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NAPOLEON

NAnostructured waterbone POLymEr films with OutstaNding properties

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José M. Asua *(PC)*
UPV

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http://www.ehu.es/napoleon/

1.- Project Execution

The development of many industrial sectors - i.e., coatings, adhesives, cosmetics, and additives for paper and textiles- is limited by the inability of existing technology to produce nanostructured polymer films via a sustainable technology. The objective of this project is to make possible a generation of radically-new products by developing a technology platform for the production of films with controlled nanostructure without the emission of organic solvents or residual monomer. The breakthrough idea is to use waterborne nanocomposite nanoparticles with carefully controlled structure as building blocks for the films. Nanoparticles are highly advantageous for processing films because they offer a means to tailor the size-scale of the nanostructure, given that the nanodomains cannot be larger than the size of the particle in which they are contained. A further benefit of the proposed technology is its compliance with impending European directives on solvent emissions. A broad range of radically-new, high-solids, waterborne nano-particles of controlled structure will be created. These are classified as (1) high-performance nanostructured polymer/polymer, and (2) polymer/inorganic nanoparticles. A key inorganic additive will be exfoliated layered silicates. These nano-structured materials can impart a wide range of attractive properties. When the project started, *there was no technology available for their controlled synthesis*.

The contractors involved are:

The University of the Basque Country	Spain
Cytec Surface Specialties	Belgium
University of Surrey	UK
CNRS (Ecole Supérieure de Physique et Chimie Industrielle)	France
CNRS (Laboratory of Chemistry and Processes of Polymerisation)	France
CNRS (Institut Charles Sadron)	France
University of Ulm	Germany
Institute for Surface Chemistry	Sweden
University of Cambridge	UK
National Institute for Applied Research (INSA-Lyon)	France
University of Clausthal	Germany
EPFL	Switzerland
University of Bath	UK
Nuplex Resins BV	The Netherlands

Wacker Chimie	Germany
BASF	Germany
Química Europea de Resinas	Spain
L'Oreal	France
Genthe-X-Coatings	Germany

The project has been coordinated by:

Professor Jose M. Asua
The University of the Basque Country
Institute for Polymer Materials (POLYMAT)
Avenida de Tolosa 72
20018 Donostia-San Sebastian, Spain
Phone: 34 943 018181 Fax: 34 943 017065
e-mail: napoleon@ehu.es

Synthesis and properties of the waterborne nanocomposite nanoparticles

a) Polymer-polymer systems

Miniemulsion polymerization was preferentially employed to synthesize high solids waterborne nanocomposite nanoparticles of controlled structure and very low VOC content because it allows the incorporation of hydrophobic components into polymer particles as the need of mass transfer through the aqueous phase is avoided.
Most of the work was carried out with alkyd-acrylic coatings and polyurethane-acrylic adhesives. In both cases, the preformed step-growth polymer (alkyd resin or polyurethane) is dissolved in a monomer mixture (polymerizable by free radical polymerization) and a miniemulsion is formed by dispersing this solution in water in the presence of emulsifiers and costabilizers using an adequate dispersion device. The miniemulsion is then polymerized maximizing the extent of droplet nucleation. The key aspects in the synthesis of the hybrid dispersions by miniemulsion polymerization are:

- to form composite droplets of small size, making them colloidally stable and stable with respect Oswald ripening,
- to polymerize most of these droplets avoiding both other nucleation mechanisms and coagulation (with particles and droplets),
- to achieve high conversion
- to control polymer architecture (composition, MWD, grafting, gel, …), and
- to achieve the desired particle morphology.

Although several homogenization devices (e.g., rotor-stator, sonicator and high pressure homogenizer) can be used to prepare the miniemulsion, only high-pressure homogenization allows the preparation of small size, high solids miniemulsions containing high concentrations of resin. A mathematical model for the miniemulsification in high pressure homogenizers has been developed.
In batch miniemulsion polymerization, droplets are efficiently nucleated provided that small size high solids stable miniemulsions and a flux of radicals high enough are used.
Miniemulsion polymerization in the presence of a preformed resin often leads to unacceptable concentrations of residual monomer due to a limiting monomer conversion. This is a serious problem that hinders the commercialization of these products. Combination of redox initiation during the main polymerization process with adequate postpolymerization strategies allows achieving a residual monomer content as low as 50 ppm in the final latex.

Polymer architecture in hybrid polymer systems is more complex than in the case of homogeneous polymers and it is case dependent. For the case of acrylic-alkyd hybrids, polymer architecture should be characterized in terms of the fraction of acrylic polymer that contained grafted resin (acrylic degree of grafting, ADG), the fraction of the resin that is grafted to the acrylic polymer (resin degree of grafting, RDG), gel content, sol MWD and fraction of unreacted double bonds (UDB) in the alkyd (Figure 1). The characterization methods are discussed elsewhere. Adequate modification of the process conditions allows obtaining a rich variety of polymer architectures (Table 1).

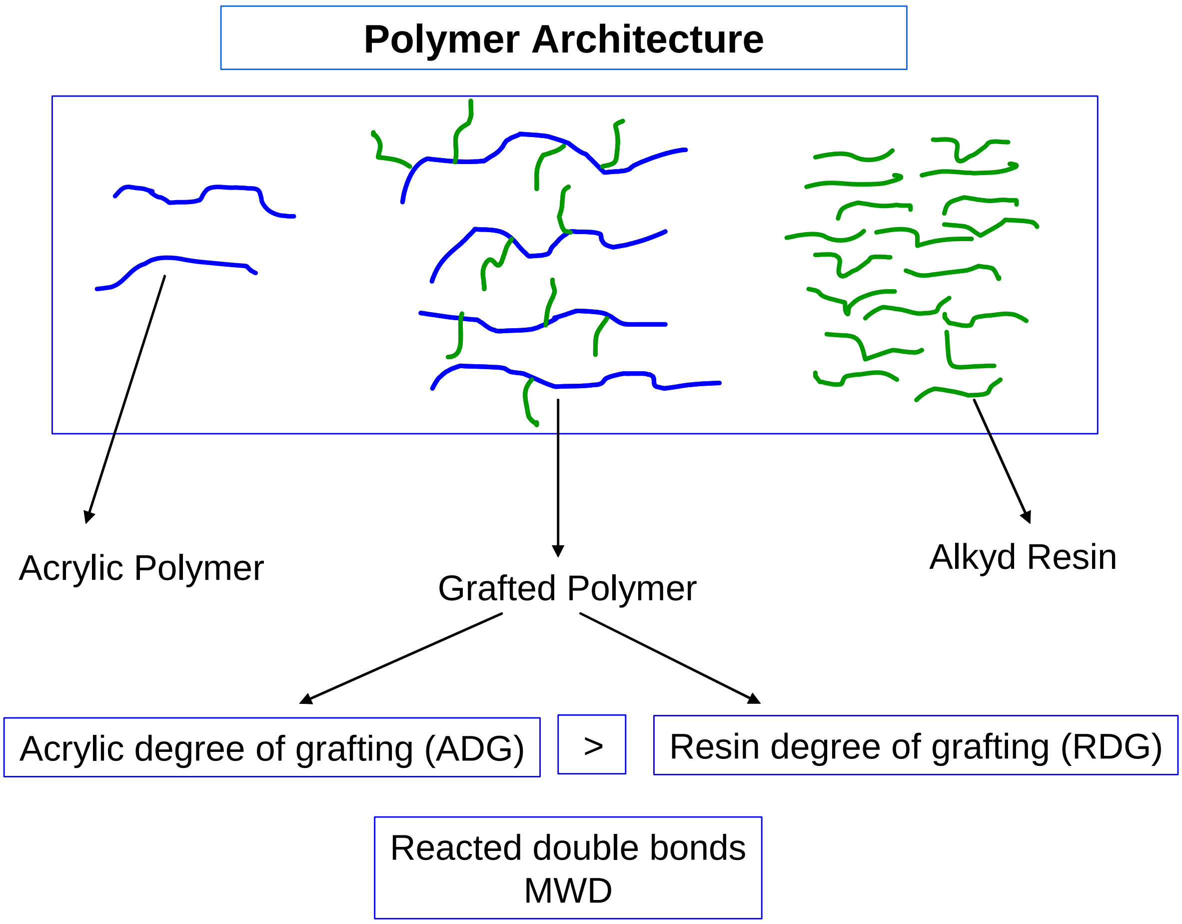

Figure 1. Polymer architecture of acrylic-alkyd hybrids

Table 1. Some examples of polymer characteristics

Hybrid	Gel (%)	ADG (%)	RDG (%)	RDB (%)	Mw (g/mol)
1	0	86	20	12	331000
2	0	> 90	47	20	>5x106
3	0	89	25	16	905000

For the case of the PU-acrylic system, the key point is the degree of crosslinking between the acrylic chains and the polyurethane chains. It has been found that this good control can be achieved by either using double bond terminated polyurethanes that are able to react with the acrylic monomer or using isocyanate terminated PUs able to react with hydroxyl acrylates.
Completely different particle morphologies can be obtained in a controlled manner by varying the characteristics of the acrylic polymers, the type of the alkyd resin and the process conditions. Figure 2 illustrates this variety for the alkyd-acrylic system.

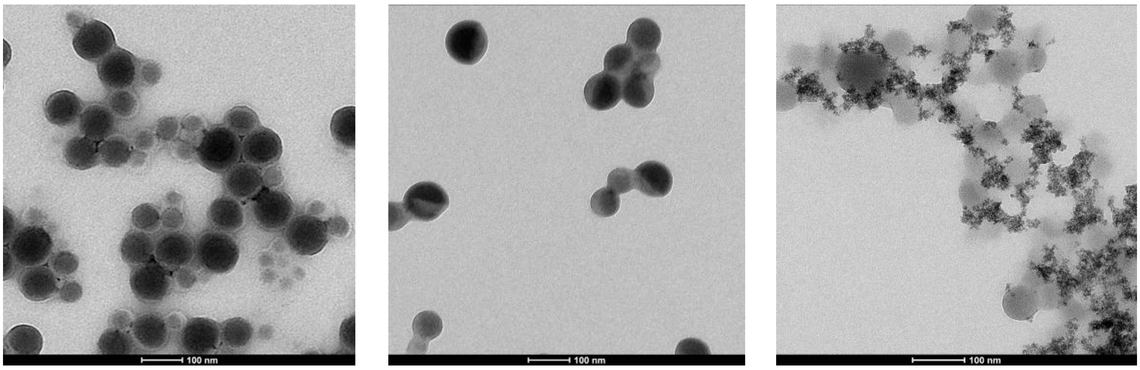

Figure 2. Particle morphologies of acrylic-alkyd nanostructured particles.

b) Polymer-clay systems

Three synthetic procedures have been investigated in order to control particle morphology (Figure 3). The three methods differ in the clay location before polymerization. In method 1, the Laponite clay platelets are functionalized with a free radical initiator and dispersed in an aqueous solution of surfactant. Monomer droplets are then formed in the presence of the organoclay and polymerized to form Laponite-armoured latex particles. In method 2, the clay is rendered hydrophobic and dispersed in the monomer mixture. Polymerization of the clay-loaded miniemulsion droplets should yield polymer-encapsulated clay platelets. In method 3, the hydrophobized clays are dispersed in a solution of a non-ionic surfactant and a separate monomeric minimemulsion stabilized with the same surfactant is prepared. In a subsequent co-sonification process, the two dispersions are combined to obtain hybrid droplets that are subsequently polymerized.

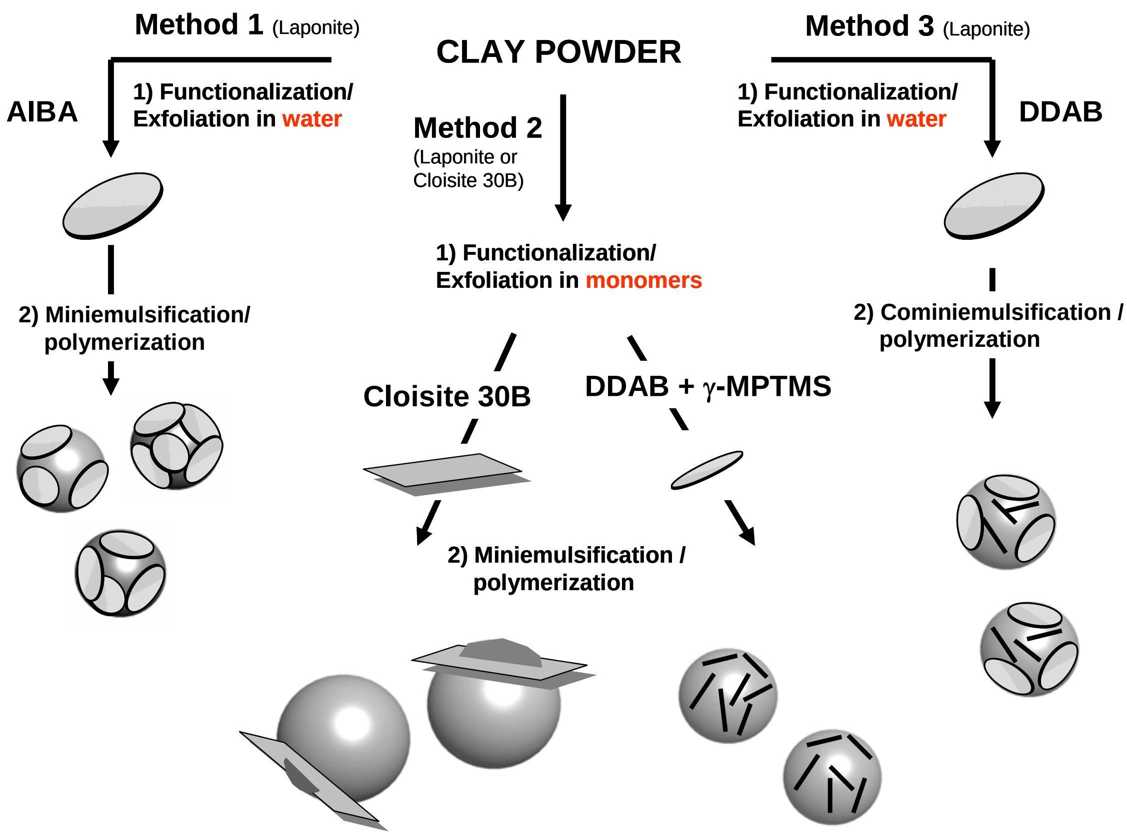

Figure 3. Synthetic strategies developed to control particles' morphology during the synthesis of polymer/Laponite or polymer/MMT composite colloids through miniemulsion polymerization.

Film formation

The waterborne nanocomposite nanoparticles were used as building blocks for the films. Film formation ensures that a high quality polymer film is attained. The process has a pronounced effect on characteristics and properties of the film, including gloss, barrier resistance, hardness, and mechanical properties.
Optimum techniques for the study of the processing of nanocomposite particles into films were established. The relevant techniques for the study of drying are the Quartz Crystal Microbalance, GARField magnetic resonance profiling, Photocorrelation Spectroscopy, and Beam/Membrane bending. Techniques for the study of particle deformation are wet scanning transmission electron microscopy (STEM), and atomic force microscopy. Finally, techniques for the study of surfactant distribution and interdiffusion are confocal Raman microscopy, X-ray photoelectron spectroscopy (XPS), and fluorescence resonance energy transfer (FRET). These techniques allowed gaining knowledge about the effect of polymer architecture and particle morphology on the three stages of film formation: (1) drying; (2) particle packing and deformation; and (3) interdiffusion across particle boundaries, as well as about surfactant migration during film formation. A mathematical model for the film morphology has been

developed. With this knowledge, important practical problems were solved including (1) controlling the rate of water loss from urethane/acrylic latex films that was exceedingly slow; (2) lowering the water sensitivity of alkyd-acrylic coatings; (3) avoiding wrinkling, blooming, poor wetting, and heterogeneity in alkyd/acrylic clear-coats; and (4) avoiding the poor adhesion of waterborne nail polish while maintaining high resistance to abrasion and scratching.

Structure-Properties

Coatings using alkyd-acrylic particles with widely different morphologies containing different polymer architectures were formulated and their application properties were measured. The morphology and polymer microstructure that led to transparent films (Figure 4) with good water resistance, dust free time and hardness were obtained.

Figure 4.- Effect of the particle morphology on film transparency.

The properties of polyurethane-acrylic adhesives were mostly determined by the polymer network in the nanoparticles. Controlling the network, adhesive films having outstanding properties in terms of shear resistance at high temperature were produced.
The role of the microstructure of polymer-clay systems on water absorption has been elucidated and it is clear that the organization of the platelets and their hydrophilicity have an important role on the macroscopic water uptake. It was generally found that the presence of clay significantly hardens the films and reduces the friction coefficient of the coatings. A phase field model of adhesives under stress as a two phase system of immiscible viscoelastic fluids has been developed.

Biocompatibility and bioavailability

The objective of this study was to answer to the following questions:

1. What happens to nanoparticles when they contact skin? Do they remain at surface or do they penetrate at all into different skin strata? Do they show particular affinity for any specific structures (e.g., hair follicles)?
2. What happens to the “active” encapsulated or associated with the nanoparticles? Does it remain with particles, or it is released? if released, where and how fast?

3. How is nanoparticle fate, and release of “active”, influenced by nanoparticle size, polymer forming the nanoparticles and physicochemical properties of “active”?

It was found that the nanoparticles lodge in skin furrows and associate with hair shafts and follicles, and there is no evidence that the nanoparticles penetrate beyond the stratum corneum. The nanoparticles are efficiently removed by cleaning. There is an initial co-localization of active and the nanoparticle on skin surface. Then, the active is released from the nanoparticles and penetrates into deeper stratum corneum. The release of the active is strongly related to the compatibility between the active and the nanoparticles surface and it is faster for larger particles.

2.- Dissemination and use

SECTION 1- Exploitable knowledge and its use

The summary of the exploitable results found in the Napoleon project can be found in the overview table below.

Overview table

	Exploitable Knowledge	Exploitable product or measure	Sectors of application	Timetable for comm. use	Patents	Owners
1	Polymer binder nanoparticles by microemulsion polymerization	Polymeric binders to improve the mechanical properties of e.g. past-like tile adhesive formulations.	Chemical (polymerization industry)	2010	Applied (2009)	Wacker
2	Post-polymerization of alkyd/acrylic waterborne latexes	Reduction of the residual harmful monomers in final products.	Chemical (polymerization industry)	2010	Applied (2009)	Nuplex
3	Construction of an agitated and thermostatized micro-cell.	Micro-reactor for on-line SAXS measurements	Analytical chemistry.	2011	Applied (2009)	UPV
4	Production of waterborne polyurethane/acrylic latexes in one step.	Binders for adhesives with very high temperature resistance.	Chemical (polymerization industry)	2011	Applied (2009)	UPV
5	Production of waterborne alkyd/acrylic latexes with a new modified alkyd resin.	Binders for clear coatings.	Chemical (polymerization industry)	2010	About to apply (2010)	Nuplex, UPV

1. Wacker has found a way to produce novel polymer binder nanoparticles by microemulsion polymerization, in order to enchance the mechanical properties of formulations that do not contain inorganic binders. The positive effect of the “reinforcing” nanoparticles on the mechanical properties can only be achieved if those particles are small enough to fit in the packing voids of the weaker binder latex particles. Wacker has developed those new nanoparticles with methyl methacrylate and hydroxypropyl methacrylate, with good stability and small particles sizes (below 35nm). Wacker has proven that the mechanical strengh has increased with these new nanoparticles compared with the benchmarks, and they have patented them.

2. One of the problems currently found when hybrid polymerizations is carried out is the limiting conversion of the harmful monomers, which will remain as

volatile molecules in the final product, coating in this case. In order to get rid of these monomers, Nuplex has developed a procedure to postpolymerize them and attach them to the polymer, not being volatile anymore. Nuplex has patented the process and will be using it in further product developments.

3. The on-line monitoring of quick reactions by Small Angel X-ray Scattering (SAXS) was not easy for reactions carried out in dispersed phase, which require agitation, together with a thermostatised environment. UPV has developed a new micrereactor, suited for the on-line measurements in SAXS, which content can be agitated and thermostatised, and with a very low reactants volume in order not to scatter too much the X-rays. UPV has already patented the micro-reactor, and is looking for commercial contacts to distribute the microreactor.

4. The expertise won by UPV during the Napoleon project in the synthesis of polyurethane/acrylic hybrids in-situ, has lead to a new series of waterborne adhesive nanocomposites having a high temperature resistance not common in waterborne adhesives. Therefore a patent has been presented by UPV in this area.

5. The close research carried out by Nuplex Resins and UPV has lead to the production of new waterborne alkyd/acrylic latex, useful as binder for high performance coatings. While UPV was carrying out the synthesis of the hybrid latexes, Nuplex was testing them. The problems in the application tests and the solutions for them were shared between both partners, reaching at the end to an optimised hybrid, starting from a modified version of the alkyd resin. The final properties of the optimised latex were better than the benchmarks, which has lead to both partners to file a patent that will soon be presented. Nuplex will probably produce the product as binder for coatings in a short term, after doing some market testings.

SECTION 2- Dissemination of the knowledge

The knowledge gained during the Napoleon project has been disseminated through different media such as a website (www.ehu.es/napoleon), a short course given to the scientific and professionals community, four articles devoted to general public, 9 PhD Thesis, 32 articles published in scientific journals and more than 50 presentations and posters in scientific congresses. See the tables below for the summary of all of them.

It has to be mentioned that the procedure for the publication of all these contributions has been the same in all the cases, i.e. the approval by all the partners before their publication. This procedure will keep on after the end of the Napoleon project (from 1 Dec 2009 on), for all the results obtained within the project.

Short course for the scientific and professional community (European Coatings Show 2009)				
N	*Authors*	*Title*	*Partners involved*	***WP***
1	C. Arnold, E. Canetta, P. Ekanayake, J. Faucheu, V. Gundabala, C. de las Heras Alarcón, A. Kőnig, M. Patel, A. Turshatov, K. von der Ehe, T. Weerakkody, H.N. Yow, J. Adams, L. Chazeau, C. Gauthier, Y. Holl, D. Johannsmann, A. Larsson, P.J. McDonald, A.F. Routh, and J.L. Keddie	Understanding the Film Formation of Waterborne Nanocomposite Coatings: Techniques to Study Latex Drying	Clausthal, Surrey, Cambridge, INSA, YKI, ICS	**4**
2	M. Goikoetxea1, R. Minari, I. Beristain, M. Manea, M. Paulis, M.J. Barandiaran, C. de las Heras Alarcón, J. Faucheu, C. Gauthier, L. Chazeau, J.L. Keddie, J.M. Asua	Controlling Polymer Architecture and Particle Morphology of Alkyd/Acrylic Waterborne Nanocomposite Coatings	UPV, INSA, Surrey	**3, 4**
3	E. Bourgeat-Lami, V. Mellon, F. Pardal, J-L Putau, T. Mc Kenna, A. Bonnefond, M. Micusik, M. Paulis, J.R. Leiza, E. Schreiber, K. Landfester, B. Lohmeijer	Acrylic/Clay Nanocomposite Latexes: Synthesis, Structure and Properties	LCPP, UPV, Ulm, BASF	**3**
4	C.M. de las Heras Alarcón, M. Goikoetxea, M.J. Barandiaran, J.M. Asua, A. Turshatov, D. Johannsmann,, S. Theisinger, M. Dass, K. Landfester, J.L. Keddie	Phase Separation in Alkyd/aAcrylic Hybrid and Blend Films for Waterborne Binders	Surrey, UPV, Clausthal, Ulm	**3, 4**
5	C. Creton, E. Degrandi, L. Sonnenberg, R. Udagama, E. Bourgeat-Lami, T. McKenna, A. Lopez, J.M. Asua	Mechanical and Adhesive Properties of Nanostructured Waterborne Pressure-Sensitive Adhesive Films	ESPCI, LCPP, UPV	**3, 5**

6	J. Faucheu, L. Chazeau, C. Gauthier, J-Y Cavaillé, C. Plummer, R. Ruggerone, G. Klein, C. Gauthier, Y. Holl	Design of polymer colloid nanocomposites for properties: some key parameters	INSA, EPFL	**3**
7	D. Mestach	Industrial Perspectives on Nanocomposites for Coating Applications.	Nuplex Resins	**10**

Articles devoted to general public					
N	*Authors*	*Title*	*Publication*	*Partners involved*	WP
1	J.M. Asua	Films nanoestructurados dispersos en agua con propiedades excepcionales	IKERTU (October 2005), for the scientific community of the UPV	UPV	
2	J.M. Asua	Un equipo de la UPV coordina un proyecto químico internacional.	“El País” on the 24th of January 2006	UPV	
3	J.M. Asua	Películas finas de polímero nanoestructuradas.	ON line in CICNetwork (www.cicnetwork.es/index.php)	UPV	2,3
4	J.L Keddie	Insights into the Drying Stage of Waterborne Nanocomposite Coatings: Results from the NAPOLEON Project	European Coatings Journal 11 (2009) 28-32	Surrey	4

PhD Thesis by students in Napoleon project					
N	*Author*	*Title*	*Partner*	*Language*	WP
1	**G. Diaconu**	Production of waterborne polymer/clay nanocomposites	UPV (Spain)	English	2,3
2	**J. Faucheu**	Relationships between microstructure and properties in nanostructured films obtained from latex	INSA (France)	English	4
3	**V. Mellon**	Synthesis and Characterization of Waterborne Polymer/Laponite Nanocomposite Latexes Through Miniemulsion Polymerization	LCPP (France)	English	2,3
4	**C. Arnold**	Formation de films minces polymères à partir de nanocolloides composites	ICS (France)	French	4
5	**X. Wu**	Characterization and Evaluation of Novel Nanoparticulate Formulations for Application to the Skin	Bath (UK)	English	6
6	**E. Schreiber**	Encapsulation of Laponite RD in Polymer Latices Aim	Ulm (Germany)	English/German	2,3
7	**Tecla G Weerakkody**	Physical Characterisation of Latex Film Formation and Film Properties	Surrey (UK)	English	4
8	**R. Ruggerone**	Structure-Property Relationships in Polymer Nanocomposite Films Derived from Novel Nanostructured Latexes	EPFL (Switzerland)	English	4,5
9	**E. Degrandi**	Latex Hybrides Urethane/Acrylique pour Applications Adhesives	ESPCI (France)	English	5

Articles published in scientific journals					
N	*Authors*	*Title*	*Publication*	*Partners involved*	WP
1	V. R. Gundabala, A. F. Routh	Thinning of drying latex film due to surfactant	**Journal of Colloid and Interface Science, *303* (2006) 306-314**	Cambridge	4
2	Xiao Wu, Bruno Biatry, Colette Cazeneuve, Richard H. Guy	Drug Delivery to the Skin From Sub-micron Polymeric Particle Formulations: Influence of Particle Size and Polymer Hydrophobicity	**Pharm. Res. 26 (2009) 1995-2001**	Bath, L'Oréal	6
3	W. Bücking, B. Du, A. Turshatov, A.M. König, I. Reviakine, B. Bode, D. Johannsmann	A Quartz Crystal Microbalance Based on Torsional Piezoelectric Resonators	**Rev. Sci. Instr. 78, 074903 (2007)**	Clausthal	4
4	Maryline Clauzel, Patrick Kékicheff, Jörg Adams, Diethelm Johannsmann	Internal dynamics in drying latex films: a study based on fluorescence anisotropy and acoustic dissipation	**Soft Materials, 2008, 6, 1-14**	Clausthal	4
5	M. Manea, A. Chemtob, M. Paulis, J. C. de la Cal, M. J. Barandiaran, J. M. Asua	Miniemulsification in high-pressure homogenizers	**AIChEJ (2008), 54(1), 289-297**	UPV	3
6	P. Ekanayake, P. J. McDonald, J. L. Keddie	An experimental test of the scaling prediction for the spatial distribution of water during the drying of colloidal films	**European Physics Journal, 166, (2008) 21-27**	Surrey	4
7	G. Diaconu, J. M. Asua, M. Paulis, J. R. Leiza	High solids content waterborne polymer-clay nanocomposites	**Macromol. Symp. 259 (2007) 305-317**	UPV	3

8	V. R. Gundabala, C.-H. Lei, K. Ouzineb, O. Dupont, J. L. Keddie, and A. F. Routh	Lateral surface non-uniformities in drying latex films	**AIChEJ (2008), 54 (12), 3092-3105**	Cambridge, Surrey	4
9	A. Turshatov, J. Adams	A new monomeric FRET acceptor for polymer interdiffusion experiments	**Polymer 48 (2007) 7444-7448**	Clausthal	4
10	K. von der Ehe, D. Johannsmann	Maps of the stress distributions in drying latex films	**Rev. Sci. Instr. 78, 113904 (2007)**	Clausthal	4
11	N. J. Glassmaker, C. Y. Hui, T. Yamaguchi, C. Creton	Detachment of stretched viscoelastic fibrils	**European Physics Journal E, 25(3) (2008) 253-266**	ESPCI	5
12	A. López, A. Chemtob, J. L. Milton, M. Manea, M. Paulis, M. J. Barandiaran, S. Theisinger, K. Landfester, W.-D. Hergeth, T. McKenna, F. Simal, J. M. Asua	Miniemulsification of monomer resin hybrid systems	**IECR 47(16) (2008) 6289-6297**	UPV, Ulm, Wacker, LCPP, CYTEC	2
13	G. Diaconu, M. Paulis, J. R. Leiza	Taking advantage of emulsion polymerization to produce high solids waterborne (PMMAcoBA)/MMT nanocomposites	**Polymer 49 (2008) 2444-2454**	UPV	3
14	R. Rodriguez, P. Ekanayake, C.M. de las Heras Alarcón, P. J. McDonald, J. L. Keddie, M. J. Barandiaran, J. M. Asua	Correlation of silicone incorporation with the hydrophobic and thermal properties of hybrid silicone-acrylic coatings	**Macromolecules 41 (2008) 8537-8546**	Surrey, UPV	3,4
15	A. Turshatov, J. Adams, D. Johannsmann	Interparticle Contact in Drying Polymer Dispersions Probed by Time Resolved Fluorescence	**Macromolecules 41(14) (2008) 5365-5372**	Clausthal	4
16	A. M. König, T. G. Weerakkody, J. L. Keddie, D. Johannsmann	Skin Formation During Drying of Polymer Dispersions: Dependence on Added Salt	**Langmuir 24(14) (2008) 7580-7589**	Clausthal, Surrey	4

17	R.J. Minari, M. Goikoetxea, I. Beristain, M. Paulis, M.J. Barandiaran, J.M. Asua	Grafting Characterization of Alkyd/acrylic Nanocomposites Prepared by Miniemulsion Polymerization	**J. Appl. Polym. Sci. 114 (2009) 3143-3151**	UPV	3
18	G. Diaconu, M. Micusik, A. Bonnefond, M. Paulis, J. R. Leiza	Macroinitiator and Macromonomer Modified Montmorillonite for the Synthesis of Acrylic/MMT Nanocomposite Latexes.	**Macromolecules 42(9) (2009) 3316-3325**	UPV	3
19	M. Goikoetxea, R. J. Minari, I. Beristain, M. Paulis, M.J. Barandiaran, J.M. Asua	Polymerization Kinetics and Microstructure of Waterborne Acrylic/Alkyd Nanocomposites Synthesized by Miniemulsion	**J. Polym. Sci. Part A: Polym. Chem. 47 (2009) 4871-4885**	UPV	3
20	J. Faucheu, L. Chazeau, C. Gauthier, J-Y Cavaillé, M. Goikoetxea, R. Minari, J.M. Asua	Latex Imaging by Environmental STEM: Application to the Study of the Surfactant Outcome in Hybrid Alkyd/Acrylate Systems	**Langmuir 25 (17) (2009) 10251-10258**	INSA, UPV	3,5
21	G. González, E. Colmenar, G. Diaconu, F. Alarcia, M. Manea, M. Paulis, M.J. Barandiaran, J.R. Leiza, J.C. de la Cal, J.M.Asua	Production of Widely Different Dispersed Polymers in a Couette-Taylor Reactor	**Macromol. React. Eng. 3 (2009) 233-240**	UPV	3
22	X. Wu, G.J. Price, R. H. Guy	Disposition of nanoparticles and an associated lipophilic permeant following topical application to the skin	**Molecular Pharmaceutics 6 (2009) 1441-1448**	Bath	6
23	X. Wu, P. Griffin, G. J. Price, R. H. Guy	Preparation and *in vitro* evaluation of topical formulations based on polystyrene-poly-2-hydroxyl methacrylate nanoparticles	**Molecular Pharmaceutics 6 (2009) 1449-1456**	Bath	6
24	X. Wu, R. H. Guy	Applications of nanoparticles in topical drug delivery and in cosmetics	**J. Drug Deliv. Sci. Tech. 19 (2009) 371-384**	Bath	6
25	J. Faucheu, C. Gauthier, L. Chazeau, J-Y. Cavaillé, V. Mellon, E. Bourgeat Lami	Miniemulsion polymerization for synthesis of structured clay/polymer nanocomposites: Short review and recent advances.	**Polymer 51(1) (2010) 6-17**	INSA, LCPP	3,5

26	R.J. Minari, M. Goikoetxea, I. Beristain, M. Paulis, M.J.Barandiaran, J.M. Asua1	Post-Polymerization of Waterborne Alkyd/Acrylics. Effect on Polymer Architecture and Particle Morphology	**Polymer 50 (2009) 5892-5900**	UPV	3
27	M. Paulis, A. Bonnefond, M. Micusik, J.R. Leiza	New Agitated and Thermostatized Cell for In-Situ Monitoring of Fast Reactions by Synchrotron SAXS.	**J. Synchrotron Radiation 16 (2009) 869-871**	UPV	3
28	J.L. Keddie	Insights into the Drying Stage of Waterborne Nanocomposite Coatings: Results from the NAPOLEON Project	**European Coatings Journal 11 (2009) 28-32**	Surrey	4
29	H.N. Yow, X. Wu, A.F. Routh, and R.H. Guy.	Dye Diffusion from Microcapsules with Different Shell Thickness into	**Mammalian Skin. Eur. J. Pharm. Biopharm., 72 (2009) 62-68.**	Bath, Cambridge	4,6
30	X. Wu, K. Landfester, A. Musyanovych and R.H. Guy.	Disposition of Charged Nanoparticles Following Their Topical Application to the Skin.	**Skin Pharmacol. Physiol., 23 (2010) 117-123.**	Bath, Ulm	3,6
31	M. J. Patel, V. R. Gundabala, F. Pardal, E. Bourgeat-Lami, and A. F. Routh	Film formation of polymer-clay nanocomposites	**Accepted in Langmuir**	LCPP, Cambridge	3,4
32	M. Mičušík, A. Bonnefond, Y. Reyes, A. Bogner, L. Chazeau, C.J.G. Plummer, M. Paulis, J.R. Leiza	Morphology of Polymer/clay Latex Particles Synthesized by Miniemulsion Polymerization: Modeling and Experimental Results.	**Accepted in Macromolecular Reaction Engineering**	UPV	3,5

Oral presentations and posters in scientific congresses					
N	*Authors*	*Title*	*Contribution*	*Partners involved*	WP
1	J. Faucheu, C. Gauthier, L. Chazeau, V. Mellon, E. Bourgeat-Lami, J.-Y. Cavaillé	Mechanical properties of P(MMA-co-BA)/Laponite films elaborated from nanostructured latexes	Abstract NPPN 2007	LCPP, INSA	3, 4
2	J. Faucheu, C. Gauthier, L. Chazeau, J.-Y. Cavaillé, V. Mellon, E. Bourgeat-Lami	Acrylic/Laponite nanocomposite films: Morphology and mechanical behavior	Abstract Eurofiller 2007	LCPP, INSA	3, 4
3	R. Ruggerone, C. J. G. Plummer, E. Bourgeat-Lami, N. L. Negrete Herrera, T. F. L. McKenna, J.-A. E. Manson	Structure-property relationships in polymer nanocomposite thin films derived from novel nanostructured latexes	Poster (SAMPE Switzerland, november 2006)	EPFL, LCPP	3,4,5
4	R. Ruggerone, C. J. G. Plummer, E. Bourgeat-Lami, N. L. Negrete Herrera, T. F. L. McKenna, J.-A. E. Manson	Structure-property relationships in polymer nanocomposite thin films derived from novel nanostructured latexes	Poster (SAMPE Europe, Paris 2007)	EPFL, LCPP	3,4,5
5	J. L. Keddie, P. Ekanayake, A. M. König, T. Weerakkody, N. Barber, D. Johannsmann, R. P. Sear, P. J. McDonald	Influence of the colloidal stability of latex particles on their distribution in drying films	234^{th} ACS-meeting Boston 2007 (honorary symposium S. Scriven)	Surrey	4
6	Xiao Wu, Bruno Biatry, Colette Cazeneuve, Richard H. Guy	Characterization and evaluation of novel nanoparticle/mesoparticle formulations for application to the skin	Abstract (Skin Forum) (_https://www.apsgb.co.uk/?Redir=/_ mostly UK based researchers working on skin,	Bath, L'Oréal	6

			2007))		
7	Xiao Wu, Bruno Biatry, Colette Cazeneuve, Richard H. Guy	Disposition of a lipophylic chemical in the stratum corneum from nanoparticulate formulations	Abstract (Gordon Research Conference on Barrier Function of Mammalian Skin, USA 2007)	Bath, L'Oréal	6
8	C. M. de las Heras Alarcón, J. L. Keddie	Structure of alkyd/acrylic nanocomposite films	Abstract 2007, poster at "Nanostructured Polymers and Polymer Nanocomposites" meeting in Prague (7 July, 2007)	Surrey	4
9	Diethelm Johansmann	Structure formation during drying of polymer dispersions	ECS in Paris Sept. 12-14, 2007	Clausthal	4
10	C.M. de las Heras Alarcón and J.L. Keddie	Structure of Alkyd/Acrylic Nanocomposite Films	Coatings Science International (COSI) Conference in Noordwijk, The Netherlands form 25-29 June, 2007	Surrey	4
11	Piyasiri Ekanayake, Peter J. McDonald and Joseph L. Keddie	Experimental Tests of Scaling Predictions of the Spatial Distribution of Particles during the Drying of Colloidal Films	Coatings Science International (COSI) Conference in Noordwijk, The Netherlands form 25-29 June, 2007	Surrey	4
12	Tecla G. Weerakkody, Peter J. McDonald, Richard P. Sear and Joseph L. Keddie	Influence of the Colloidal Stability of Latex Particles on their Distribution in Drying Films	Coatings Science International (COSI) Conference in Noordwijk, The Netherlands form 25-29 June, 2007	Surrey	4
13	W. Bücking, B. Du, A. Turshatov, A.M. König, I. Reviakine, B. Bode, D. Johannsmann	A Quartz Crystal Microbalance Based on Torsional Piezoelectric Resonators	Contribution to the European Time and Frequency Control Symposium in Geneva (May 29 - June 1) 2007	Clausthal	4
14	J. L. Keddie, T. G. Weerakkody, A. M. König, D. Johannsmann, R. P. Sear, P. J. McDonald	Influence of colloidal stability on the uniformity of drying in waterborne colloidal coatings (see 5)	European Coatings Symposium 07, 12-14 September in Paris	Surrey	4

15	Venkata Gundabala, Chun-Hong Lei, Joseph L. Keddie, A.F. Routh	Drying of Latex Dispersions	UKPCF 2007 international conference on colloids, Warwick UK.	Surrey, Cambridge	4
16	G. Diaconu, J. M. Asua, M. Paulis, J. R. Leiza	High solids content waterborne polymer-clay nanocomposites	9^th International Workshop on Polymer Reaction Engineering in Hamburg, in October 2007 Macromol. Symp. 259 (2007) 305-317	UPV	2,3
17	G. Diaconu, J. M. Asua, M. Paulis, J. R. Leiza	High solids content waterborne polymer-clay nanocomposites	ILP (Industrial Liaison Programme, between Polymat and 9 international companies: Arkema, BASF, Cray Valley, Cytec, Euroresin, ICI Paints, Nuplex, Rohm & Haas and Wacker) meeting to be held in September in San Sebastian	UPV	2,3
18	V. Mellon, N. Negrette-Herrera, J.-L. Putaux, T. McKenna, E. Bourgeat-Lami	Preparation of waterborne acrylic/Laponite nanocomposite latexes by miniemulsion polymerization	Club Emulsion – 20-21 Septembre 2007 Lyon – France	LCPP	2,3
19	T. G. Weerakkody, P. J. McDonald, R. P. Sear and J. L. Keddie	Influence of the Colloidal Stability of Latex Particles on their Distribution in Drying Films	UK Polymer Colloids Conference at the University of Warwick on 16-18 September 2007.	Surrey	4
20	J. Adams	Coalescence Dynamics of Drying Latex Films	9th Arab International Conf. on Polymer Science & Technology (18-22 Nov 2007).	Surrey	4
21	A.M. König, P. McDonald, J.L.Keddie, D. Johannsmann	Influences of Added Salt on the Drying Behavior of Polymer Dispersions – Simultaneous Use of Magnetic Resonance Profiling and Diffusing-Wave Spectroscopy	Macromolecular Symposium Freiburg February 2008	Clausthal	4

22	E. Degrandi, C. Creton, E. Bourgeat-Lami, R. Udagama, T. McKenna, J. M. Asua, A. Lopez	Mechanical and adhesive properties of nanostructured waterborne polymer films prepared by miniemulsion	Abstract: Euradh 2008 conference on adhesion and adhesive phenomena	ESPCI, LCPP, UPV	3,5
23	E. Degrandi, C. Creton, A. Lopez, J.M. Asua, R. Udagama, E. Bourgeat-Lami, T. McKenna, E. Canetta, J.L. Keddie.	Waterborne polyurethane acrylic hybrid nanoparticles by miniemulsion polymerization: Mechanical properties of nanostructued films	Colloids conference Prague 2008	ESPCI, LCPP, UPV	3,5
24	H. N. Yow, X. Wu , A. F. Routh, and R. H. Guy	Dye diffusion from microcapsules with different shell thickness into mammalian skin	European Journal of Pharmaceutics and Biopharmaceutics 72 (2009) 62–68	Cambridge, Bath	4,6
25	V. Mellon, N. Negrete-Herrera, J-L. Putaux, T. McKenna, E. Bourgeat-Lami	Incorporation of laponite clay platelets into polymer latexes; Evidence of clay localization by Cryo-TEM imaging.	Abstract Particles 2008 conference	LCPP	3
26	L. Sonnenberg, E. Degrandi, R. Udagami, E. Bourgeat-Lami, C. Creton	Waterborne Polyurethane-Acrylic Nanoparticles by Miniemulsion Polymerization: Mechanical Properties of Nanostructured Films	Abstract UK polymer colloid forum (UKPCF 2008)	LCPP, ESPCI	3,5
27	T.G. Weerakkody, C.-H. Lei, A.B. Foster, A. M. König, D. Johannsmann, P.J. McDonald, Peter A.	Influence of pH and Acrylic Acid on the Drying and “Water Whitening” Resistance of Waterborne Adhesive Films Lovell, and Joseph L. Keddie	Abstract UKPCF 2008	Surrey, Clausthal	4
28	E. Canetta, A. Lopez, J. M. Asua, J. L. Keddie	Film formation and structure of waterborne polyurethane-acrylic nanocomposite adhesives	Abstract UKPCF 2008	Surrey, UPV	3, 4
29	C. Arnold, V. Mellon, E. Bourgeat-Lami, G. Klein, P. Marie, Y. Holl	Distribution of SDS in acrylic composite latexes and in waterborne films	Abstract UKPCF 2008	ICS, LCPP	3,4
30	C.M. de las Heras Alarcón, M. Goikoetxea, M.J. Barandiaran, J. M. Asua,	Interdiffusion and phase separation studies of alkyd/acrylic hybrid films	Abstract UKPCF 2008	Surrey, UPV	3,4

	J.L. Keddie				
31	T. Wang, E. Canetta, T. G. Weerakkody, J. L. Keddie	The effects of ionic and hydrogen-bonding interactions on adhesive properties of acrylic latex	Abstract Colloids Prague 2008	Surrey	4
32	M. Goikoetxea, I. Beristain, R. Minari, M. Paulis, M. J. Barandiaran, J. M. Asua	Preparation of waterborne alkyd–acrylic nanoscale hybrid systems	Abstract UKPCF 2008	UPV	3
33	A. Bonnefond, M. Micusik, G. Diaconu, M. Paulis, J. R. Leiza	Waterborne polymer/clay nanocomposites	Industrial Liaison Meeting 2008 (San Sebastián)	UPV	4
34	I. Beristain, M. Goikoetxea, R. Minari, C. de las Heras Alarcón, M. Paulis, M.J. Barandiaran, J.L. Keddie, J. M. Asua	Preparation of waterborne alkyd–acrylic nanoscale hybrid systems	Industrial Liaison Meeting 2008 (San Sebastián)	UPV, Surrey	3,4
35	E. Degrandi, C. Creton, L. Sonnenberg, R. Udagama, E. Bourgeat-Lami, T. McKenna	Mechanical and Adhesive Properties of Waterborne Polyurethane-Acrylic Hybrid Nanostructured Films	Adhesion Society	LCPP, ESPCI	3,5
36	M. Micusik, A. Bonnefond, M. Paulis, J. R. Leiza	Preparation of Waterborne Adhesives Containing Exfoliated Clay Platelets	"Hybrid Materials" Congress, Tours, France, 2009	UPV	3
37	J.R. Leiza (invited speaker)	Synthesis of Hybrid Acrylic/Montmorillonite Adhesives by Miniemulsion Polymerization	Invited Lecture - 2nd International Symposium in Advanced Particles ISAP 2009 Yokohama (Japan)	UPV	3
38	A. López, E. Degrandi, L. Sonnenberg, C. Creton, E. Canetta, J.L. Keddie, J.M. Asua	Waterborne Polyurethane-Acrylic Hybrid Nanoparticles by Miniemulsion Polymerization	IPCG 2009	UPV, ESPCI, Surrey	3,4,5

39	M. Goikoetxea, R. Minari, I. Beristain, M. Paulis, M. J. Barandiaran, J. M. Asua	Preparation of waterborne alkyd–acrylic nanoscale hybrid systems	IPCG Meeting in Polymer Colloids, Lucca, Italy	UPV	3
40	M. Patel, V. Gundabala, A.F. Routh	Film formation from aqueous suspensions of polymer-silica nanocomposites	AIChE National meeting 2009	Cambridge	4
41	J.M. Asua	Waterborne Polymer-Polymer Hybrid Nanoparticles	IPCG 2009 (Lucca)	UPV	3
42	M. Goikoetxea, R.J. Minari, I. Beristain, M. Paulis, M.J. Barandiaran, C. de las Heras Alarcón, J. Faucheu, C. Gauthier, L. Chazeau, J.L. Keddie, J.M. Asua	Alkyd/acrylic Nanocomposite Latexes	French Club Emulsion (Mulhouse, 2009)	UPV, Surrey, INSA	3,4,5
43	H.N. Yow, A.F. Routh	Film Stress Detection via Beam Bending	UK Polymer Colloids Conference (2009)	Cambridge	4
44	R.J. Minari, M. Goikoetxea, I. Beristain, M. Paulis, M.J. Barandiaran, J.M. Asua	Production of Waterborne Alkyd-acrylic Hybrid Latexes with Controlled Polymer Architecture and NANOParticle Morphology	ARCHIPOL Conference (Argentina, Oct 2009)	UPV	3
45	D. Johannsmann	Film Formation from Polymer Dispersions: A Detailed View on Solidification	IPCG Meeting in Polymer Colloids, Lucca, Italy	Clausthal	4
46	M. Goikoetxea, R.J. Minari, I. Beristain, M. Paulis, J.M. Asua, M.J. Barandiaran	Production of High Solids and Low VOC Alkyd/Acrylic Latexes	ARCHIPOL Conference (Argentina, Oct 2009)	UPV	3
47	R. Rodríguez, C. de las Heras Alarcón, P. Ekanayake, P.J. McDonald,	Waterborne Silicone-Acrylic Hybrid Coatings: Correlation of Structure with Hydrophobic and Thermal Properties	European Coatings Conference on Waterborne Clear Coats, Berlin 2009	UPV, Surrey	3,4

	M.J. Barandiaran, J.M. Asua, and J.L. Keddie				
48	M.J. Patel, V.R. Gundabala, A. F. Routh	Session: Colloidal dispersions I Film formation from aqueous suspensions of polymer-silica nanocomposites	AIChE Conference, Tenesse, November 2009	Cambridge	4
49	Y. Reyes-Mercado, M. Goikoetxea, I. Beristain, R.J. Minari, M. Paulis, M.J. Barandiaran, J. M. Asua	From Particle Morphology to Film Morphology	ILP Meeting 2009	UPV	3
50	A. Bonnefond, M. Micusik, M. Paulis, J.R. Leiza	Production of Waterborne Polymer/Clay Nanocomposites	ILP Meeting 2009	UPV	3
51	I. Aranberri, M. Goikoetxea, A. Chemtob, J.M. Asua	Synthesis of Nanostructured Hybrid Particles via Miniemulsion Polymerization Suitable for Drug Delivery	UKPCF 2009	UPV	3
52	I. Nikiforow, A.M. König, A. Turshatov, J.Adams, A. Langhoff, M. Zoromba, J.L. Keddie, T. Weerakkody, D. Johannsmann	Vertical Segregation between Charged and Neutral Particles During Film Formation from Polymer Dispersions	Workshop on Waterborne Coatings, Berlin, Nov 2009	Clausthal, Surrey	4