7.30 Workshops on Topics I, II, III, and IV

Thursday, 3 July
9.00 Topic V POLYMER COLLOIDS IN THE BIOMEDICAL FIELD
Plenary Lecture: C.D.Flatsoucas (Houston)
10.45 J.Ugelstad (Trondheim) 'Uniform Magnetized Polymer Particles Applied in Selective Cell Processes'
11.45 J.Singer (Bronx) 'Immunoassay for the Rapid Detection of Infectious Antigens or Antibodies using Polystyrene Latex Particles'
2.00 Panel Discussion V: C.D.Flatsoucas,J.C.Daniel (Rhone Poulenc, Aubervilliers), K.Mustad (Oslo), M.Papamichail (Athens), C.Owen (Philadelphia), T.Wilkins (Brussels)
4.00 Workshops on Topics I, II, III, and V.
7.30 Workshops on Topics I, II, III, and IV.

Friday, 4 July
Reports back from Workshops: I, 9.00; II 9.30; III 10.00; IV 11.00; V 11.30.

Attendance is by invitation only: any members of the Polymer Colloid Group who have not yet accepted the invitation but wish to attend should contact Mohammed El-Aasser without delay.

EMULSION POLYMERIZATION AND POLYMER EMULSIONS

The Symposium, held in New York 16-17 April 1986, comprised the 24 papers listed below. Preprints appear in 'Polymeric Materials: Science and Engineering' 54 (1986) 354-380, 439-464, 510-534, 587-617. Copies of this volume are available to non-members of the PMSE Division at $15 including postage from the Distribution Office, ACS, 1155 sixteenth St. NW, Washington D.C. 20036. Collective publication is not planned but as the Symposium was co-sponsored by the Division of Colloid and Surface Chemistry, Bob Rowell has suggested that papers might be submitted for publication in 'Langmuir' - the Division's new journal.

I - The Role of Surfactant in Emulsion Polymerization
1 - Polymeric Surfactants based on Hydroxyethyl Cellulose as Stabilisers in Emulsion Polymerization. D.H.Craig (Hercules, Wilmington).
2 - Emulsion Polymerization with Pluronic Polyols. M.Jain & I. Piirma (Akron).
3 - Uniform Polymer Particles by Dispersion Polymerization in Alcohol. C.M.Tseng, Y.Y.Lu, M.S.El-Aasser, & J.W.Vanderhoff (Lehigh).
4 - Microencapsulation of Emulsified Oil Droplets by in situ Polymerization. J.Berg, D.Sundberg, & B.Kronberg (University of New Hampshire and Swedish Institute of Surface Chemistry).
5 - Monomer Grafting Reactions of Hydroxyethyl Cellulose in the Presence of Non-Oxidizing Radical Initiators. D.H.Craig (Hercules, Wilmington)
6 - Inverse Emulsion Polymerization of Acrylamide: Anomalous Behavior of Tetronic 1102 Emulsifier. J.W.Vanderhoff, D.L.Visioli, & M.S.El-Aasser (Lehigh).

II - Polymerization Kinetics
7 - The Effect of Reaction Variables on Particle-Size Distribution in the Emulsion Polymerization of Styrene. A.S.Dunn & S.A.Hassan (UMIST, Manchester, UK).
8 - Miniemulsion Copolymerization of Vinyl Acetate and Butyl Acrylate. J.Delgado, M.S.El-Aasser, C.A.Silebi, & J.W.Vanderhoff (Lehigh).
9 - Emulsion Polymerization of p-Methylstyrene. S.Lee & I.Piirma (Akron).
10 - Emulsion Copolymerization of 2-Ethylhexyl Acrylate with Acrylic Acid and Methacrylic Acid. F.V.Loncar, M.S.El-Aasser, & J.W.Vanderhoff (Lehigh).
11 - Effect of Monomer and Water Soluble Impurities on Emulsion Polymerization Case I and Case II Kinetics. B.P.Huo, D.Campbell, A.Penlidis, J.L.MacGregor, and A.E.Hamielec (McMaster).
12 - Free Radical Exit from Latex Particles. M.Adams, D.H.Napper, R.G.Gilbert, & D.F.Sangster (Sydney, Australia).

III - Emulsion Polymerization Latex Modifications
13 - N-substituted Acrylamides-Styrene Copolymer Latices. H.Kawaguchi, F.Hoshino, T.Fujimoto, & Y.Ohtsuka (Keio University, Yokohama, Japan).
14 - Electrophoresis of Expandable Layer Copolymer Latices. A.A.Morfesis & R.L.Rowell (Massachusetts).
15 - The Dilute Solution and Emulsion Properties of Model Water-Soluble-Dispersible Copolymers. D.Bode, B.Gedeon, & D.McIntyre (Akron).
16 - New Developments in Production and Application of Monosized Polymer Particles. J.Ugelstad, T.Ellingsen, A.Berge, H.B.Steen, & K.Nustad (NTH, Trondheim, Norway)
17 - Hydrophilic Microspheres for Bio-medical Applications. M.Chang, M.Colvin, J. Holt Rose, G.Richards, & A.Rembaum (JPL, Pasadena, California)
18 - Emulsifier-free Copolymerization of Styrene and Butyl Acrylate in the Presence of Functional Comonomers. J.L.Guillaume & C.Pichot (CNRS, Vernaison, France).

IV - Emulsion Polymerization Process Variables and Latex Properties
19 - Preparation of Large-particle-size Monodisperse Latexes in Space. J.W.Vanderhoff, M.S.El-Aasser, F.J.Micale, E.D.Sudol, C.M.Tseng, A.Silanowics, & D.M.Kornfeld. (Lehigh and George C. Marshall Space Flight Center)
20 - Preliminary Estimate of the Diffusion Coefficient of Polystyrene during Film Formation from Latex. M.A.Linne, A.Klein, L.H.Sperling, & G.D.Mignall(Lehi
21 - Polymethyl Methacrylate Grafting Reaction inside Polybutadiene Seeded Latexes M.P.Merkel, V.L.Dimonie, M.S.El-Aasser, & J.W.Vanderhoff (Lehigh)
22 - Effect of Process on Latexes from Monomers of Different Water Solubilities. M.H.Andrus Jr. (3M Center, St Paul, Minnesota)
23 - Semicontinuous Emulsion Polymerization of Styrene/Methyl Methacrylate. Kinetics and Microstructure of Copolymer. J.Palacios, G.Osorno, & L.Rios (Mexico).
24 - Comparative C-13 NMR Study of Alkyl Acrylate-Styrene Copolymer Latexes with Different Alkyl Groups. Relations between Microstructure and the Emulsion Process. [illegible], C.Pichot, M.Ramires, & J.Guillot

FURTHER DEVELOPMENTS IN THE THEORY OF COMPARTMENTALISED FREE-RADICAL POLYMERISATION REACTIONS

Recd 6 MAY

D. C. Blackley, London School of Polymer Technology,
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In our published papers[1-5] on the theory of compartmentalised free-radical polymerisation reactions, we have endeavoured, using the locus-population generating function approach, to obtain explicit analytic solutions for the time-dependent Smith-Ewart differential difference equations for various special cases. These equations describe the non-steady-state behaviour of a compartmentalised free-radical polymerisation reaction in which polymerisation is occurring in a fixed number of reaction loci which are dispersed in an external phase, and in which any new free radicals generated within the system are formed within the external phase. In our previous work, the assumption has been made that any radicals which are lost from the reaction loci to the external phase are not available for subsequent re-initiation. Whilst this assumption may be justified for some reaction systems, it is clearly unduly restrictive when considering reaction systems in general.

We are currently investigating the feasibility of a modified approach in which we introduce the concept of a two-dimensional array of locus-occupancy probabilities, $\nu_{i,j}$, where $\nu_{i,j}$ is the probability that a single reaction locus selected at random from the reaction system contains exactly i active radicals, and that, at the same instant, the arbitrary volume of external phase in the reaction system contains exactly j active radicals. This two-dimensional array of locus-occupancy probabilities replaces the one-dimensional array, ν_i, of our previous work, in which ν_i denoted the probability that a single reaction locus selected at random contains exactly i active radicals regardless of the number of active radicals present in the external phase at that instant. Thus the relationship between the ν_i of the previous work and the $\nu_{i,j}$ of our current investigation is

$$\nu_i = \sum_{j=0}^{\infty} \nu_{i,j}$$

We then introduce a time-dependent bivariate locus-population generating function, $\Psi(\xi, \zeta, t)$, defined as

$$\Psi(\xi, \zeta, t) = \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} \nu_{i,j}(t)\, \xi^i \zeta^j$$

where ξ and ζ are auxiliary variables. The function $\Psi(\xi, \zeta, t)$ can provide much useful information concerning the distribution of radical populations within the reaction loci and within the external phase. Thus the various moments of the joint distribution for i and j can be obtained from the general expression

$$E(i^l j^m) = \frac{1}{l!\,m!} \left\{ \frac{\partial^l}{\partial \xi^l} \frac{\partial^m}{\partial \zeta^m} \Psi(\xi, \zeta, t) \right\}_{\xi=\zeta=1}$$

In particular, the mean values for i and j can be obtained as

$$\bar{i}(t) = \left(\frac{\partial \Psi}{\partial \xi} \right)_{\xi=\zeta=1} \quad \text{and} \quad \bar{j}(t) = \left(\frac{\partial \Psi}{\partial \zeta} \right)_{\xi=\zeta=1}$$

We are currently investigating the feasibility of applying this approach to reaction systems more complex than those which we have considered hitherto, e.g., reaction systems in which radicals lost from the reaction loci to the external phase are available for subsequent re-entry into the reaction loci.

References

1. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc., Faraday Trans. I, 1977, 73, 1998

2. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc., Faraday Trans. I, 1978, 74, 2051

3. D. T. Birtwistle, D. C. Blackley and E. F. Jeffers, J. Chem. Soc., Faraday Trans. I, 1979, 75, 2332

4. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc., Faraday Trans.I, 1981, 77, 413

5. D. T. Birtwistle and D. C. Blackley, J. Chem. Soc., Faraday Trans.I, 1981, 77, 1351

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28 APR Recd

Contribution from the Institut Charles Sadron (CRM-EAHP) CNRS-ULP
6, rue Boussingault, 67083 Strasbourg Cedex, France

by F. CANDAU

The following are abstracts of papers in press

Copolymerisation of water-soluble monomers in non ionic bicontinuous microemulsions (F. Candau, Z. Zekhnini and J.P. Durand, J.Colloid and Int. Sci.)

Water-soluble copolymers of acrylamide and sodium acrylate of variable compositions were prepared by radical copolymerization in microemulsions stabilized by a nonionic emulsifier blend and dispersed in an isoparaffinic oil. Addition of monomers increases considerably the microemulsion region in the phase diagram. A close correlation exists between the optimum HLB value of the blend, the minimum emulsifier concentration and the acrylate content in the feed. A too high concentration of the latter produces a salting out of the hydrophilic moiety of the emulsifier, leading to a phase separation. The microemulsions of interest i.e. with high monomers contents (∿25%) exhibit a bicontinuous character. Polymerization in these systems produces a transformation of the random disordered structure towards a concentrated dispersion of spherical latex particles. The inverse latexes are highly stable and show no settling over months. The dimensions of the particles are rather low (d∿60nm) with a narrow size distribution.

Characterization of poly(acrylamide-co-acrylates) obtained by inverse microemulsion polymerization (F. Candau, Z. Zekhnini, F. Heatley and E. Franta, Colloid and Polymer Sci.)

Two series of poly(acrylamide-co-acrylates) with compositions ranging from 10 to 55 mol % acrylate units have been prepared by radical polymerization in inverse microemulsions. The compositional analyses of the samples have been performed using elemental analysis, potentiometry

and ^{13}C NMR. The comparison between the three methods indicates that ^{13}C NMR is the most reliable one, avoiding errors which often arise from associated water in hydrophilic polymers. The copolymer viscosity exhibits a maximum behavior around 40mol % acrylate content, a lower value than that already observed for copolymers prepared in homogenous solution. The production of copolymers presenting high intrinsic viscosities (∿3700 cm^3g^{-1}) is achieved using an inverse microemulsion as the polymerization medium operating at lower temperature.

We are presently investigating salt effects in solutions of non ionic emulsifiers and their applications as stabilizers in microemulsion polymerization (in collaboration with C. Holtzscherer). The results will appear in the next report.

References

"A ^{13}C NMR study of the sequence distribution of poly(acrylamide-co-sodium acrylates) prepared in inverse microemulsions". F. Candau, Z. Zekhnini and F. Heatley (Macromolecules, in press)

CONTRIBUTION TO THE POLYMER COLLOIDS GROUP NEWSLETTER

21 APR Recd

from
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1. The degree of dispersion of poly(vinylalcohol) in water/n-propanol solutions (F.P. Vercauteren).

Poly(vinylalchohol) (PVOH) and poly(vinylalcohol-co-vinylacetate) (PVOH-Ac) are widely used in industry. It is well known that it is difficult to make aqeuous solutions of this product in which the polymer is molecularly dispersed. Furhtermore, the properties of these solutions change on ageing because of aggregate formation. Wolram and Nagy (Kolloid Z.Z. Polymere 227, 86 (1968)) reported that addition of n-propanol to aqueous PVOH en PVOH-Ac solutions stops their ageing and suggested even that the polymers were molecularly dispersed in such solutions.
We reexamined this effect of n-propanol addition. The same PVOH as mentioned in the previous newsletter was first reacetylated to PVAc. Its molar mass was determined from GPC, osmotic pressure, light scattering and viscosity measurements.
GPC and osmotic pressure measurements gave an average value for the number average molar mass M_n of 97 kg. mol^{-1}. GPC, light scattering and viscometry gave an average value for the weight average molar mass M_w of 206 kg. mol^{-1}. From these data the corresponding values for PVOH were calculated to be 50 and 105 kg. mol^{-1}.
From turbidity measurements it was found that addition of n-propanol concentrations of 2 % and higher essentially stops ageing of the aqueous solution of this PVOH, irrespective of polymer concentration. This proves that no specific n-propanol-PVOH interaction is responsible for this effect.
Light scattering however gave a molar mass of 2700 kg. mol^{-1}, clearly showing that the polymer is not molecularly dispersed in 2 % n-propanol solutions.
Osmotic pressure measurements of both aqueous and 2 % n-propanol solution of PVOH showed erratic behaviour.
Intrinsic viscosity measurements resulted in a M_w value of 122 kg. mol^{-1}, surprisingly close to the value derived from the PVAC measurements.

One must keep in mind however that the Mark Houwink Kuhn Sakurada constants used have been determined by use of PVOH samples of which the molar mass was determined by light scattering of the corresponding PVAc. This means that the fact that PVOH is not monomolecularly dispersed is automatically taken into account in the k and a values of the MHKS equation.
It is therefore concluded that:
- unequivocal values for M_n or M_w of PVOH must be obtained via molar mass determination of the parent PVAc;
- n-propanol stops ageing of PVOH-solutions but does not lead to molecularly dispersed solutions.

More details of this work, carried out in cooperation with the universities of Osnabrück (FRG) and Bradford (UK) (prof. Lechner and dr. Eagland respectively) will appear soon in European Polymer Journal.

2. The effect of emulsifier-polymer complexformation on particle nucleation in emulsion polymerization

Complexation between water soluble polymers like polyethyleneoxide (PEO) and polycarboxylic acids like polymethacrylic acid (PMAA) is a well known phenomenon. In emulsion polymerizations comprising recipes with (meth)acrylic acid (M)AA and ethoxylated emulsifiers this complexation might be of importance in the particle nucleation stage, as the complexes formed are water insoluble. Therefore complexation might lead for instance to particle nucleation in an earlier stage in the polymerization thus influencing particle size and particle size distribution.
Results of model studies with MAA and MMA containing systems indeed do show interesting effects of addition of PEO. The molar mass of the PEO as well as the MAA/MMA ratio appear to be very important, effects being observed for PEO molar masses from 200-20.000 g.mol^{-1} and for all MAA/MMA ratios ranging from pure MAA to pure MMA. For the low MAA recipes the observed effects cannot be explained by PEO-polyacid complexation. The results suggest that oligomers formed upon initiation with persulfate interact with PEO in a manner that has been observed for anionic sufactants.

More details are described in an article submitted to J. Polym. Sci. Polym. Letters Ed.

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NUCLEATION AND STABILITY OF LATEX PARTICLES IN THE STYRENE EMULSION POLYMERISATION

The primary function of the emulsifier in all emulsion polymerisations is to stabilise the latex particles which form the principal locus of polymerisation. Emulsifier micelles do not appear to have any specific role in the polymerisation of the more water-soluble monomers where the latex particles are nucleated by the Fitch-Roe Oligomeric Precipitation Mechanism. Does this also apply to the less water-soluble monomers (typically styrene) in the presence of micellar emulsifier? Recent results from Sydney based on the skewness of the particle size distribution curve at low conversions suggest that the latex particles are also formed by a coagulative mechanism in that case (Lichti, Gilbert, & Napper, J.Polym.Sci. Polym. Chem. Edn. 21 (1983) 269). But how general is this result? It is difficult to catch polymerisations at sufficiently low conversions to obtain valid data but we did obtain a similarly shaped particle size distribution curve at 19% conversion with styrene at 90 °C at a phase ratio of 1:13.5 using 'Aerosol' MA at 0.0412 mol dm^{-3} (1.6 x c.m.c. under the conditions of the experiment) and potassium persulphate 1.85×10^{-3} mol dm^{-3}. On the other hand our previous work on the effects of different emulsifiers (J.Polym.Sci. Polym. Chem. Edn. 16 (1978) 677: p. 617 in Fitch ed. 'Polymer Colloids II' Plenum, 1980) and on the effect of added electrolyte (Polymer 23 (1982) 1172) shows that it is the concentration of micellar emulsifier which is important rather than the total emulsifier concentration as would be expected if the Smith-Ewart criterion for the cessation of latex particle formation - that the surface of the latex particles should have increased sufficiently to adsorb all the emulsifier present when the emulsifier exponent can only be 0.60 exactly - were correct. However, apart from the effect of the increase of micelle size with emulsifier concentration, these effects may be a result of increases in the amount of emulsifier adsorbed at the polymer/water interface. The most convincing evidence for the dominance of micellar nucleation above the c.m.c. with styrene is the large increase in the number of latex particles formed (and consequently in the Interval II polymerisation rate) observed at the c.m.c. Latex particles are certainly formed by a coagulative mechanism at lower concentrations so that an alternative explanation of this effect could be that it represents a transition from limited coalescence to stability of the primary latex particles. However we find (as reported at the New York Symposium) that slow coalescence continues when a completely polymerised latex is held at polymerisation temperature even when the initial emulsifier concentration was above the c.m.c. Although we have results for only one emulsifier ('Aerosol' MA), it appears that similar results have been obtained in unpublished work in industrial laboratories. Thus the alternative explanation may be excluded. It appears that under the commonly chosen conditions in which the latex particle number during Interval II is constant this is a result of a steady state in which the rate of particle nucleation (by oligomeric precipitation in absence of micelles) is equal to the rate of slow coalescence of latex particles. At lower emulsifier concentrations slow coalescence predominates and catastrophic coagulation may eventually ensue. At higher emulsifier concentration the surface of the latex particles is saturated with adsorbed emulsifier and a low concentration of micelles remains enhancing the rate of nucleation so that the particle number increases slowly (cf. Kincaid & Piirma: paper presented at the 1985 Philadelphia A.I.Ch.E. 'Emulsion Polymers' Symposium). It is possible that the rate of particle growth by polymerisation may actaly exceed the rate at which emulsifier can be adsorbed to stabilise the interface formed so that micelles are destabilised by polymerisation and undergo limited coalescence to form latex particles.

COLLOID RESEARCH AT MCMASTER UNIVERSITY - RECENT DEVELOPMENTS

by

Archie Hamielec

18 APR

1. HIGH CONVERSION BATCH AND SEMI-BATCH SUSPENSION POLYMERIZATION OF VINYL CHLORIDE:

The kinetics of high conversion polymerization of vinyl chloride (X > 0.75) are being investigated to better understand the control of particle porosity, resin bulk density and PVC thermal stability.

2. MICROSUSPENSION COPOLYMERIZATION OF ACRYLAMIDE WITH ANIONIC AND CATIONIC MONOMERS USING BATCH, SEMI-BATCH AND CONTINUOUS PROCESSES:

The kinetics of aqueous free-radical copolymerization of various comonomer systems are being investigated to optimize the production of high molecular weight products. Work is continuing on the use of airstops to control the polymerization rate.

3. EMULSION POLYMERIZATION OF VINYL ACETATE AND VINYL ACETATE/ACRYLIC ACID USING PARTIALLY HYDROLYZED POLY(VINYL ACETATE) AS STABILIZER:

Partition coefficients for the stabilizer on poly(vinyl acetate) particles have been measured for a range of conditions including, particle concentration, monomer concentration, electrolyte level and pH. This information permits one to accurately predict the bulk viscosity of the latex during polymerization.

The investigation of PVAc grafting on PVOH stabilizer is continuing.

Some of the work reported herein is being done in collaboration with Dr. J.F. MacGregor.

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POLYMER COLLOIDS AT THE UNIVERSITY OF SYDNEY

Reporters: D. H. Napper/R. G. Gilbert

1. Surfactant-free Polymerizations

Mr. P. J. Feeney has applied coagulative nucleation theory to describe nucleation in surfactant-free polymerizations of styrene. This theory considers the rate of production of precursor latex particles (i.e., particles that are too small to exhibit colloid stability and to swell fully with monomer):

$$\frac{dv_k}{dt} = \sum_{i=1}^{k-1} B_{i,k-1} v_i v_{k-i} - 2v_k \sum_{i=1}^{m} B_{ki} v_i - 2v_k B_{Nk} N_c$$

(k=1,2,..,m)

FORMATION BY COAGULATION OF PRECURSORS	LOSS BY COAGULATION WITH OTHER PRECURSORS	LOSS BY COAGULATION WITH MATURE LATEX PARTICLES

$$+K_{k-1} \bar{n} \frac{v_{k-1}}{V_p} - K_k \bar{n} \frac{v_k}{V_p} + \delta_{k,1} g(t)$$

GAIN FROM PRECURSOR GROWTH	LOSS BY PRECURSOR GROWTH	INJECTION OF PRIMARY PRECURSORS

Here v_k is the number of precursor particles containing k-fold primary precursor particles, N_c is the number concentration of mature latex particles, containing at least m primary precursor particles, K_k is the growth rate coefficient for a k-fold precursor, g(t) is the production rate for primary particles of volume V_p and $\delta_{k,1}$ is the Kronecker delta.

The theory then considers the rate of production of "true" (mature) latex particles by aggregation of precursor particles and by growth:

$$\frac{dN_c}{dt} = \sum_{i=1}^{m} v_i \left(\sum_{j=m-i-1} B_{ij} v_j \right) + K_m \frac{\bar{n} v_m}{V_p}$$

The growth by polymerization of latex particles is, of course, ignored here since particle number is conserved under growth.

The B_{ij}'s in the above equations are the rate coefficients for the slow coagulation of the aggregating species; their values may be estimated using DLVO theory in conjunction with Smoluchowski-Müller-Fuchs aggregation kinetics.

Although the for-going kinetic equations cannot be solved analytically, numerical solutions to these stiffly coupled equations can be obtained. The coagulative nucleation theory predicts with modest accuracy the dependencies of the number of particles generated in surfactant-free systems upon the initiator concentration and upon the ionic strength of the system that were reported by Ottewill et al. (Colloid and Polymer Sci., 252, 464 (1974)). It also predicts with fair precision the correct absolute number concentration of particles formed. For example, Ottewill et al. found experimentally that at a particular ionic strength N_c depends upon the initiator concentration [I] viz:

$$\log N_c = 0.717 \log [I] + 16.7$$

whereas coagulative nucleation theory predicts for the same conditions:

$$\log N_c = 0.77 \log [I] + 20.8$$

The agreement, while not perfect, is sufficiently good to suggest that the theory embraces the correct physical principles in a reasonably quantitative fashion. The experimental dependence of N_c on the electrolyte concentration

$$\log N_c \alpha -0.71 \log [E]$$

is reasonably well reproduced by coagulative nucleation theory:

$$\log N_c \alpha -1.1 \log [E]$$

Coagulative nucleation can thus explain a broad range of latex phenomena in styrene systems: the skewness of latex particle size distributions (which virtually eliminates the possibility of nucleation by micellar entry); the occurrence of periodic nucleation phenomena (Liesegang rings), also inexplicable by micellar entry theory; the plateau effect at high surfactant concentrations for the particle number concentration generated in emulsion polymerization; and the effects of initiator concentration and ionic strength on particle size (or number) in surfactant-free systems. Such broad applicability to a wide range of experimental data engenders confidence in the validity of the theory.

2. Butyl Acrylate Emulsion Polymerization

Mr. I. Maxwell has used our now-standard kinetic procedures to study the seeded emulsion polymerization of butyl acrylate. These combine chemically initiated studies of the approach to the steady state in non-nucleating systems with relaxation studies in γ-irradiated systems. These procedures allow unique values to be determined for the entry rate coefficient (ρ), the exit rate coefficient (k), the propagation rate coefficient (k_p) and the bimolecular termination rate coefficient (c or k_t). Butyl acrylate is a system where even for relatively small particles ρ, k and c are all active in determining the overall kinetics.

2 MAY Rec'd

CONTRIBUTION TO POLYMER COLLOID GROUP NEWSLETTER
FROM
LABORATOIRE DES MATERIAUX ORGANIQUES (CNRS)
SUBMITTED BY C.PICHOT

1-KINETIC STUDIES IN STYRENE-ALKYL ACRYLATE EMULSION COPOLYMERIZATIONS (W.RAMIREZ-S.DJEKKABA)
Extensive experimental work is carried out in order to get qualitative and quantitative informations on the polymerization mechanism in the emulsion polymerization of styrene with different acrylate monomers (methyl, ethyl) having appreciable water solubility

2-FUNCTIONALIZATION OF COPOLYMER LATEXES (C.BONARDI-F.LEVY-P.CRISTOU)
Recent studies in the lab (thesis of J.L.GUILLAUME) pointed out that water-phase polymerization is of critical importance in the polymerization mechanism (particle formation and stabilization). In the current works with the different systems (BuA/MMA; BuA/Styr) a preliminary objective is to determine the various parameters which control such aqueous phase polymerization (partition coefficients; polymerization rate data; etc). The next step deals with the modelization, with a view to predicting several kinetic parameters, such as the surface incorporation of the functional monomer

3-STRUCTURE-PROPERTIES RELATIONSHIPS IN EMULSION COPOLYMERS
Two research projects are currently investigated on the effect of the particle morphology on the mechanical properties of latex films. A first study deals with vinyl acetate-butyl acrylate copolymer latexes (X.Z.KONG) for which different particle morphologies were obtained with varying the composition and the process. The characterization of such particles is under way by electron microscopy using staining techniques or by the soap titration method (using the sodium hexadecyl sulfate as emulsifier probe). Micromechanical properties of these different films were investigated as a function of temperature (from 100°K to 340°K) and of frequency (from 5.10^{-5} Hz to 5 Hz). A second study is directed on a series of styrene-butyl acrylate latexes prepared by emulsion polymerization using various types of process (composition-controlled batch, core-shell, multilayered) and comonomer compositions (A.CRUZ-B.SCHUNLD)

4-INVERSE EMULSION (CO)POLYMERIZATION (C.GRAILLAT-M.LEPAIS)
Our activity in this area have been focused on the preparation of stable inverse emulsions at low emulsifier content (1 to 3% based on organic phase) using a mixture of two emulsifiers. Such emulsions are being tested for the synthesis of hydrophilic gels with acrylic acid or/and dimethyl aminoethylacrylate, using oil or water soluble initiators.

Newsletter Contribution
from University of Akron

I. Piirma

8 MAY Rec'd

Work carried out by A. Parker

SYNTHESIS OF POLYVINYL ALCOHOL-g-4-VINYLPYRIDINE HYDROCHLORIDE) FOR APPLICATION AS A SURFACTANT IN THE EMULSION POLYMERIZATION OF METHYL METHACRYLATE

ABSTRACT

Studies of the emulsion polymerization of methyl methacrylate were carried out in the presence of a novel graft copolymer, poly(vinyl alcohol-g-4-vinylpyridine hydrochloride) (PVA-g-4VPyHCl). The graft copolymer was synthesized under aqueous acidic conditions in the presence of a ceric ion/poly-(vinyl alcohol) redox initiation system. MMA emulsion polymerizations were found to exhibit two constant rate regions when they were formulated with solutions of the PVA-g-4VPyHCl emulsifier. The particle size distribution remained narrow in both regions, indicating that the dual rate region phenomenon might be a manifestation of the gel-effect. It was also found that PVA-g-4VPyHCl copolymers exhibit no critical micelle concentrations, and that PVA-g-4VPyHCl solutions become turbid and viscous upon standing. PMMA latices were unstable when they were formulated with turbid surfactant solutions; but when the turbid solutions were heated before use, the turbidity disappeared, and stable latices wqere readily formulated. This behavior may be a result of a tendency for PVA-g-4VPyHCl molecules to form thermally reversible crystalline-like aggregates in solution.

CONTRIBUTION TO THE POLYMER COLLOID GROUP NEWSLETTER

Submitted by F. L. Saunders, Dow Chemical Co., Midland, MI - U.S.A.

24 APR Recd

INTERPENETRATING POLYMER NETWORK LATEXES: SYNTHESIS, MORPHOLOGY, AND PROPERTIES*

D. I. Lee, T. Kawamura, E. F. Stevens

Dow Chemical U.S.A.
1604 Building
Midland, MI 48674

A B S T R A C T

Semi- and full IPN latexes were synthesized by emulsion polymerizing styrene and mixtures of styrene and butadiene, respectively, in the presence of crosslinked, carboxylated polymer latexes as seeds. Their particle morphology was studied by electron microscopy in conjunction with both hydrazine/OsO_4- and OsO_4- staining techniques. It was found that their particle morphology was a cellular structure typical of IPN's composed of two immiscible polymers, and the domain size of polymer II decreased with increasing crosslinking of polymer I. Indeed, as the crosslinking of polymer I seed latexes increased, two distinctive Tg's gradually disappeared and converged into a broad glass transition temperature. Dynamic mechanical spectroscopy (DMS) also provided information on the extent of interactions and mixing between the two polymers I and II. These IPN latexes exhibited unique mechanical properties and improved heat and light stability.

*To be presented at NATO Workshop, June 1986

DEVELOPMENT OF LOW GLOSSING PAPER COATING LATEXES: THEORIES AND CONCEPTS*

D. I. Lee, R. E. Hendershot
Dow Chemical Company
Midland, MI 48674

ABSTRACT

Theories relating to the gloss of paper coatings predict that very low coating gloss can be achieved with a microscoopic surface roughness without resorting to macroscopically rough coatings. Our earlier study (TAPPI Coating Conference, 97 (1974) has shown that the roughness of the coating surface is affected by the extent of the film shrinkage of binders: the greater shrinkage, the rougher surface. Also, it has been found that highly shrinkable latexes can result in microscopically rough coating surface, thus lowering the coating gloss. Combining the above theories and observations, we have developed low glossing paper coating latexes. This paper will discuss theories and concepts involved in the development of new, unique latexes for matte and dull paper applications.

THE EFFECT OF COATING COLOR SOLIDS ON PROPERTIES AND SURFACE UNIFORMITY*

R. L. Van Gilder, R. D. Purfeerst

Dow Chemical Company
Midland, MI 48674

ABSTRACT

The manufacturers of high quality coated printing papers are interested in higher solids containing coating colors for faster coater speeds, heavier coat weight applications and improved coated properties. Our earlier work (TAPPI 66 (11), 49 (1983) with high solids coatings showed good blade coater runnability using a specific high solids carboxylated styrene/butadiene latex.

Recently, higher solids coatings using a high solids latex were run successfully on the blade coater. Coatings containing a high kaolin clay composition were compared to coatings containing a high calcium carbonate pigment composition.

Coating at the highest practical solids level gave definite property advantages. Coating gloss, ink gloss and coating smoothness were significantly improved at the higher solids levels.

Surface structure analysis of the higher solids coatings indicated improved fiber coverage and superior structure uniformity without significant binder migration.

*To be presented at 1986 TAPPI Coating Conf., May 1986, Washington, D.C.

Microencapsulation of Emulsified Oil Droplets by In-Situ Polymerization

30 APR Recd

Johan Berg, Donald Sundberg* and Bengt Kronberg
Swedish Institute for Surface Chemistry
Stockholm, Sweden

This paper reports on the preparation and evaluation of microcapsules formed by the polymerization of methyl metacrylate in the presence of an oil/water emulsion. The oil phase was composed of alkanes (e.g. decane or hexadecane) and the oil/water emulsions were stabilized by a variety of surfactants. Both oil soluble and water soluble initiators were used and the monomer was introduced either in solution with the oil or as a dispersion in the water. The objective of the work was to study the effects of both formulation and process variables on the nature of the microcapsules formed.

In-situ polymerization of a vinyl polymer shell about an emulsified oil droplet is quite different than other methods of microencapsulation. These include the so-called "interfacial polymerization" in which a condensation polymer is formed at the oil/water interface by using a system in which one monomer is only soluble in the oil phase and the other is only soluble in the water phase. In such a system the polymer can only form at the interface. On the other hand, the use of free radical polymerization of a vinyl mononer does not rule out the formation of polymer in either the oil phase or the water phase, and certainly does not automatically guarantee the formation of polymer at the interface where it is needed. The authors view this system to be an opportunity to study morphological characteristics of polymeric microparticles at the 1-100 micrometer size range in which the core of the intended particle is a simple, low viscosity liquid.

Thermodynamic Considerations

An approximate thermodynamic analysis of the morphological nature of the microcapsules may be obtained by viewing the free energy changes taking place for the following hypothetical pathway. The initial state is that of a pure oil phase and a pure polymer phase completely separated. The final state is that of one of the microcapsule morphologies shown in Figure 1. Since no

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phase changes or mixing or demixing are involved, the only contribution to the free energy change is that of the creation of new interfaces. For capsules suspended in a continuous phase of water, those interfaces are water/oil, water/polymer and polymer/oil. It must be noted that the practical need for a stabilizing agent will greatly affect the interfacial tension at the water interface.

The free energy change can be expressed as

$$\Delta G = \sum_i \gamma_i A_i \qquad (1)$$

where γ_i is the interfacial tension of the i-th interface and A_i is the corresponding interfacial area. Each of the morphologies depicted in Fig. 1 will have different combinations of $\gamma_i A_i$ due only to their geometric features. This makes the analysis quite straightforward as long as the interfacial tensions are constant and can be measured. The first case to be treated is that of the CSOP (core-shell, oil as core, polymer as shell) where the interfacial tensions involved are that between the water and polymer, γ_{wp}, and that between the polymer and oil, γ_{po}. In this case

$$(\Delta G)_{CSOP} = \gamma_{pw}\, 4\pi R^2 + \gamma_{po}\, 4\pi R_c^2 \qquad (2)$$

where R_c is the radius of the core, or oil droplet, and R is that of the overall microcapsule. Using the core surface area $4\pi R_c^2$, to place the analysis on a surface energy per unit area basis, and defining the volume ratio of polymer to oil as VRPO,

$$VRPO = (R/R_c)^3 - 1 \qquad (3)$$

the modified interfacial energy change is SECSOP,

$$SECSOP = (\Delta G)_{CSOP}/4\pi R_c^2$$

$$= \gamma_{po} + \gamma_{pw}\,(1 + VRPO)^{2/3} \qquad (4)$$

A similar analysis for the case of the inverted structure CSPO (core-shell, polymer as core, oil as shell) results in

$$SECSPO = \gamma_{wo} (1 + VRPO)^{2/3} + \gamma_{po} (VRPO)^{2/3} \quad (5)$$

Similar analyses were done for the remaining morphologies depicted in Figure 1 but are not detailed here.

An analysis of the comparative free energy changes for the various morphologies was carried out. In so doing, it was found that for all cases of practical interest for this project the CSOP and hemispherical morphologies would be most probable. Further, it was found that changes in the values of the interfacial tensions would not have to be too great in order to invert the relative probabilities of forming core-shell structures versus hemispherical structures. What has become clear from this analysis is that one should expect better chances of making the desired core-shell morphology the greater the difference between the γ_{wo} and the sum of γ_{wp} and γ_{po}. Stated quantitatively, we project than an approximate quantitative guide should be that when $\gamma_{wo} > (\gamma_{wp} + \gamma_{po})$, one should obtain the proper core-shell structure. Thus it appears that one should choose the components used in the formulation carefully so as to obtain the greatest difference between γ_{wo} and $(\gamma_{wp} + \gamma_{po})$. In particular, the influence of the type and concentration of the stabilizing agent upon γ_{wo} and γ_{wp} (particularly the former) must be recognized.

Experimental

The bulk of our experiments utilized methyl methacrylate as the monomer and decane as the oil. A wide range of surfactants were used and the majority are listed below;

Aerosol-OT	Polyethylene oxide
Lignosulfonate	Polystyrene sulfonate
Phospholipid	Xanthate
Polyvinyl alcohol	Polyacrylic acid
Polyvinyl pyrolidone	Carboxymethyl cellulose
Polyvinyl sulfate salt	Hexpectin
Polyethylene imine	

Not all of the surfactants provided good emulsion stability and simultaneously attractive values for the interfacial tensions, but the last three in the table offered reasonable balances.

Polymerizations were conducted in the 50-80°C range and the monomer was either dissolved in the oil prior to emulsification or dispersed in the water after emulsification. Both water soluble and oil soluble initiators were used, but experience resulted in a preference for oil soluble initiators with very low water solubilities. Experiments were run with monomer to oil ratios as high as 1:1. Typical emulsified droplet sizes were 1-10 micrometers.

Results

By choosing to operate with several surfactants which led to very different values of γ_{wo} and γ_{po}, we were able to obtain both the core-shell and hemispherical microparticles. As a result we were able to provide experimental verification of the thermodynamic projections, ableit in a limited fashion. Systems which utilized the pectin stabilizers yielded the proper type of microcapsules while those which gave much lower interfacial tensions (such as AOT and phospholipids) yielded the hemispherical structure.

An interesting observation made while viewing these particles in the microscope is that they are seldom, if ever, truly spherical once the polymer shell begins to form. Very shortly after the beginning of the polymerization the particles tend to become dimpled (many looking like blueberries) and the existence of fragments of the sphere (e.g. half-spheres) coated by polymer are not uncommon. Photographs of the various particle structures will be presented during the discussion at the meeting.

Acknowledgements

The authors are grateful for the financial support provided by the Swedish Board for Technical Development.

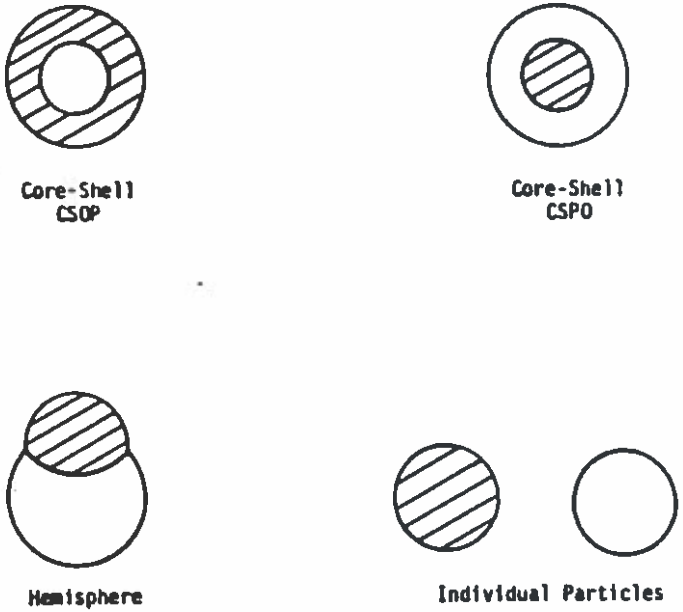

Figure 1

29 APR Recd

April 21,1986

Contribution to the Polymer Colloid Group Newsletter.

Mohamed S. El-Aasser, Andrew Klein, F. J. Micale, Cesar Silebi and J. W. Vanderhoff.

Emulsion Polymers Institute, Sinclair Lab.#7
Lehigh University, Bethlehem, Pennsylvania 18015

We have currently twentyeight active projects, the titles of which are included in the enclosed Index of our Graduate Research Progress Reports, issue No. 25, January, 1986. Requests for the full abstracts for any of the given topics should be directed to Ms. Karen Hicks at the above address.

The titles of recently completed Ph.D. and M.S. thesis are enclosed. Copies of these thesis are available on request.

At the 191st ACS meeting in New York, April 13-18, 1986, the following papers were delivered:

M.P.Merkel, V.L. Dimonie, M.S. El- Aasser and J.W Vanderhoff.
Polymethyl methacrylate grafting reactions inside polybutadiene seeded latexes.

M.A. Linne, A. Klein and L.H. Sperling.
Preliminary estimates of the diffusion constant of polystyrene during film formation from the latex.

J.W. Vanderhoff, M.S. El-Aasser, F.J. Micale, E.D. Sudol, C.M. Tseng, A. Silwanowitz, and H.R. Sheu.
Preparation of large-particle size monodisperse latex in space.

J.W. Vanderhoff, D.L. Visioli, and M.S. El-Aasser.
Inverse emulsion polymerization of acrylamide.

C.M. Tseng, Y.Y. Lu, M.S. El-Aasser and J.W. Vanderhoff.
Uniform polymer particles by dispersion polymerization in alcohol.

F.V. Loncar, M.S. El-Aasser and J.W. Vanderhoff.
Emulsion copolymerization of 2-ethylhexyl acrylate with acrylic acid and methacrylic acid.

The NATO Advanced Research Workshop will be held from June 30-July 4, at Racine, Wisconsin. Questions should be directed to M.S. El-Aasser.

Our 17th Annual Short Course on "Advances in Emulsion Polymerization and Latex Technology." will be held at Lehigh on June 2-6, 1986 and at Davos, Switzerland on August 18-22.

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M.S. Theses and Research Reports:

1. "Inverse Emulsion Polymerization of Acrylamide in a Tubular Reactor," Thomas Bash, 1985.

2. "Latex Aggregation with Methylcellulose," Kendall Brown, 1985.

3. "Computer Interfacing for Hydrodynamic Chromatography," Jose G. Dos Ramos, 1985.

4. "The Covalent Binding of beta-Glucosidase to Activated Polystyrene Latexes," Katharine Lawrence, 1985.

5. "Investigation of the High Conversion Range in Styrene-Butadiene Copolymerizations," Thomas Kauffman, 1985.

6. "Interactions Between Offset Printing Inks and Fountain Solutions during the Process of Offset Printing," Sanjay Sathaye, 1985.

7. "The Effect of Initial Pressure on Coagulation during the Emulsion Polymerization of Styrene," Debra Bartsch, 1985.

8. "The Slide Agglutination Assay: A Study of the Factors Affecting Sensitivity," Mark Smith, 1984.

9. "The Preparation of Aqueous Silicon Carbide Dispersions" Gary Carl, 1984.

10. "The Effects of Prepolymer Contamination on Coagulation During the Emulsion Polymerization of Styrene Monomer," Vern Lowry, 1983.

11. "The Cathodic Electrodeposition of Polymer Latexes," J. Andrew Hadley, 1983.

12. "Freezing of Coal," Manju Agrawal, 1983.

13. "Freezing of Coal," Neal Earhart, 1983.

14. "The Effect of Hydroquinone on the Kinetics of the Seeded Emulsion Polymerization of Styrene," Anthony Silvanowicz, 1983.

15. "The Interfacial Characterization of Mixed Emulsifier Systems," Craig D. Lack, 1983.

16. "The Binding of Protein Molecules to Modified Polystyrene Latexes," Eric S. Daniels, 1983.

17. "Drying and Curing of Epoxy Films," Ata-Ur Rahman, 1983.

18. "Seeded Suspension Polymerization," Douglas Bloom, 1982.

Theses Titles

The following is a list of Ph.D. Theses and M.S. Theses and Research Reports which have been written by graduate students affiliated with the Emulsion Polymers Institute at Lehigh University.

Ph.D. Theses:

1. "Morphology of Core/Shell Latexes and their Mechanical Properties," Michael Markel, 1986.

2. "Emulsion Formation and Stabilization with Mixed Emulsifier Liquid Crystals," Craig D. Lack, 1985.

3. "Analysis, Kinetics and Alkali-Swellability of Carboxylated Latexes," Francis V. Loncar, Jr., 1985.

4. "New Free Radical Initiators and Their Use in the Preparation of Polystyrene Polymer Colloids," William H. Guthrie, 1985.

5. "Nuclear Magnetic Resonance Characterization of Polymer Colloids," Rohitha Jayasuriya, 1985.

6. "Agitation-Induced Coagulation of High-Solids Latexes," Vern Lowry, 1985.

7. "Covalent Binding of Biological Macromolecules to Activated Polystyrene Latexes," Theresa Michael, 1985.

8. "Adsorption and Stabilization Studies of Polymers on Latex Particles," Maqsood S. Ahmed, 1984.

9. "Formation and Stabilization of Inverse Emulsion Polymers," Donna Visioli, 1984.

10. "Mechanism of Core-Shell Emulsion Polymerization," Deborah R. Stutman, 1984.

11. "Kinetics of Successive Seeding of Monodisperse Latex," E. David Sudol, 1983.

12. "Toward the Production of Large-Particle-Size Monodisperse Latexes -- Studies of Swelling and Polymerization Parameters," Chi-Ming Tseng, 1983.

13. "Fundamental Studies of the Effect of Particle Size and Particle Stability on Critical Pigment Volume Concentration (CPVC) in a Model Latex Coating," Ajay Ranka, 1983.

14. "Ink Transfer in a High-Speed Electrostatic Printer," Suda Kiatkamjornwong, 1983.

15. "Electrokinetics, Particle Diffusion, and Particle-Bubble Interaction in the Flotation Process," Ken Chiang, 1983.

Contribution to Polymer Colloid Group Newsletter

T.G.M. van de Ven

Pulp and Paper Research Institute of Canada
and
Department of Chemistry, McGill University
Montreal, Quebec, Canada, H3A 2A7

6 MAY Recd

The following are abstracts of recent papers (submitted and in press).

1. Creeping Flow over a Composite Sphere: Solid Core with Porous Shell
J. Masliyah, G. Neale, K. Malysa and T.G.M. van de Ven

Creeping flow past a solid sphere with a porous shell has been solved using the Stokes and Brinkman equations. The dimensionless solid core and shell radii, normalized by the square root of the shell permeability, are the two parameters that govern the flow. In the limiting cases, the analytical solution describing the flow past the composite sphere reduces to that for flow past a solid sphere and a homogeneous porous sphere.

The settling rates of a solid sphere with attached threads are measured experimentally. This system can be considered a model for rigid linear molecules anchored or adsorbed onto a colloidal particle. The analytical solution for the composite sphere is in remarkable agreement with the experimental results.

The theory allows predictions of the effective hydrodynamic radius of colloidal particles covered with a homogeneous polymer layer.

2. Deposition of Latex Particles on Glass Surfaces in an Impinging Jet
T. Dabros and T.G.M. van de Ven

The deposition of latex particles has been studied in an impinging jet cell, which provides well-controlled hydrodynamic conditions, covering a wide range of flow intensities with Reynolds number Re in the range 20–1600. For Re > 350 instabilities of the flow occurred and the coating was found to be non-uniform, in contrast to even deposition observed for less intense flows.

A fairly good agreement was found between experimental and calculated values of the Sherwood number (dimensionless deposition rates) for regions near the symmetry axis in the entire range of flow intensities studied. The nature of the deviations from non-uniformity observed for large Reynolds numbers indicates that aging can play an essential role in the coating process. Rough estimates of the energy minimum in which the particles are captured indicate that within one second the depth can change from about - 7 kT to values well over - 20 kT.

Contribution to the Polymer Colloid Group Newsletter.

28 APR Recd

Submitted by A. Vrij,
van 't Hoff Laboratory of Physical and Colloid Chemistry,
University of Utrecht, Padualaan 8, 3584 CH Utrecht.

We are synthesizing already for several years silica spheres which are made lyophilic ("oil-soluble") by etherification of the surface hydroxyls with octadecylalcohol [1]. The spheres, which are in the colloidal size range of ~ 20-300 nm, can be dispersed in organic solvents like cyclohexane and toluene. Attractive forces between the particles were studied by Jansen in his thesis work. Stearylsilica shows a phase separation in toluene below 9°C. Concentrations in the separated phases were determined and discussed. The characterization of the attractive forces was also studied above 9°C (where the phase is still homogeneous) with turbidity measurements. Because the interpretation of turbidity is not disturbed by multiple scattering effects (in contrast to measurements of light scattering) it was possible to extract values of the second virial coefficient as a function of temperature. It turns out that the positive second virial coefficient at higher temperatures drops to zero and even becomes negative at lower temperatures. These results were compared with the "adhesive hard sphere" model [2].

1) A.K. van Helden, J.W. Jansen and A. Vrij, J. Colloid Interface Sci., 81 (1981) 354.
2) J.W. Jansen, C.G. de Kruif and A. Vrij, J. Colloid Interface Sci., accepted for publication.