

The 35th Annual Short Course

"ADVANCES IN EMULSION POLYMERIZATION AND LATEX TECHNOLOGY"

A One-Week Short Course
held at the Hotel Belvédère
in the Davos resort area
of Switzerland

August 13-17, 2012

COURSE DIRECTORS

Dr. Mohamed S. El-Aasser
Professor of Chemical Engineering
And Vice President, Lehigh University

Dr. F. Joseph Schork
Professor Emeritus
Chemical & Biomolecular Engineering
Georgia Institute of Technology

COURSE DESIGN

The course is an in-depth study of the synthesis, characterization, and properties of high polymer latexes. The subject matter includes a balance of theory and practical problems. Lectures will begin with introductory material and will progress through recent research results. Lectures will be given in English, and are held in the morning, the late afternoon, and the evening, with a large break in the afternoon to enjoy the recreational activities of the area and allow for interactions between the participants. Organized hikes and visits to points of interest in and around Davos will be arranged for some of the afternoons.

PARTICIPANTS

The course is designed for engineers and scientists who are actively involved in emulsion work, as well as for those who wish to develop expertise in the area. A basic background in chemistry will be assumed. All participants will receive a set of course notes for the lectures.

COURSE FEE

The Registration Fee for the short course is US \$1,500. Registrations paid before June 30 will receive a 5% discount. A 10% discount is offered for multiple participants from the same company, if all register at the same time. The Registration Fee will cover attendance, coffee breaks, a welcome reception Sunday evening, a final reception on Thursday evening, and a set of course notes. Payment may be made by check, wire transfer or credit card. Please contact us at DavosCourse@gmail.com for information on wire transfer or credit card payment.

Course Fee is due on June 30. Refund requests received before this date will be honored in full.

COURSE SCHEDULE

MONDAY, August 13, 2012

- 08:30 - 10:00 Kinetics of Free Radical-Initiated Polymerization (F. J. Schork)
10:00 - 10:30 Coffee Break
10:30 - 12:00 Emulsion Polymerization Mechanisms and Kinetics (G. W. Poehlein)
16:30 - 18:00 Semi-Continuous Emulsion Polymerization and Structured Latexes
(M. F. Cunningham)
20:00 - 21:45 The Role of Surfactants in Emulsion Polymerization (M. S. El-Aasser)

TUESDAY, August 14, 2012

- 08:30 - 10:00 Engineering of Emulsion Polymerization Reactors (G. W. Poehlein)
10:00 - 10:30 Coffee Break
10:30 - 12:00 Branching and Grafting in Emulsion Polymerizations (P. A. Lovell)
16:30 - 18:00 Latex Rheology (F. J. Schork)
20:00 - 21:30 Discussion of Applications and Problems Submitted by Course Participants

WEDNESDAY, August 15, 2012

- 08:30 - 10:00 Stabilization Mechanisms in Aqueous and Non-Aqueous Latexes
(M. S. El-Aasser)
10:00 - 10:30 Coffee Break
10:30 - 12:00 Biopolymer-Based Nanoparticle Latexes for Industrial Applications
(D. I. Lee)
16:30 - 18:00 Film Formation and Cohesive Strength Development from Latex Systems
(A. Klein)
20:00 - 21:45 Advances in Miniemulsion Polymerization (M. S. El-Aasser)

THURSDAY, August 16, 2012

- 08:30 - 10:00 Living-Controlled-Radical Polymerization in Bulk, Miniemulsion and Emulsion
(M. F. Cunningham)
10:00 - 10:30 Coffee Break
10:30 - 12:00 Water-Borne Pressure-Sensitive Adhesives (P. A. Lovell)
16:30 - 18:00 Mixing and Scale-Up in Emulsion Polymerization Reactors (A. Klein)
20:00 - 21:00 Discussion of Applications and Problems Submitted by Course Participants

FRIDAY, August 17, 2012

- 08:30 - 10:00 High Solids Latex Technology (D. I. Lee)
10:00 - 10:30 Coffee Break
10:30 - 12:00 Sensors and Control of Emulsion Polymerization Reactors (F. J. Schork)
12:00 End of Course

LOCATION

The course will be held at the Hotel Belvédère in Davos Platz in the Graubünden resort area of Switzerland. Numerous recreational opportunities are available to both participants and their guests during the short course.

The Steigenberger Belvédère Hotel is a five-star hotel located in the center of Davos, 0.8 km from the railway station. The hotel, built in 1875, is a harmonious combination of grand past with lively present, of international standards with traditional Swiss hospitality. The view is magnificent in any season in this sumptuously appointed hotel centrally located near all of Davos' many attractions and sports facilities. Spacious, comfortable rooms decorated in romantic-rustic fashion with wooden paneling or in an elegant, modern style, wish you a warm and homely welcome. Large commons areas allow informal conversations between course participants and course lecturers outside of the formal sessions.

Davos is about 100 km north of St. Moritz in southeastern Switzerland. It can be reached by air by flying into Zurich, and then taking Swiss Rail to Davos Platz, with a change of trains in Landquart. From northern Europe, the most common rail route is via Zurich and Landquart to Davos Platz. Driving to Davos should be no problem, since the roads into Davos, although mountainous, are good.

HOTEL RATES

Short Course room rates are:

CHF 187 for superior single rooms with bath

CHF 156 for standard rooms with bath

CHF 123 supplement for a double room (second person)

Rates for children are available from the hotel.

Rates include a buffet breakfast, a three course fixed-menu dinner elegantly served in the Main Dining Room with the course participants, and free use of the public transportation system in Davos (including selected mountain railways and cable cars). Conference rates will also apply for early arrival or extended stays.

LECTURE ABSTRACTS

Kinetics of Free Radical-Initiated Polymerization

F. Joseph Schork (Georgia Institute of Technology)

A review of the principles of free radical-initiated polymerization, including the basic reactions of initiation, propagation, termination and transfer; inhibition; molecular weight and molecular weight distribution, effect of temperature and pressure, auto-acceleration and diffusion control of termination and propagation, and copolymerization including copolymerization reactivity ratios and copolymer sequence distribution.

Emulsion Polymerization Mechanisms and Kinetics

Gary W. Poehlein (Georgia Institute of Technology)

Reaction mechanisms and kinetics of free radical polymerization will be reviewed. The unique features of emulsion polymerization will be outlined and the influence of the colloidal size of the reaction sites

discussed. Kinetic theories due to Smith and Ewart, Stockmayer, O'Toole, Roe, Fitch, Ugelstad, and Gilbert will be discussed.

Semi-Continuous Emulsion Polymerization and Structured Latexes **Michael Cunningham (Queens University)**

Semi-continuous (or semi-batch) polymerizations in which the monomer is added incrementally during the course of reaction are commonly used in industrial processes because they allow control of the polymerization rate, and because they can be used to control the particle morphology. "Structured latexes" are emulsion polymer particles in which the internal morphology and/or composition vary through the particle. Examples include core-shell particles, and particles with radial composition gradients between the particle core and surface. The discussion will describe how semi-continuous processes are run, the unique features of operating an emulsion polymerization in semi-continuous mode, and how structured latexes can be synthesized.

The Role of Surfactants in Emulsion Polymerization Processes **Mohamed S. El-Aasser (Lehigh University)**

Surfactants play major roles during the particle nucleation and growth stages, with direct impact on latex particle size, size distribution, polymerization rate, molecular weight and particle morphology. Surfactants are also essential during post polymerization processes: stripping, storage, shipping, and formulation for several applications. The general characteristics of surfactants and their adsorption profiles on latex particles will be reviewed. The specific role of surfactants in determining the particle number according to the various nucleation mechanisms will be described. Three alternatives to conventional surfactants will be reviewed.

Engineering of Emulsion Polymerization Reactors **Gary W. Poehlein (Georgia Institute of Technology)**

The various types of reactors (batch, semi-batch and continuous), used to produce synthetic latexes will be reviewed. Pros and cons of various types of processes will be discussed and theoretical reactor models will be presented where appropriate. Reactor design and operating factors that influence product properties will also be reviewed.

Branching and Grafting in Emulsion Polymerizations **Peter Lovell (University of Manchester)**

Branching in polymers produced by free-radical polymerization arises from chain transfer to polymer and has important effects on polymer properties. In emulsion polymerization, intermolecular chain transfer to polymer can lead to grafting of water-soluble polymers to latex particles, facilitating control of colloidal stability and latex rheology. Such branching and grafting is used to good effect in the emulsion polymer industry to control the end-use performance of latexes and emulsion polymers. This lecture will begin with an overview of the chemistry of branching and grafting. Case studies of branching in acrylate and vinyl acetate homopolymerizations and synergistic effects in copolymerization will then be presented, together with strategies for controlling the level of branching. This will provide the basis for considering grafting of water-soluble polymers used as colloid stabilizers in emulsion polymerizations. The chemical processes which the most commonly-used water-soluble polymers may undergo during emulsion polymerization will be illustrated through case studies that highlight the key principles for their control.

Latex Rheology

F. Joseph Schork (Georgia Institute of Technology)

This introduction to the rheology of latexes covers the type of rheological measurements that can be made and the effects of the many variables found in latexes; solids concentration, particle size and distribution, surface charges, adsorbed surfactants, particle aggregation, non-spherical particle morphology, swellable particles, and the use of water-soluble polymer thickeners.

Stabilization Mechanisms in Aqueous and Non-Aqueous Latexes

Mohamed S. El-Aasser (Lehigh University)

The basic concepts and terminology of colloid science will be introduced. The principles of electrostatic and steric stabilization mechanisms will then be reviewed. The inverse problem of coagulating and flocculating latexes will also be discussed.

Biopolymer-Based Nanoparticle Latexes for Industrial Applications: I. Development of New Starch-Based Nanoparticle Latex Binders for Paper Coating Applications

Do Ik Lee (Western Michigan University)

Biobased latex binders adopted in the paper industry in 2008 were the first use of biopolymer-based microgels and nanogels for large-scale industrial applications [1], although they had been explored and used for drug delivery and other bio-medical applications for a long time [2]. Both biobased latex binders and biopolymer-based microgels and nanogels can be broadly classified as a special type of latexes whose particles are made up of water-swollen crosslinked hydrophilic polymers. Since the biobased latex binders currently used in the paper industry are water-swollen crosslinked starch nanoparticles, their wet and dry properties depend mainly on their particle size and crosslink density. The crosslink density of starch molecules forming the nanoparticles is especially important because it controls the extent of water swelling (swell ratio), that is, as the crosslink density increases, the swell ratio of crosslinked starch nanoparticles decreases. Varying swell ratios of the water-swollen starch nanoparticles not only set them apart from conventional starches and synthetic latexes in their rheological behavior, but also differentiate themselves in paper coating performance. Their unique rheological behavior and paper coating performance will be discussed based on theoretical considerations as well as some laboratory testing, pilot coater and mill trial results.

Film Formation and Cohesive Strength Development from Latex Systems

Andrew Klein (Lehigh University)

The cohesive properties of polymer films from latexes are dependent on the film formation mechanism. Polymer film formation from latex occurs either when: (a) the molecules from the individual polymer particles interdiffuse and entangle as the particle boundaries gradually disappear, or, when (b) the molecules partially interpenetrate and cross-link, forming interparticle spot welds, or when (c) water-soluble molecules react or interact with functional groups on the particle surface. In the last two cases, the particle boundaries remain distinct. The role of interpenetration depth and the diffusion rate on cohesive strength development will be discussed, using model latex systems.

Advances in Miniemulsion Polymerization

Mohamed S. El-Aasser (Lehigh University)

Despite the fact that the first miniemulsion polymerization was carried out at Lehigh University in 1972, the word "miniemulsion" was coined only in 1981. The number of publications on miniemulsions has been increasing exponentially over the past decade, including a few patents.

Miniemulsions are relatively stable oil-in-water emulsions with average droplet diameters ranging from 50 to 500 nm. These are typically prepared using a mixture of a surfactant and a low-molecular weight, highly water-insoluble costabilizer (referred to as cosurfactant). In miniemulsion polymerization, the submicron size monomer droplets are the main sites for particle nucleation and growth via free radical initiation using oil-soluble or water-soluble initiators. The theory of miniemulsions has been developed based on the well-known concepts of Ostwald ripening and thermodynamics. Miniemulsions have been exploited in making new types of polymer colloids (latexes) that were difficult and sometimes impossible to make by using conventional emulsification or emulsion polymerization processes. These include preparation of artificial latexes and hybrid latexes, high solids latexes, polymerization of highly water-insoluble monomers and macromonomers, controlled polymer microstructure and morphology, encapsulation of pigments and dyes, and controlled molecular weight via living free radical polymerization. In this lecture both the theory and practice of miniemulsions will be discussed.

Living-Controlled-Radical Polymerization in Bulk, Miniemulsion and Emulsion **Michael Cunningham, Queens University**

“Living” (or “controlled”) radical polymerizations provide a novel and potentially inexpensive route to designing polymers with controlled microstructure (e.g. block copolymers, star polymers) and narrow molecular weight distributions. While extensive research has been conducted into homogeneous bulk and solution living radical polymerizations, investigations into aqueous dispersed phase systems (emulsion and miniemulsion polymerization) have only recently appeared. Although little progress has been realized with emulsion polymerization, considerable success has been achieved using miniemulsion polymerization with living radical systems. This presentation introduces the three major living radical polymerization chemistries (nitroxide-mediated radical polymerization (NMRP), atom transfer radical polymerization (ATRP) and reversible-addition-fragmentation-transfer polymerization (RAFT)), and summarizes recent progress of these systems in bulk, miniemulsion and emulsion. The emphasis will be on heterogeneous systems, and more specifically on those aspects of operating in a heterogeneous environment that influence the polymerization rate, the molecular weight distribution and the livingness of the system.

Water-Borne Pressure-Sensitive Adhesives **Peter Lovell (University of Manchester)**

Pressure sensitive adhesives (PSAs) are viscoelastic materials which adhere to substrates on the application of slight pressure over short periods of time. They are ubiquitous in everyday life as self-adhesive tapes and labels used in a wide variety of applications (e.g., bonding, signing and marking, healthcare, automotive, electronics, furniture, security, food packaging and retailing). Over the past few decades, water-borne PSAs based on latexes prepared by emulsion polymerization have gained market share at the expense of flammable, environmentally-unfriendly solvent-borne PSAs and now comprise the largest proportion of the overall PSA market. The growth has arisen not only because they replace solvents with water, but also because the latexes have low viscosity at high solids contents which brings benefits in formulation, handling, transport and coating. This lecture will describe the different types of PSAs before focusing on the principle components used in preparation of acrylic water-borne PSAs and their roles in controlling latex properties and adhesive performance. Effects of latex particle composition/morphology, polymer properties and branching on the performance of PSA films will be discussed. A case study will be presented to demonstrate principles for control of adhesive performance through careful design of structured latex particles that determine the sub-micron and nanoscale morphology of PSA films as a consequence of the mechanism of film formation from latexes.

Mixing and Scale-Up in Emulsion Polymerization Andrew Klein (Lehigh University)

The scale-up of the mixing process in emulsion polymerization involves breaking the process down into individual but interrelated steps. The effect of mixing on the microscopic heterogeneity of the continuous phase, fluid shear rates and heat transfer allows each to be considered separately. A few of these effects will be discussed and illustrated with specific examples. The utility of bench scale experimentation, with a view toward scale-up with some early experimental results, will also be discussed.

High Solids Latex Technology Do Ik Lee (Western Michigan University)

High-solids latex technology is based on three basic considerations from the viewpoints of dispersion rheology: (1) The maximization of latex particle packing volume fractions, (2) The minimization of the effective volumes of latex particles, and (3) The minimization of latex medium viscosity. With these considerations at hand, the technology is concerned with the maximization of the volume solids of latexes, while meeting their respective end-use property requirements for a variety of applications. For this reason, its objective is to increase the volume solids of the existing latexes by 5 to 15% by considering a bimodal approach only for the packing efficiency, although the technology is capable of achieving 70% or higher volume solids latexes. This talk will describe the three basic considerations involved in the high-solids dispersion technology, and then discuss post-polymerization blending (i.e., blending large and small particle size preformed latexes) and in-situ emulsion polymerization methods (i.e., bimodal emulsion polymerization by either surfactant or seed addition) for the preparation of high-solids bimodal latexes. Some high-solids latex examples will be also presented.

Sensors and Control of Emulsion Polymerization Reactors F. Joseph Schork (Georgia Institute of Technology)

Recent developments in the area of on-line sensors, coupled with the availability of high-performance digital control systems has opened up new opportunities for the efficient operation and control of latex reactors. Available sensors for on-line analysis will be discussed. The use of such measurements in the application of advanced control techniques to batch and continuous polymerization reactors will be reviewed, with special emphasis on controlling the undesirable process dynamics associated with continuous emulsion polymerization, and optimizing controllers for batch polymerization.

LECTURERS

Michael Cunningham Professor of Chemical Engineering, Queens University, Kingston, Ontario

Ph.D. in Chemical Engineering from the University of Waterloo. Industrial experience with the Xerox Corporate Research Group developing new processes for small, composite particles. Research program is in polymer reaction engineering, with an emphasis on emulsion polymerization. Primary focus of current research is living radical polymerization in heterogeneous systems, and the design of functionalized latex particles for applications such as bioseparations.

Mohamed S. El-Aasser Vice President, Lehigh University and Professor of Chemical Engineering, Lehigh University

Ph.D. from McGill University and Pulp and Paper Research Institute in 1972. Research interests include emulsion polymerization, emulsification, surface and colloidal properties of latexes, and latex film formation, adsorption from solutions, and stabilization of colloids.

Andrew Klein
Professor of Chemical Engineering, Lehigh University

Ph.D. in Chemical Engineering from North Carolina State University at Raleigh. Industrial experience in emulsion polymers with GAF, and National Starch and Chemical Company. Research interests include colloid and surface chemical aspects of heterogeneous polymerization kinetics, related thermodynamics, engineering and applications.

Do Ik Lee
Adjunct Professor of Paper Engineering, Chemical Engineering and Imaging,
Western Michigan University

B.S. degree in Chemical Engineering from Seoul National University in 1959 and both M.S. and doctoral degrees in Chemical Engineering from Columbia University in 1964 and 1967, respectively. Currently, Adjunct Professor in the Department of Paper Engineering, Chemical Engineering and Imaging at Western Michigan University and a TAPPI Fellow. Formerly, Senior Scientist in Emulsion Polymers R&D at The Dow Chemical Company for 35 years. His research interests are latex technology, emulsion polymerization, structured latex polymerization, controlled free-radical emulsion polymerization, solid and hollow plastic pigments, paper coating technology, paper chemistry, colloid science, particle packing, dispersion rheology, and associative alkali-soluble latexes. He holds 27 U.S. patents. He received several awards, including the 2003 Distinguished Service Award from Korea TAPPI.

Peter A. Lovell
Professor of Polymer Science in the School of Materials, University of Manchester, UK

Founding Chairman of the UK Polymer Colloids Forum, which was established in 1993, and was Chairman of Macro Group UK from 2004-2007. His research focuses mainly around aspects of emulsion polymerization and related processes. Prominent in this research has been synthesis of core-shell and multi-layer particles (for applications in toughening plastics and as soft adhesives) and studies of the chemistry (and extent) of branching and grafting, including grafting to water-soluble polymeric colloid stabilizers.

Recent research includes a novel chemistry for room-temperature crosslinking during latex film formation, synthesis of new nitroxides for use in controlled miniemulsion polymerization, development of click chemistry for latex particle fictionalization and the lead role in a European collaborative research program for development of high-performance water-borne pressure-sensitive adhesives.

Gary W. Poehlein
Professor Emeritus of Chemical & Biomolecular Engineering, Georgia Institute of Technology

Ph.D. in Chemical Engineering from Purdue University. Industrial experience with the Proctor and Gamble Company. Research interests include kinetics of emulsion polymerization and continuous reactor systems.

F. Joseph Schork
Professor Emeritus of Chemical & Biomolecular Engineering, Georgia Institute of Technology

Ph.D. in Chemical Engineering from the University of Wisconsin working in the field of emulsion polymerization reactor dynamics. Industrial experience with E.I. DuPont de Nemours & Company in the areas of emulsion polymerization and digital process control. Research interests in polymerization reaction engineering, digital control of polymerization reactors, system dynamics and control. Consultant to various companies in the area of polymerization reaction engineering.

REGISTRATION

Registration will be limited to 60 course participants. A participant may register by sending the information on the attached Registration Form to Professor Schork by mail, e-mail or fax. On-line registration is available at our website (see below). Checks payable to the Emulsion Polymer Course may accompany registration requests. Alternatively, participants will be invoiced for the course fee upon receipt of a registration form. Payment by bank transfer or credit card can be arranged on request. Only the registration fee will be collected by the course organizers. The conference organizers will make hotel reservations for each participant at the time of registration. Confirmations of the reservation will be sent to the participant by the Hotel Belvédère. Participants needing changes to hotel reservations should deal directly with the Hotel Belvédère. Each participant will be charged directly by the hotel for room costs and extras.

Please register as early as possible so that a course opening can be reserved in your name.

**For more information, or to register,
please contact:**

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OR

visit our web site (including on-line registration) at:

<http://www.DavosCourse.com>

REGISTRATION FORM
"ADVANCES IN EMULSION POLYMERIZATION AND LATEX TECHNOLOGY"
August 13-17, 2012

Dr. Mr. Ms. (Circle one)

First Name: _____

Family Name: _____

Company: _____

Address: _____

Country: _____

Fax: _____

E-mail: _____

Hotel Reservations:

Arrival Date: _____ Departure Date: _____

Number of Rooms:

Superior: _____ Standard: _____

Number of Persons:

Adults: _____ Children: _____

Course Fee:

Enclosed: _____ Please Invoice: _____

Make Checks Payable to:

"EMULSION POLYMERS COURSE"

If possible, please attach a business card and Mail or Fax to:

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