

Dispersion Polymers

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Decade of Progress

Isolated articles from the emerging literature are often difficult to put into context in terms of their relative importance. Although the introductions to many articles contain mini-reviews, these naturally are only intended to lead in to the subject matter of the contribution. A good overall review article is therefore always welcome and such a review, focussing on studies relating to emulsion polymerisation over the last ten years, has recently been published. It covers all aspects of the process and

highlights a number of controversial issues, such as nucleation mechanisms. References are given to source work on some of the sophisticated analytical techniques and methodologies used to study aspects of the polymerisation process, often mentioned in passing in this journal. I have made this review the first item this month and commend it to readers engaged in emulsion polymerisation.

Particular Assemblies

Featured in this issue is a collection of papers loosely falling under the heading 'inorganic/organic polymer composites'. The fabrication of hybrid nanoparticles continues to be a major field of endeavour and it is interesting to see the various particle morphologies, creatively named by authors, that may be produced by experimental design. Four of these articles describe studies of silica/acrylate copolymer systems.

A section on 'living free radical polymerisation' is also included this month. Two articles describe the problems of conducting RAFT emulsion polymerisation and address the issue of transportation of the RAFT agent into the latex particles. One of these (Gilbert et al.) describes a RAFT-controlled self-assembly process, avoiding the presence of monomer droplets during the nucleation

stage. The other (Lubnin) describes the use of 'tailored' RAFT agents to achieve the desired balance of hydrophilic and hydrophobic character to facilitate transport.

Other noteworthy items this month are papers on the influence of monomers on persulphate decomposition rate in emulsion polymerisation, design parameters for high solids, low viscosity latices and items on silane functional polymers. On the Applications side, several interesting patents on pressure sensitive adhesives are included. A patent describes the fabrication of heat resistant microspheres and other contributions describe coatings for leather, one of these focussing on the use of polycarbodiimide crosslinking agents.

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Formerly Emulsion Polymer Technologies

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1 Polymerisation General

Emulsion Polymerisation, Mechanisms and Kinetics

This review article covers main developments in emulsion polymerisation (EP) which have taken place over the last ten years. It commences with a general overview of the subject covering pioneering studies such as the well-known Smith-Ewart theory. A number of techniques useful for studying polymerisation mechanisms are discussed. These include methods for isolation and characterisation of oligomers and precursor particles, on-line monitoring techniques, polymer chain end-group analysis and probe techniques to determine particle nucleation loci. EP using different stabilisers has been extensively reported in recent years and a number of representative articles are featured in the review. These include items on polymerisable surfactants, surface-active initiators and degradable stabilisers. It is noted that, dependent on recipe and conditions, one or more particle nucleation mechanisms may be operative in EP, and accordingly the complexity of the evolution of latex particle size and distribution has become appreciated. Controversy remains over the particle nucleation process, which merits further study. It is observed that the number of recent studies covering the growth of latex particles during polymerisation is small compared to particle nucleation investigations.

A number of reports of work to produce and characterise non-uniform latex particles have recently been published and the origin of such particles is discussed from both kinetic and thermodynamic standpoints, including the influence of reaction parameters on the development of particle morphology. Several reported studies illustrate how reaction variables may be used to control the development of particle morphology as polymerisation proceeds on a case by case basis.

Significant attention is given to the industrially important semi-batch EP process, with aspects of polymerisation mechanism, kinetics and colloidal stability being comprehensively reviewed. Methods for producing high solids (>70%) latices and bimodal particle size distributions are included. Finally the subject of removal of residual free monomer by chemical post treatment following polymerisation is touched on, with the need for more definitive studies stated. This 43-page article contains over 200 references, putting a number of recent studies into collective context.

Chern C.S. Progress in Polymer Science 2006, vol.31(5), pp443-486

High Solids / Low Viscosity Latices

In this conference paper, the production of high solids content, low viscosity (HSLV) latices without employing intermediate seeds is described. These authors have published a review of the subject (Prog. Polymer Sci. 2002, 27, 1573). Reported studies indicate that highest solids contents, at minimum viscosity, are achieved with latices having a bimodal particle size distribution, where the large particles represent 80-85 vol% of the organic phase and the ratio of the diameters of large to small particles is in the range 6:1 to 8:1. Where this 'ideal' cannot be achieved, it is preferable that fewer small particles are present.

Two general methods have been described in the academic press for achieving HSLV latices. In the first, a bimodal distribution is produced by the addition of a seed of small particles to an initial population of large particles. In the second, *in situ* nucleation is used to produce a second population of fine particles, thereby creating a bimodal distribution. In the work described in this article, the second approach was adopted. Latices comprising copolymers of MMA/BA were prepared by initially producing coarse particle size latex (60% solids), followed by the formation of a second particle population by *in situ* nucleation, followed by a physical concentration stage. A H₂O₂/ascorbic acid redox couple was used as initiator in the first stage. APS was used in the second stage. The use of an electrically neutral initiator and judicious choice of surfactants (combined anionic/non-ionic system) in the first stage prevented the stabilisation of fine particles at the start of the process. Limited flocculation of the small particles formed by homogeneous nucleation (due to the presence of MMA) contributes to a relatively rapid growth of the large particles in the first stage. Switching to persulphate initiator in the second stage, while maintaining low levels of surfactant, enabled stabilisation of the homogeneously initiated particles, resulting in a new generation of small particles. The process is said

to be capable of yielding latices with solids contents over 75% vol% and with viscosities less than 1.5 Pa.sec (at a shear rate of 20 sec⁻¹).

McKenna T.F.L. et al. Proc. PRA "Waterborne & High Solids Coatings", March 2006, Paper 7, 12pp

Persulphate Dissociation Rate – Influence of Monomer

It is recognised that the thermal dissociation of persulphate in emulsion polymerisation systems is quite a complex process. The rate of disappearance of persulphate ions is greatly influenced by the presence of water-soluble alcohols, many vinyl monomers, some surfactants and the presence of contaminants. Despite extensive literature on the subject, it is claimed there are no reported systematic studies of comparative measurements of the dissociation rate coefficient (k_d) of persulphate in a single system, using specific vinyl monomers and their saturated analogues. The object of this article is to report on such an investigation focussing on St and MMA and their saturated analogues, ethyl benzene (EB) and methyl isobutyrate. Experimental conditions were chosen to mimic those of emulsifier-free emulsion polymerisation with regard to temperature (50°C), monomer level and initiator concentration. The dissociation of persulphate (KPS) was followed using iodometry.

It was found that the presence of St (and to a lesser extent EB) greatly increased k_d , whereas the presence of MMA had little effect (a slight reduction in k_d being observed). It was clear from the measurements that the saturated monomer analogues could not be used to model the influence of monomer on k_d . The large influences that certain monomers have on the dissociation rate of persulphate have implications for the interpretation of data for radical entry in emulsion polymerisations. Finally it was noted that traces of metal ions, such as may derive from the use of a stainless steel agitator, greatly enhanced k_d .

Gilbert R.G. et al. Polymer 2006, vol.47(13), pp4667-4675

Miniemulsion Polymerisation

One of the limitations of miniemulsion polymerisation that has restricted its commercial exploitation is the high level of surfactant required to stabilise the small emulsion droplets prior to and during polymerisation. A process is described whereby the use of undesirable surfactants may be eliminated, or significantly reduced by employing an amphiphilic stabilising polymer in their stead. The stabilising polymer is required to possess an adequate balance of hydrophilic/hydrophobic character to stabilise oil-in-water emulsions at relatively low levels of addition. The preferred types are St/maleic anhydride copolymers or St/ α -methylstyrene/AA terpolymers. They should preferably have a MW of 1000-25000 Da, a water solubility >1g/L and an acid number between 150-300 mg KOH/g. Typical levels of addition are in the region 2-5 wt% of monomer.

Miniemulsion polymerisations are described where a mixture of monomer and hydrophobe (e.g. hexadecane) is dispersed in a solution of the amphiphilic polymer. The mixture is then subjected to high shear emulsification to produce the miniemulsion, polymerisation being initiated in the conventional manner. A number of examples are given using proprietary amphiphilic polymers to prepare a variety of polySt, polyMMA and poly(MMA-co-BA) dispersions, having mean particle diameters in the range 100-300nm. Coatings prepared from film forming latices (e.g. MMA/BA copolymers) exhibit superior water resistance, improved gloss and higher block resistance than equivalent latices prepared using conventional surfactant stabilisers.

*Do Amaral Martins M. et al. European Patent 1594903 (Cytec Surface Specialities S.A. (BE))
Publication Date 16 November 2005. Also published as US Patent Application 20050052529*

2 Living Free Radical Polymerisation

RAFT Emulsion Polymerisation – Self Assembly

A well-referenced short historical account of emulsion polymerisation is presented at the start of this article, leading into the scope offered by living free radical polymerisation with particular emphasis on RAFT emulsion polymerisation and its potential to be a major industrial process. Transportation of the RAFT agent into the latex particles has been one of the major obstacles. RAFT agents are fairly water-insoluble, making the transportation process very slow and prone to variability. The use of more water-soluble RAFT agents has given rise to significant inhibition or retardation, probably due to interference with the process of radical entry into particles.

Recently a method has been developed for applying the RAFT process in *ab initio* emulsion polymerisation where the presence of monomer droplets in the particle formation stage is avoided. Tri-thiocarbonate RAFT agents are used to form short stabilising blocks from a water-soluble monomer, from which di-blocks can be prepared by the subsequent polymerisation of a hydrophobic monomer. These di-blocks self-assemble to form micelles. Initial polymerisation conditions are controlled to avoid the presence of monomer droplets during the nucleation stage or until the hydrophobic ends of the di-blocks have become sufficiently long to prevent desorption from the particles. A model is developed to predict the particle size formed by this new method of emulsion polymerisation. A process involving the formation of BA/St core/shell particles is described to illustrate the technique. Using the RAFT process, the sequential addition of hydrophobic monomers leads to two distinct hydrophobic blocks. The polymerisation of BA followed by St gives a core/shell structure with the core and the shell polymers being attached by the same chains.

It is concluded that the ongoing development of RAFT emulsion polymerisation is making it feasible to design structured nanoparticles with a wide range of monomer compositions, having potential for industrial use.

Gilbert R.G. et al. Macromolecular Symposia 2006, vol.231(1), pp84-93

RAFT Emulsion Polymerisation of Methyl Methacrylate

On the basis of theoretical simulations, the present authors have previously proposed that ‘super swelling’, occurring during the initial stages of controlled living radical miniemulsion polymerisation, is the primary cause of colloidal instability. In this article, a theoretical simulation of the swelling of particles during the initial stage of controlled living radical emulsion polymerisation is presented. It is predicted that increasing the surfactant level, initiation rate and targeted MW will help to improve the colloidal stability.

In order to test this hypothesis, RAFT emulsion polymerisation of MMA was conducted employing 2-cyanoprop-2-yl dithiobenzoate as RAFT agent, KPS as initiator and SDS as stabiliser. In general close agreement between experimental results and theoretical predictions was obtained. Poor control of the MW and polydispersity index was found to have a close relationship with colloidal instability. It was demonstrated that by employing high surfactant levels and initiation rates, RAFT polymerisation could be successfully conducted with little coagulum formation and good control of MW and polydispersity index, using a standard emulsion polymerisation procedure.

Luo Y. et al. J. Polymer Science Part A: Polymer Chemistry 2006, vol.44(9), pp2837-2847

Novel RAFT Agents

This conference paper commences with a short review (25 references) of RAFT emulsion polymerisation and the problems that have beset the technique. Primarily the article describes a family of RAFT agents developed by Noveon Inc. (the affiliation of the author). These RAFT agents have the generic formula



[where Z= -SR (trithiocarbonate) or -NR₂ (dithiocarbamate) or -OR (xanthate)]

It is shown that only RAFT agents with the right balance of hydrophilic/hydrophobic character are suitable for emulsion polymerisation. By careful selection of the R* group, it is possible to achieve sufficient hydrophilic character to just enable diffusion through the aqueous phase, with the RAFT agent retaining enough hydrophobic character to phase separate into the particles. References to the synthesis of these compounds are given. Eight different RAFT agents were evaluated with the best results being obtained using a RAFT agent where Z derives from a dithiocarbamate and R* is -CH₂CH₂OH.

Using the favoured RAFT agent, a variety of odourless, telechelic acrylic, methacrylic and styrenic latices, covering a range of MWs and containing only low levels of coagulum were prepared by emulsion polymerisation. Attempts to prepare polyVA latices produced unsatisfactory results. In addition microemulsion and solution/dispersion (RAFT mediated pre-polymer formed in solution) polymerisation of acrylic monomers was conducted, yielding clean and stable dispersions.

Lubnin A. Proc. PRA "Waterborne & High Solids Coatings" Conference, Brussels, March 2006, Paper 9, 20pp

Core/Shell Nanoparticles Prepared by ATRP

Surface initiated polymerisation is one of the emerging techniques used to functionalise surfaces via growth of polymer brushes. In this report the use of surface initiated ATRP to produce core/shell morphology is described. Crosslinked acrylic copolymer nanoparticles were synthesised by persulphate initiated emulsion polymerisation. By adding a small level of a functional methacrylate comonomer, containing a dormant ATRP living free radical initiator (2-bromo isobutyrate type) to the aqueous phase during polymerisation, the surface of the nanoparticles could be functionalised with ATRP groups. Subsequently surface initiated ATRP of St was conducted to grow polymer brushes emanating from the crosslinked nanoparticles (achieved via Cu(I)/pentamethyldiethylene triamine). This technique is claimed to be suited for the design of a wide variety of polymeric shells surrounding the crosslinked core, while keeping good control of the size of the nanostructures.

Jhavari S.B. et al. Polymer Materials, Science & Engineering, 2006, vol.94, pp106-107

Atom Transfer Radical Polymerisation of Styrene by a Nano-Precipitation Technique

A nano-precipitation technique has been previously reported by the authors to enable the preparation of polySt latices under stable free radical polymerisation (SFRP) conditions. Macroinitiator particles were prepared by the precipitation of a nitroxide-terminated oligomer dissolved in acetone, into an aqueous solution of pVOH. Subsequent particle swelling and heating of the emulsion mixture resulted in stable latex containing a polymer that increased in MW with time. In this article the adaptation of the nano-precipitation technique to the ATRP process is described. A solution of low MW polySt in acetone was again precipitated into a solution of a surfactant in water to create a macroinitiator. The resulting particles were swollen with St and then heated. The effects of various surfactants and hydrophobic ligands, the reaction temperature and the ligand/copper(I) bromide ratio were studied.

Adding fresh copper complex to the macroinitiator just before the nano-precipitation step in the process was shown to be beneficial in ensuring a reproducible process. In general good final latex stability was obtained when a macroinitiator with a MW <4000g/mol was used. It was shown to be necessary to use a hydrophobic ligand (N,N-bis(2-pyridylmethyl)octadecylamine) for controlled polymerisation. A non-ionic surfactant [polyoxyethylene(20) oleyl ether] proved to be the most effective stabiliser. Under optimum conditions, latices with good colloidal stability having average particle diameters of around 200nm were obtained.

Chan-Seng D. et al. J. Polymer Science Part A: Polymer Chemistry 2006, vol.44(13), pp4027-4038

Metathesis Polymerisation of Norbornene in Miniemulsion

Recently the synthesis of a novel, ruthenium carbene (Ru-C) that promotes homogeneous ring-opening metathesis polymerisation (ROMP) in aqueous media has been reported. Building on this study, the present authors have synthesised a water-soluble Ru-C macroinitiator and used it in the miniemulsion polymerisation of norbornene (NB). The synthesis of the macroinitiator involved the reaction between a hydrophobic Ru complex, $(PCy_3)_2(Cl_2)Ru=CHPh$ and α -norbornenyl-polyEO. The latter compound was synthesised by anionic polymerisation from 5-norbornene-2-methanol. The miniemulsion ROMP of NB was carried out by first forming a miniemulsion of NB and hexadecane by ultrasonication, using a non-ionic surfactant (polySt-b-polyEO), followed by addition of the polyEO-based initiator. Particles with diameters in the range 200-250nm were produced at high conversion.

Heroguez V. et al. J. Polymer Science Part A: Polymer Chemistry 2006, vol.44(9), pp 2784-2793

3 Inorganic / Organic Polymer Composites

Organic/Inorganic Hybrid Colloidal Particle Assemblies

There is considerable interest in the synthesis of organic/inorganic hybrid particles with controlled morphology due to their potential for deployment in areas of material science. In this article the synthesis of hybrid nanoparticles, comprising polySt particles associated with single silica particles leading to controlled morphologies, is reported. Silica particles were first synthesised by controlled hydrolysis of tetraethoxysilane in alcohol, followed by dialysis to generate an aqueous dispersion. The particles were surface modified with a hydrophilic oxyethylene methacrylate macromonomer. Subsequently emulsion polymerisation of St was conducted in the presence of these particles, using NaPS as initiator and a non-ionic surfactant as stabiliser.

The location of the resulting polySt particles was shown to occur at the silica surface, due to the presence of the adsorbed macromonomer. It was shown that the morphology of the hybrid particles could be adjusted by varying the ratio of silica seed particles to the number of polySt particles generated during polymerisation. A range of particle shapes was produced, being characterised by terms such as 'daisy-shaped', 'raspberry-like' and 'snowman-like'. A number of photoelectron micrographs (TEM) illustrate these morphologies. This approach is seen as a route to construct more complex supra-particle assemblies, possibly by introducing reactive groups at the surface of the polymer component.

Ravaine S. et al. Colloids & Surfaces A: Physicochemical & Engineering Aspects 2006, vol.284-285, pp 78-83

Organic/Inorganic, Core/Shell Nanoparticles

Recently the layer-by-layer self-assembly technique for fabricating core/shell particles has attracted much interest. The basis of the method is the electrostatic association between alternately deposited, oppositely charged species. Multi-layered shells of polyelectrolyte, inorganic particles or proteins have been deposited onto particle templates to create novel entities. Organic/inorganic composite particles comprising latex cores and silica nanoparticles, luminescent semi-conductors and iron oxide nanoparticles are among the multi-layer coatings that have been fabricated.

This paper describes the formation of polymer core/inorganic shell particles by a two-stage process. Initially an acrylic latex was prepared by the emulsion copolymerisation of n-butyl methacrylate (97%)/MAA/AA. The type/level of acidic monomer was chosen to best promote the interaction between the surface of the particles and the subsequently formed inorganic shell. In the second stage, dispersions of inorganic powder in water were added slowly to the heated latex, resulting in encapsulation of the core particles. The powders used were pectin coated precipitated calcium carbonate, alumina and silica. The morphology of the particles was determined using SEM and TEM. The silica-shell particles were used to illustrate how, by thermal decomposition of the organic core, hollow nanospheres may be produced. This was achieved by calcination of the pre-dried nanospheres at 500°C. The approach is claimed to allow the fabrication of hollow, inorganic microspheres of tailored composition and with predetermined diameters and size distribution.

Naderi N. et al. J. Applied Polymer Science 2006, vol.99(6), pp2943-2950

Ceramic Powder/Polymer Composites

There has been considerable recent interest in the fabrication of composites prepared from ceramic powders and polymer dispersions. The processing and properties of these composites are of potential interest to both the coatings and ceramics industries. In this article, a study of the film formation of compositions prepared from alumina and surfactant-free polySt latex is reported. The method used was the mixing together of pyrene-labelled polySt latex (prepared by surfactant free, batch-process, emulsion polymerisation, using KPS as initiator) and alumina dispersion (prepared by hydrolytic condensation of aluminium tri-*sec*-butoxide in acidified media). Nine different compositions were prepared with latex contents ranging from 27% to 100%. Coatings were applied to glass plates and annealed at elevated temperatures (up to 300°C). The films were characterised by AFM and UV-VIS spectroscopy.

It was observed that light transmission through the coatings increased dramatically above an onset temperature (MFFT) for samples containing up to 33 wt% alumina. Below this critical value, conventional latex film formation takes place, although the presence of alumina particles in a polySt matrix does influence the film formation process. If the alumina is present at a level above this critical value, the polySt latex particles are encapsulated by alumina particles and no variation in transmitted light intensity is observed on annealing the coatings.

Pekcan O. et al. J. Colloid & Interface Science 2006, vol.295(2), pp457-463

Magnetic Latex Particles

A number of alternative strategies have been reported for the encapsulation of magnetic nanoparticles within latex particles. Where the latex particles comprise hydrophobic polymer (e.g. polySt), the magnetic particles must be hydrophobic to disperse in the monomer (St) and miniemulsion polymerisation is a preferred synthetic route. Properly executed this method avoids the formation of pure polymer particles (excluding magnetic nanoparticles) and free magnetic nanoparticles (not coated by polymer). This article describes the preparation and characterisation of magnetic polymeric composite particles (MCPs) by miniemulsion polymerisation. The synthetic technique involved the initial production of a Fe₃O₄ ferro-fluid, containing particles with an average size of 10nm by the coprecipitation of ferrous and ferric salts, by the addition of ammonia to a solution of their chlorides. This was followed by acidification of the resulting Fe₃O₄ nanoparticles and dispersion in St. Miniemulsion polymerisation of St, containing MAA as comonomer was conducted in the presence of the ferro-fluid using hexadecane as a hydrophobe, AIBN as initiator, SDS as emulsifier and hydroxyethyl cellulose and polyvinyl pyrrolidone as co-stabilisers. Experimental conditions were varied to maximise encapsulation and obtain the narrowest particle size distribution (PSD) of the MCPs.

It was shown possible to include up to 10% Fe₃O₄ before the formation of uncoated magnetic particles became apparent. The presence of MAA facilitated the encapsulation of Fe₃O₄ but broadened the PSD. The presence of the auxiliary stabilising colloids narrowed the PSD. The MCPs prepared here were shown to exhibit superparamagnetism and possessed some magnetic response.

Forcada J. et al. J. Polymer Science Part A: Polymer Chemistry 2006, vol.44(13), pp4187-4203

Silica/(Meth)Acrylate Copolymer Nanocomposite Particles

The preparation of nanocomposite particles of silica/acrylate copolymer, using miniemulsion polymerisation, is described in this article. The production method involved the use of a pre-dispersion of silica in a mixture of MMA and BA, to which a silane coupling agent [3-(trimethoxysilyl)propyl methacrylate (MPS)] was added. The mixture was ultrasonicated with hexadecane (stabiliser) and AIBN (initiator) in a solution of SDS (emulsifier/stabiliser), prior to thermal initiation (60°C). The 'encapsulation efficiency' of the silica particles was determined by elution and acid (HF) etching. The particle size distribution and morphology of the particles were determined using DLS and TEM respectively.

The formation of MPS modified silica particles in the organic phase was shown to improve the encapsulation efficiency of the silica and the degree of grafting of the polymer onto the silica. This resulted in the formation of coarser latex particles with a broader size distribution. As the weight fraction of silica was increased, the morphology of the particles exhibited a structure resembling a 'guava-like' shape, with a silica particle-rich interlayer at the surface of the latex particles. By varying the composition of the polymerisation recipe (monomers, acrylate/silica ratio), nanocomposite latex particles suitable for coatings or for use as impact modifiers for plastics may be obtained using this method. For both applications, good dispersion of the silica and good interfacial adhesion between the silica and the polymer phase are of particularly importance.

Bao Y-Z. et al. Polymer 2006, vol.47(13), pp4622-4629

Most silica/polyMMA nanocomposite particle studies reported in the literature have utilised methodology involving surface treatment of the silica particles prior to polymerisation. In this study, a series of SiO₂/polyMMA composite particles with different morphologies were prepared by conventional emulsion polymerisation, with acid-base interaction between silanol groups of the unmodified SiO₂ particles and the amino groups of 4-vinyl pyridine (4-VP) employed as comonomer ensuring adequate bonding. The method utilised involved the addition of a MMA (75)/4-VP (25) monomer mixture to an aqueous pre-prepared silica sol, in the presence of a non-ionic surfactant. The mixture was emulsified prior to thermal initiation using APS. The resulting latex was purified (centrifugation/redispersion cycles) and characterised by TEM, SEM, TGA and zeta potential measurements.

It was shown that the morphology of the particles could be multi-core/shell, raspberry-like or conventional core/shell, dependent on emulsifier content, monomer/SiO₂ ratio, SiO₂ particle size and monomer feed method. In principle this simple method, that enables control of morphology, could be applied to prepare other ultrafine sols.

Wu L. et al. J. Polymer Science Part A: Polymer Chemistry 2006, vol.44(12), pp3807-3816

Silica/Acrylic Copolymer Composite Coatings

In this study, the preparation and characterisation of organic/inorganic composite films, containing colloidal silica are reported. Two acrylic dispersion polymers (MMA/EHA/MAA) were prepared for this study by emulsion polymerisation, one including a silane monomer (3-methacryloxypropyltrimethoxysilane) at a level of ~0.7 wt% on total monomers. The acrylic dispersions were mixed with colloidal silica (at various ratios) and coalescing solvent. Films were cast and dried at room temperature. Films were characterised by SEM, TEM, contact angle and optical measurements (gloss and transparency).

It was demonstrated that the composite films derived from the silane-functional acrylic dispersion and colloidal silica were more hydrophobic than those derived from the unmodified acrylic polymer. The hydrophilic character of films prepared using the silane-functional acrylic dispersion increased as the particle size of the colloidal silica decreased (to below 100nm). TEM observations indicated the presence of densely dispersed aggregations of silica particles on the surface of the composite films.

Wada T. et al. J. Applied Polymer Science 2006, vol.101(3), pp 2051-2056

4 Polymer Developments

Silane-functional Core/Shell Latex

The preparation of structured latex particles with a lightly crosslinked poly(St-co-BA) core and a poly(St-co-MMA, containing vinyltriethoxysilane) shell is described. The core particles were prepared by the delayed addition of a St/BA monomer mixture to a solution of disodium isodecyl sulphosuccinate, containing diethyleneglycol diacrylate. KPS was used as initiator. Subsequently the shell was formed by delayed addition of St/MMA, containing variable amounts of silane, no extra surfactant being added.

It was shown possible to include up to 8 wt% silane in the shell before the latices became unstable. Latex particle structures were investigated using FTIR, TGA, DSC, TEM and DLS. Films cast from the latices exhibited good water repellence, water uptake decreasing with increasing silane content. The tensile strength of films cast from the silanated polymers was markedly higher than those derived from unmodified controls. The relationship between the particle structure and the film properties was also investigated in this work.

Guo T. et al. J. Applied Polymer Science 2006, vol.100(3), pp1824-1830

Silane-functional Vinyl Acetate/Acrylic Ester Copolymers

Silanated latices potentially offer a number of advantages when used as binders for aqueous paints. Derivative paint films may possess enhanced water resistance, UV resistance, adhesion and all round durability. In this study the effect of including a silane-functional monomer (triethoxyvinylsilane (TVES)) in the emulsion copolymerisation of VA and EHA (also containing MAA) is investigated. The polymerisations were carried out employing a semi-continuous monomer addition procedure, using APS as initiator and a combined anionic/non-ionic stabiliser system. TVES levels were varied up to 4 wt% of total monomers.

This article focuses mainly on the influence of reaction conditions (initiator concentration, reaction temperature and stirring speed) on polymerisation rate. By and large predictable results were observed. It was found that increasing the level of TVES caused a decrease in polymerisation rate and corresponding increase in mean particle size and narrowing of distribution (SEM). TGA studies showed the presence of TVES enhanced thermal stability and the DSC curves indicated a reduction in the thermoplasticity of coatings as the TVES level is raised.

Naghsh H.J. et al. Progress Organic Coatings 2006, vol.55(4), pp375-381

Reactive Polymeric Nanoparticles

A short communication outlines a programme of work to study the formation of reactive, crosslinked nanoparticles by the emulsion polymerisation of St and trimethylolpropane trimethacrylate (TMPTA). Samples were taken during the course of the polymerisation and precipitated in methanol to remove residual monomer. Particle sizes ranged from 25-500nm. It was shown that the particle size depended on the comonomer ratio. The reactivity of the crosslinked particles is due to the presence of residual double bonds, the reactivity increasing with the level of TMPTA. This type of system has potential use as a filling material in dentistry, where minimal volume shrinkage at the final photopolymerisation stage (crosslinking the residual double bonds) is essential.

Borbely J. et al. Polymeric Materials: Science & Engineering 2006, vol.94, pp 783-784

Dye-labelled Latex Particles

Hydrophobic dyes are difficult to incorporate into latex particles using conventional emulsion polymerisation due to difficulty in diffusion through the aqueous phase from the monomer droplets to the loci of polymerisation. The problem can be circumvented by the use of miniemulsion polymerisation and in this short article, the synthesis of carboxyl-functional polySt particles containing a hydrophobic blue dye (copper

phthalocyanine) is described. The procedure used involved the pre-homogenisation of a monomer solution (St/MAA/dye) in a surfactant solution to create a miniemulsion, polymerisation being initiated by a redox system (KPS/NaHSO₃). It was shown that as the dye content increased, monomer conversions decreased and mean particle size increased. Increasing the dye content also reduced the MAA content of the particles, by reducing the level of 'buried' acid groups within the particles.

Yuan B. et al. Polymeric Materials Science & Engineering 2006, vol.94, pp238-239

Monodisperse Carboxyl-functional Microspheres

A novel approach to the synthesis of carboxyl-functional polyMMA microspheres is reported. The method involved deployment of the heterocyclic vinyl monomer (2-vinyl-4,4'-dimethylazolactone) (VDMA) as stabiliser in the emulsion polymerisation of MMA. Emulsion polymerisations were monitored as a function of VDMA content and initiator concentration. VDMA was shown to copolymerise with MMA, accompanied by rapid hydrolysis of the azolactone ring. The resulting carboxyl functionality served to stabilise the microspheres during the emulsion polymerisation, thereby controlling the particle size and distribution and influencing the morphology. KPS proved to be an efficient initiator for this system, consistent MWs and particle sizes being obtained, irrespective of initiator level, within the range studied. The ability to prepare monodisperse microspheres, with carboxyl-functional groups, in the sub-micron range, offers scope for further chemical modification that may be particularly suited to the bio-medical field.

Gleason W.B. et al. Colloid & Polymer Sci. 2006, vol.284(6), pp586-595

Polyurethane Dispersions, Stability Studies

There are few reported systematic investigations of the factors influencing stability of anionic PUDs. In this study, a large range of PUDs based on isophorone diisocyanate, dimethylol propionic acid, two alternative polyester glycols and short chain glycol chain extenders were prepared by a pre-polymerisation process. The resulting dispersions were characterised by IR, NMR, and PCS. The parameters investigated were carboxyl content, hard segment content, and influence of solvents, chain extender type and methodology employed. Their influence on pot life (stability) and particle size of the PUDs was examined.

The particle size of the dispersions was shown to decrease with increasing carboxyl content and a water-soluble ionomer was obtained when the carboxyl content was above 1.5%. Particle size also decreased with decreasing hard-segment content. The type of polyester diol used was shown to influence the stability of the resulting PUDs. On the other hand the type of glycol chain extender employed and addition sequence did not influence stability. Stability results are discussed, particularly with reference to spectroscopic measurements conducted on the polymers.

Zhang S. et al. J. Applied Polymer Science 2006, vol.101(1), pp597-602

5 Surface Coating Applications

Silica/Polyacrylate Hybrid Paint Binder

The use of an organic/inorganic nano-hybrid copolymer as a paint binder is examined in this article. The two nano-composite copolymer dispersions (NCDs) used in this study were prepared using primary monomer ratios of MMA(35)/BA(65) and MMA(50)/BA(50). A delayed addition procedure was adopted, with a silica sol present in the initial aqueous phase. A combined anionic/non-ionic surfactant system was used as stabiliser. Silica-free dispersions were also prepared by conventional emulsion polymerisation, using the same monomer ratios.

The NCDs were shown to comprise a silica core (30nm diameter) and a polymer shell, having a mean diameter of 60nm. Paints were formulated around the two NCDs, the two silica-free controls and 1/1 blends of the NCDs and controls. The NCD-bound paints exhibited superior solvent resistance, although adhesion

was inferior to the controls. The lower organic binder content of the NCD-based paints is seen as advantageous, particularly for the formulation of fire-resistant coatings.

Mizutani T. et al. Progress in Organic Coatings 2006, vol.55(3), pp276-283

Colour Shifts in Drying Latex Coatings

The colour changes that occur during film formation of pigmented acrylic latex coatings are investigated in this article. During film formation, colour shifts are caused by changes in the scattering and reflection of light within the film, which takes place as coalescence of particles and polymer network formation occurs. In this study, an acrylic dispersion was compounded with chromatic pigments with light absorption at different regions of the visible spectrum. Coatings were applied on paper substrates and were dried at different temperatures. The optical properties during film formation were investigated using a system that combined simultaneous, real-time measurements of the optical characteristics of the coatings and their weight loss during film formation in a controlled temperature environment.

On drying the coatings at 20°C (above the MFFT, but below the T_g of the acrylic binder) three phases of colour change were observed. The first phase was represented by a rapid colour change, the second phase was a transitional region and in the last stage a slow colour change was observed. The three stages corresponded to distinct stages of weight loss. When dried at 35°C, an induction period was observed prior to the three stages of colour change. This induction period was attributed to the opposing effects of polymer network development and pigment particle migration. In the final stages of coating formation, the colour properties of the dry coating were found to approach those of the liquid layer prior to drying, for both temperatures.

Zvonkina I.J. et al. European Coatings Journal 2006, vol.4, pp40-43

UV Curable Coatings

A study of the influence of low levels of functional acrylic monomers, incorporated into a core/shell acrylic copolymer, on UV curing characteristics, is reported. The polymerisation was conducted by first forming a MMA (25)/ BA (60)/ MAA (15) terpolymer seed, followed by the second-stage addition of St/BA, including carboxyl- and hydroxyl-functional monomers, along with the UV crosslinking monomer. The crosslinking monomers examined were isobornyl acrylate and methacrylate, tripropyleneglycol diacrylate, pentaerythritol triacrylate and 1,6-hexanediol diacrylate. They were incorporated at a typical level of 2.3 mole percent of total second stage monomer. The influence of type of functional monomer in the shell, concentration of photoinitiator and extent of UV exposure on film properties was examined.

T_g measurements (DSC) showed that although some crosslinking of the polymer took place during polymerisation and processing, further UV curing of the dried film occurred, dependent on the above mentioned parameters. Due to the relatively low level of unsaturation in the cast film, no significant changes in the infra-red spectra (FTIR) were observed during curing of the film. UV crosslinking of the film was shown to increase resistance of the film to swelling in alkali, despite no changes in gel content being measured.

Gan S.N. et al. J. Applied Polymer Science 2006, vol.100(3), pp2317-2322

Coatings for Flexible Packaging

Compositions are described that are able to provide coatings that can withstand substantial elongation without breaking, be applied at low coat weights to a variety of flexible substrates and confer desirable visual characteristics, such as gloss. The coatings comprise dispersions of resin coated nanoparticles, which are applied and heat cured onto the flexible substrate. A wide variety of systems are described in this patent application, but the nanoparticles invariably comprise organic or inorganic pigments. The resin-coated nanoparticles are prepared by *in situ* polymerisation, using either solvent or waterborne systems. Two examples describe the preparation of composite microparticles from phthalocyanine blue and carbon black pigments, using respectively a urethane/acrylic hybrid copolymer, prepared by the emulsion polymerisation

of MMA/BA in the presence of a PUD. The use of resin coated nanoparticles avoids problems of flocculation and produces more durable coatings.

Faler D.L. et al. (PPG Industries Inc.), US Patent Application 20050287348, Publication Date 29 December 2005

Can Coatings

A coating composition, suitable for use on food and beverage cans is described. The coating is derived from a polymer dispersion, prepared by the emulsion polymerisation of selected ethylenically unsaturated monomers in the presence of a pre-formed water-soluble polymer. The pre-polymer may typically be an acid-functional acrylic terpolymer, partially neutralised with an amine to enable full water solubility. One example describes the solution polymerisation of a St (30)/EA (25)/MAA (45) monomer mixture to yield a terpolymer that was subsequently partially neutralised with dimethylethanolamine, creating a polymer solution with a solids content of 22% and having an acid number of 302 mgKOH/g.

It is claimed that a wide range of primary monomers may be used in the subsequent emulsion polymerisation but the monomer mixture should contain a functional monomer containing an oxirane group [e.g. glycidyl methacrylate (GMA)]. An example describes the preparation of a St (41)/BA (30)/butyl methacrylate (21)/GMA (8) emulsion polymer in the presence of 25% dry weight of the above mentioned acrylic pre-polymer, based on total monomer weight. A H₂O₂/benzoin redox system is the preferred initiator for this class of product. The use of persulphate is said to compromise water resistance. A large number of representative examples are contained in this 30 page patent application and detailed testing of the dispersions as can coatings is described.

O'Brien R.M. et al. (Valspar Sourcing Inc.) PCT WO2006045017, Publication Date 27 April 2006 also US Patent Application 20060100366

6 Adhesive Applications

Universal Adhesive for Difficult Surfaces

A very broad based patent application describes a 'universal' adhesive composition, comprising one or more polymerisable surfactant monomers as part of an emulsion copolymer system, that claimed to exhibit superior adhesion to difficult surfaces compared to conventional systems. More specifically, acrylic dispersion polymers containing a level of above 0.4 wt% of polymerisable surfactant are claimed to be suitable as pressure sensitive adhesives able to bond to a variety of surfaces (e.g. polyolefins, thermoplastics and recycled paper/board). Good elevated temperature adhesive performance is claimed which is maintained at low temperatures (below 15°C).

Compositional details are described broadly but no specific examples are given, other than the use of one proprietary polymerisable surfactant (Polystep-NMS1, ex Stepan Co., described as the amine salt of an allyl-functional alkyl benzene sulphonate). Superior performance is in evidence compared to a control dispersion using SDBS as stabiliser. Reading between the lines, the use of a polymerisable surfactant enables minimisation or elimination of the use of conventional surfactants, which can migrate to interfaces and reduce adhesive performance. A variety of performance advantages are claimed to be achievable when this approach is adopted covering a wide range of adhesive types.

Bunn A.G. (Rohm & Haas Co.), US Application 20060100357, Publication Date 11 May 2006

Pressure Sensitive Adhesives Containing Silicon Compounds

Maximising adhesive properties of coatings, whilst maintaining cohesive strength, is key to formulating pressure sensitive adhesives (PSAs). In this patent it is claimed that by incorporating silicon compounds, in the form of discrete particles (5-200nm diameter), in PSA grade polymer dispersions, adhesion may be improved without detracting from cohesive strength. The silicon compounds may comprise either polymeric

silicates or be silicones, formed by condensation of silanes. The composition of suitable polymer dispersions, which form the primary components of PSAs is broadly defined, as are emulsion polymerisation procedures used to fabricate the latices. Two proprietary BASF PSA grades (Acronal™ A220 and Acronal™ V215) are used in the examples. The polymeric silicates are typically obtained by condensing water-soluble alkali metal salts (such as ‘water glass’). Amino-functional silanes (4-amino-3,3'-dimethylbutyltrimethoxysilane being specifically mentioned) are the preferred precursors for the silicones. It is suggested that the silicon compounds be pre-dispersed in water and then added to the polymer dispersion. Inevitably a broad range of addition levels of the silicon compounds are stated, the preferred range being 0.1-3% by weight based on polymer content. Optionally tackifying resins and other components may be post added to formulate the PSAs.

It is claimed that self-adhesive articles based on the disclosed composition possess a good balance of adhesive properties. Among the advantages stated for these adhesives are tolerance to compounding ingredients (including wetting agents), good apolar adhesion, minimal tendency to ‘adhesive transfer’ (e.g. label applications) and good water resistance.

Aydin O. et al. (BASF Ag), United States Patent 7041720, Publication Date 9 May 2006, also published as EP1479744

Pressure Sensitive Adhesive Adhesion Promoter

A synthetic polymer dispersion modifier claimed to significantly improve the adhesive properties of acrylic pressure sensitive adhesives (PSAs) is described. The composition of this adhesion promoter is 15-35 parts of a C₆-C₁₂ diester of a dicarboxylic acid (e.g. dioctyl maleate), 15-35 parts of a C₂-C₁₆ vinyl ester(s) (e.g. VA), 35-65 parts of a C₄-C₈ alkyl (meth)acrylate (e.g. BA) and 0.1-2.0 parts of an acetoacetoxy-functional monomer (e.g. acetoacetoxyethyl methacrylate). In the examples, the adhesion promoter is prepared by the emulsion polymerisation of the corresponding monomers, using a delayed pre-emulsion addition procedure, a mixed anionic/non-ionic emulsifier system being used. The resulting latices have a mean particle diameter in the region 100-400nm, a T_g between -30 and -50°C and a non-volatile content between 50 and 70%.

Relative to the amount of PSA, the modifier is added at a level of 5-30 parts. Results are presented showing that as the level of modifier is increased across this range, corresponding increases in polythene adhesion, loop tack (steel plate) and the holding power (cohesive strength) can be achieved.

Yang B-Y. et al. (Chief Investment Corp. (TW)), United States Patent 7041754, Publication Date 9 May 2006

Pressure Sensitive Adhesive with Superior Application Properties

A pressure sensitive adhesive (PSA) composition is described, suitable for application on high speed coating lines, which does not cause coating problems such as ‘cissing’ and ‘retraction’ when applied to a release paper. The key to this is to design a system with a dynamic surface tension $>59\text{mN}\cdot\text{m}^{-1}$, whilst achieving a suitable solids (50-70%)/viscosity (100-1000mPa.s) balance. It is argued that the adhesive is in a dynamic state throughout the high speed coating operation (i.e. does not reach equilibrium) and that defect-free coatings can be achieved by ensuring wettability of the discharge outlet by the adhesive is poor. Experiments have shown that if the dynamic surface tension (measured by a ‘bubble pressure’ method) is less than $59\text{mN}\cdot\text{m}^{-1}$, the PSA forms a meniscus and ‘wraps around’ the reverse side of a doctoring blade, forming part of the adhesive discharge system, which can give rise to defects.

To achieve high dynamic surface tension values, careful selection of emulsion polymerisation components is essential. The use of a combined anionic/non-ionic emulsifier system is advocated. The anionic surfactant should be the ammonium salt of a polymerisable, ethoxylated compound. The non-ionic surfactant should contain an alkylene oxide chain with the number of repeat units exceeding 50; it may also optionally be polymerisable. Examples and structures of suitable surfactants are described. Choice of chain transfer agent is also important with a thioglycolic acid ester, containing methoxy groups (e.g. methoxybutyl thioglycolate)

being preferred. A number of examples of the preparation of acrylic copolymer dispersions, all utilising the monomer ratios BA (48)/EHA (48)/AA (3)/MAA (1) and containing various suitable surfactants and chain transfer agents, are included. Good coating performance compared to control systems of lower dynamic surface tension systems is demonstrated.

Matsumoto M. et al. (Toyo Ink Mfg Co. (JP)), US Patent Application 20060094806, Publication Date 4 May 2006

7 Miscellaneous Applications

Polycarbodiimide Crosslinking Agents

A review of recent developments of polycarbodiimide (pCDI) crosslinkers, with particular reference to their application in leather/artificial leather coating, is presented. This area of application typically uses PUDs, acrylic latices or the two in combination. The chemistry of pCDI crosslinking involves mainly the reaction of carboxylic acid groups in acrylic latices or PUDs with pCDI ($-N=C=N-$), an N-acyl urea being formed. This reaction can be quite fast under ambient or mild thermal cure conditions. When pCDIs are used as crosslinkers, it is not necessary or even advisable to get to a 1:1 stoichiometry between pCDI and carboxyl groups. Optimum dosage should be determined empirically.

In a reported study, three types of oligomeric, water-dispersible pCDI crosslinker were evaluated in combination with various PUD and acrylic latices. The types of pCDI used were a solvent-based pCDI, an aqueous pCDI and a multi-functional, higher performance solvent-based, pCDI. Among the tests carried out were mechanical property measurements and solvent resistance of dried (cured) coatings as well as pot life. The work was extended to examine the respective systems in practical leather coating formulations. Graphically presented results indicate the improvements in tensile strength and ethanol uptake that can be achieved as a function of level of crosslinker. The multi-functional, solvent-based pCDI (no further details given) proved the most efficient crosslinker. The test results with actual basecoat and topcoat formulations have demonstrated that pCDI cured systems are practical for leather finishing. In this respect, the aqueous pCDI proved most advantageous since pot life was superior to the solvent-based pCDIs, and the ease of handling and absence of VOC are key features.

Hesselmans L.C.J. et al. Progress in Organic Coatings 2006, vol.55(2), pp142-148

Coatings for Leather and Elastomers

The formulation of a fast-drying, durable, glossy coating for flexible substrates such as leather and synthetic elastomers is disclosed. The formulation comprises an anionic stabilised dispersion polymer(s), a polyfunctional amine and a volatile base. It appears that composition of the polymer dispersion is not critical, however the ability of the polymer to be crosslinked is essential. The T_g of the dispersion polymer should be 21°C or higher. The presence of carboxylic groups to facilitate crosslinking by polyvalent metal ions or reaction with aziridines, carbodiimides etc is specifically mentioned. The use of polyvalent metal cations to crosslink the formulation is specifically mentioned in the claims. No specific details of formulations are disclosed in the patent. It does appear however that the key feature of these coatings (when polyvalent metal cations are deployed), is that on loss of the volatile base, co-ordination complexes rapidly form from both amine and carboxyl functionality, resulting in a rapidly cured coating (cf. polish technology)

Guaraldi F.L. et al. (Rohm & Haas (US)), European Patent 1627903, Publication Date 22 February 2006

Ultra Violet Blocking Fabrics

There is currently interest in designing and modifying fabrics to achieve high UV resistance. Coatings containing zinc oxide nanoparticles are one approach that shows particular promise. In this article a novel approach to fabricate ZnO/polySt nano-hybrid coatings on cotton fabrics is reported. The process involved

dispersing hydrophobic ZnO in the monomer phase [St (95)/MAA (5)], using a low HLB surfactant [poly(ethylene-alt-maleic anhydride)]. The resulting mixture was ultrasonicated in the water phase, using SDS as stabiliser. By this route, miniemulsion droplets were formed which were subsequently polymerised using AIBN as oil-soluble initiator.

TEM analysis indicated good dispersion of the ZnO particles in monomer prior to polymerisation and efficient encapsulation within polymer shells afterwards. Cotton fabrics were subsequently treated with the hybrid latex. By adding a latent acid catalyst (NaH_2PO_2), bonding between the carboxyl groups of the polymer and the hydroxyl groups of the cotton could be achieved on heating the coated fabric. It was subsequently demonstrated that the fabrics exhibited excellent UV blocking properties and good wash fastness, illustrating the viability of the process to produce protective fabrics.

Xin J.H. et al. J. Colloid & Interface Science 2006, vol.300(1), pp 111-116

Paper Coatings

A conference paper describes an investigation into the influence of filler systems on the morphology and properties of pigmented coatings. The coating formulations examined in the study comprised a filler system of kaolin (plate-like particles) and precipitated calcium carbonate (PCC) and utilised an SBR latex binder. The compounds were prepared using different blend ratios of pre-dispersed fillers, at two binder levels equating to 10 and 20 parts per hundred of filler. Coatings were applied to adsorbent (ink jet paper) and non-adsorbent (plastic) substrates and air-dried. The coatings were characterised by X-ray photo-electron spectroscopy (XPS), gloss measurements and profilometry (surface roughness).

Coatings applied to the non-porous substrate exhibited higher gloss and lower surface roughness than those applied to the porous surface. Increasing the PCC content of the filler system caused a decrease in gloss over the non-porous surface, but an increase in gloss over the porous one. This latter observation was attributed to improved 'filler packing'. The XPS results showed that as the PCC content was proportionally increased, the surface of the coating became enriched in polymer, explained by the plate-like structure of the kaolin layers being disrupted, opening channels for movement of the polymer particles following coating application. It is concluded that both filler composition and particle shape of the components play a crucial role in determining the surface structure of coatings.

Al-Turaif H. Proc. PRA "Waterborne & High Solids Coatings", Brussels, 7-8 March 2006, Paper 20, 17pp

Heat Resistant Hollow Sphere Polymers

A Rohm & Haas patent describes the design and application of heat resistant voided latex particles suited for use in a variety of applications where thermal processing is involved. Traditionally used hollow polymeric particles tend to soften and collapse on exposure to high temperatures, resulting in the partial or complete loss of the void within the particles. The voided particles described here are of the well-known alkali-swellaible core/hard shell type, produced by a two-stage sequential emulsion polymerisation process. A broad description of this technology is given with numerous references to prior patented processes. Typically the core component contains at least 10% by weight of copolymerisable acid. The shell may be a carboxyl-functional MMA/butyl methacrylate copolymer, with a $T_g > 70^\circ\text{C}$ and the voided fraction of the particles in the region 30-55%. It is disclosed that if a fixed base (e.g. KOH) is used to neutralise/swell the core polymer, as opposed to a volatile base (e.g. NH_4OH), the thermal stability of the voided particles is much enhanced, with processing temperatures up to 150°C being achievable. By crosslinking the shell (and optionally the core) by including a difunctional monomer (e.g. DVB, allyl methacrylate) in the emulsion polymerisation, it is claimed to be possible to process the voided particles at temperatures up to 350°C .

A number of examples are given illustrating the use of a proprietary product of this type (RhopaqueTM AF1055, ex Rohm & Haas) in a variety of heat resistant textile applications (e.g. non-wovens, pigment printing). The retained opacity of coatings/sizes containing this product, after heat processing is shown to be

vastly superior to equivalents containing a control voided polymer latex (Rhopaque™ HP1055), swollen with a volatile base. Applications for heat resistant voided particles extend to their use in thermoplastics, powder coatings and metal coatings (e.g. coil coatings, automotive coatings).

Brown J.T. et al. (Rohm & Haas Company), European Patent 1632537, Publication Date 8 March 2006, also US Application 20060046056

Food Coating Composition

Aqueous coatings applied to foods such as cheese, vegetables and sausages etc. are required to possess anti-fungal properties to prevent the unwanted growth of mould and yeast. These compositions, usually based on polymer dispersions contain polyene fungicides, such as natamycin. These are expensive components often lacking chemical stability, such that degradation and loss of activity occur in compounded formulations, necessitating the addition of excess biocide. Polymer dispersions, characterised by excellent polyene fungicide tolerance are described in this patent application. The key to achieving this appears to be setting the pH of the composition in the preferred range 4.2-5.5, including an antioxidant (e.g. ascorbic acid) and preferably avoiding the use of cellulose ether stabilisers. The primary polymers used in such formulations are VA/di-butyl maleate copolymers (used in the examples). Alternatively polyVA, VA/E copolymers and acrylic copolymers may be used. pVOH is the preferred colloid stabiliser, with non-ionic surfactants also included in the emulsion polymerisation. Comonomer composition is adjusted to yield a dispersion with an MFFT below 15°C. Ideally free VA levels in the final dispersion should be less than 100ppm. Natamycin was post added to the dispersion as the final addition in the compounding stage.

Subsequent natamycin recovery testing, performed on samples of dispersion aged at 40°C for one week, gave values greater than 90%, significantly higher than controls.

Jakob M. et al. (Celanese Emulsions GmbH), European Patent 1642929, Publication date 5 April 2006. Also published as US 20060047069

Glossary

CHEMICALS

AA	Acrylic acid
ACN	Acrylonitrile
AIBN	2,2'-Azobisisobutyronitrile
APS	Ammonium persulphate
BA	Butyl acrylate
Bd	Butadiene
Cy	Cyclohexyl
DVB	Divinyl benzene
EA	Ethyl acrylate
EHA/2-EHA	2-Ethylhexyl acrylate
EO	Ethylene oxide
KPS	Potassium persulphate
MA	Methyl acrylate
MAA	Methacrylic acid
MMA	Methyl methacrylate
Ph	Phenyl
PU	Polyurethane
PUD	Polyurethane dispersion
pVOH	Polyvinyl alcohol
SBR	Styrene butadiene (rubber)
SDBS	Sodium dodecylbenzene sulphonate
SDS	Sodium lauryl sulphate, Sodium dodecyl sulphate
SFS	Sodium formaldehyde sulfoxylate
St	Styrene
tBHP	t-butyl hydroperoxide
TDM	t-dodecyl mercaptan
TEMPO	2,2,6,6-tetramethylpiperidinyloxy
UF	Urea formaldehyde resin
VA	Vinyl acetate

TERMINOLOGY

AFM	Atomic force microscopy
ATRP	Atom radical transfer polymerisation
CMC	Critical micelle concentration
DLS	Dynamic light scattering
DMA	Dynamic mechanical analysis
DSC	Dynamic scanning calorimetry
FTIR	Fourier transform infra-red spectroscopy
GC	Gas chromatography
GPC	Gel permeation chromatography
HLB	Hydrophilic lipophilic balance
MFFT	Minimum film forming temperature
MW	Molecular weight, Mn and Mw, number and weight average MW
NMR	Nuclear magnetic resonance
PCS	Photon correlation spectroscopy
PSD	Particle size distribution
RAFT	Reversible addition fragmentation transfer
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
Tg	Glass transition temperature
TGA	Thermogravimetric analysis
VOC	Volatile organic compound

Other abbreviations are explained in the text of the journal

Courses, Meetings, Conferences

The **11th Meeting of the UK Polymer & Colloids Forum** will take place on 11-12th September 2006 at the University of Manchester, England. The sessions fall under the headings: Synthesis, stabilisation & properties of polymer latices; Microgels & colloidsomes and Biomedical applications of polymer colloids. Details at <http://www.uk-pcf.org/06%20Final.pdf>

The **20th European Colloid & Interface Science Society** Conference will take place on 17-22nd September 2006 in Budapest, Hungary. The conference will focus on many aspects of this subject, embracing material science and nanotechnology. Included in the topics are self-supporting organic/inorganic films, polymer gels, colloidal polymer aggregates and nanoparticles. Details at <http://koll1.chem.u-szeged.hu/colloids/20thecis>

The **78th Annual Meeting of the Society of Rheology** will take place on 8-12th October 2006. The meeting will comprise ten thematic sessions that will include Suspensions, colloids & granular materials: Rheology & structure of entangled polymer systems and Paper, pulp & industrial processes. Details at http://www.rheology.org/sor/annual_meeting/2006Oct/program.htm

The IUPAC International Symposium on **Advanced Polymers for Emerging Technologies** will be held on 10-13th October 2006 in Bexco, Busan, Korea. Commemorating the 30th anniversary of the Polymer Society of Korea, the content of the symposium will embrace a wide range of topics including Smart polymers, Polymer nanomaterials & nanotechnology, Polymer synthesis & reactions and Industrial polymers. Details at <http://www.psk30.org/>

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purpose of the congress is to build on the previous four congresses held in this series, by bringing together experts in the fields of the protection and preservation of wood, to present and discuss new developments, which will lead to a greater understanding of the problems the industry faces and the possible solutions. The congress also provides an ideal opportunity for establishing new business contacts, consistent with the current interest in “partnering” as a means of enhancing the new product development process.

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