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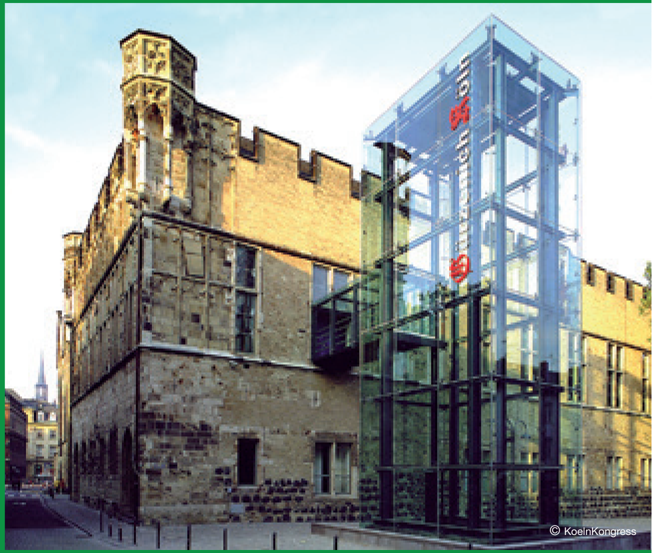
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EUROPEAN TECHNICAL COATINGS CONGRESS 2014 · COLOGNE

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EUROPEAN TECHNICAL COATINGS CONGRESS 2014

New Functions and Sustainability – Drivers for Future Coatings

3 – 5 September 2014

Gürzenich · Cologne · Germany


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BOOK OF ABSTRACTS

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TABLE OF CONTENTS

SCIENTIFIC PROGRAMME 4

- Wednesday, 3 September 2014 4
- Thursday, 4 September 2014 7
- Friday, 5 September 2014 10

POSTER PROGRAMME 13

LECTURE ABSTRACTS 17

- Plenary Lectures 17
- Functional coatings/Nano technology 21
- Corrosion protection 45
- Sustainability in the coatings field/Saving resources/Biobased coatings 57
- Polymers, pigments and other raw materials 69
- Advances in coatings and inks sciences/Crosslinking an hardening 87
- Progress in production, application and processes 113
- Measuring and testing/New optical properties in coatings 121

POSTER ABSTRACTS 137

Editor:
Gesellschaft Deutscher Chemiker e.V.
Postfach 90 04 40
60444 Frankfurt am Main, Germany

E-Mail: tg@gdch.de
Homepage: www.gdch.de

Layout/Typesetting: PM-GrafikDesign, Wächtersbach, Germany
Print: Seltersdruck GmbH, Selters/Ts., Germany

(Date: August 11, 2014)

Großer Saal

09:00	**CONGRESS OPENING**	Großer Saal	Page
09:30	PLENARY LECTURE 1 **Smart and functional materials** J. Baghdachi, Ypsilanti/US, H. Perez, Freiburg/DE	Großer Saal	19
10:10	PLENARY LECTURE 2 **Strategies for a more sustainable coatings industry** K. Watson, Collegeville/US, H. Kheradmand, Valbonne/FR	Großer Saal	20
10:50	COFFEE BREAK		
	FUNCTIONAL COATINGS		
11:20 1.1	**Ordered liquids from molecular mess: Self-assembly of novel bola-amphiphiles** H. Hintze-Bruening, Münster/DE, T. Lohmeier, Münster/DE		23
11:50 1.2	**Ionic Liquids as Conductivity Promoters in Coatings Applications** A. Eichfelder, Ludwigshafen/DE, S. Shah, Charlotte/US, J. Zuurveld, Heerenveen/NL		24
12:20 1.3	**Ionic liquids as innovative materials for the stabilization of multifunctional nanofluids** T. J. S. Schubert, Heilbronn/DE, J. Wimberg, Heilbronn/DE		25
12:50	LUNCH BREAK		
13:50 1.4	**Nanofibrillated cellulose in wood coatings – a feasibility study** T. Künniger, Dübendorf/CH, F. Grüneberger, Dübendorf/CH, T. Zimmermann, Dübendorf/CH, M. Arnold, Dübendorf/CH		26
14:20 1.5	**The use of functionalized nanoparticles for surface properties enhancement of coatings for wind energy and aerospace** G. Durand, Cambridge/GB, A. Taylor, Cambridge/GB, D. De Bono, Middlesbrough/GB		27
14:50	COFFEE BREAK		
15:20 1.6	**Controlled synthesis and application of silver nanoparticles in coatings for inhibition of microbial growth and biofouling formation** T. Szabó, Budapest/HU, J. Telegdi, Budapest/HU, L. Nyikos, Budapest/HU		28
15:50 1.7	**Towards more reliable sol-gel coatings by combined extrinsic and intrinsic healing** M. Abdolah Zadeh, Delft/NL, S. van der Zwaag, Delft/NL, S. J. Garcia, Delft/NL		29
16:20 1.8	**Scratch resistant and outdoor weatherable coatings – applied nanotechnology and functional properties** C. Hilgers, Leverkusen/DE, A. Haeuseler, Leverkusen/DE, R. Hayes, Waterford, NY/US		30
17:00	**General Meeting VILF**	Großer Saal	
18:30	BREAK		
19:30	**GET-TOGETHER** FARBEUNDLACK // PREIS 2014 by Vincentz Network Get-together, sponsored by BASF SE and Bayer MaterialScience	Brauhaus Sion	

Kleiner Saal

			Page
09:00	**CONGRESS OPENING**	Großer Saal	
09:30	PLENARY LECTURE 1 **Smart and functional materials** J. Baghdachi, Ypsilanti/US, H. Perez, Freiburg/DE	Großer Saal	19
10:10	PLENARY LECTURE 2 **Strategies for a more sustainable coatings industry** K. Watson, Collegeville/US, H. Kheradmand, Valbonne/FR	Großer Saal	20
10:50	COFFEE BREAK		
	CORROSION PROTECTION		
11:20 2.1	KEYNOTE LECTURE ***In-situ* analytical and electrochemical evaluation of interfacial bonding and performance of corrosion protective coatings** J. M. C. Mol, Delft/NL		47
11:50 2.2	**New substrates influencing the pretreatment process** P. Kuhm, Düsseldorf/DE, J. Kroemer, Düsseldorf/DE		48
12:20 2.3	**What happens during the swelling of a coating?** M. Dornbusch, Krefeld/DE, C. Deschamps, Krefeld/DE, C. Henzel, Krefeld/DE, S. Overmeyer, Krefeld/DE		49
12:50	LUNCH BREAK		
13:50 2.4	**New aspects in corrosion protection with polymer dispersions** U. Christ, Stuttgart/DE, R. Nothhelfer-Richter, Stuttgart/DE		51
14:20 2.5	**New 2-layer epoxy coating system achieving excellent corrosion protection and UV-stability** M. Gerlitz, Basel/CH, A. Dureault, Basel/CH, A. Napoli, Basel/CH, P. Luethi, Basel/CH		52
14:50	COFFEE BREAK		
15:20 2.6	**Effective sol-gel derived protective coatings to prevent the corrosion of steel in marine environment** S. Pfeifer, Freiberg/DE, E. Kroke, Freiberg/DE		53
15:50 2.7	**A wishing well – DTM coatings with anticorrosive pigments** L. Kirmaier, Langelsheim/DE		54
16:20 2.8	**Electrochemical stability of the metal/paint interface: A combined impedance spectroscopy and scanning Kelvin probe study** P. Keil, Münster/DE		55
17:00	**General Meeting Lackchemie**	Kleiner Saal	
18:30	BREAK		
19:30	**GET-TOGETHER** FARBEUNDLACK // PREIS 2014 by Vincentz Network Get-together, sponsored by BASF SE and Bayer MaterialScience	Brauhaus Sion	

Isabellensaal

09:00	**CONGRESS OPENING**	Großer Saal	Page
09:30	PLENARY LECTURE 1 **Smart and functional materials** J. Baghdachi, Ypsilanti/US, H. Perez, Freiburg/DE	Großer Saal	19
10:10	PLENARY LECTURE 2 **Strategies for a more sustainable coatings industry** K. Watson, Collegeville/US, H. Kheradmand, Valbonne/FR	Großer Saal	20
10:50	COFFEE BREAK		

SUSTAINABILITY IN THE COATINGS FIELD

11:20 3.1	**Feedstock in transition – a manufacturer's perspective on petrochemical trends and the downstream impact to the coatings market** K. Kohlhammer, Burghausen/DE	59
11:50 3.2	**CO_2 based polyols: A new polymer backbone for polyurethane coatings** S. Waddington, Waltham/US, J. Anderson, Waltham/US, W. Willkomm, Erie/US	61
12:20 3.3	**Influence of isosorbide to polyurethane dispersions for wood coatings application** C. Schirp, Braunschweig/DE, S. Eschig, Braunschweig/DE	61
12:50	LUNCH BREAK	
13:50 3.4	**Investigation the cathodic electrodeposition behaviour of chitosan biopolymer in different solid content** S. Heydarian, Tehran/IR, Z. Ranjbar, Tehran/IR, S. Rastegar, Tehran/IR	63
14:20 3.5	**Silicone-hybrid technology for modern and resource efficient high solid coatings** S. Herrwerth, Essen/DE, D. Hinzmann, Essen/DE, M. Siemens, Essen/DE	65
14:50	COFFEE BREAK	
15:20 3.6	**Lactide-modified polyester resin with enhanced resin- and coating performance** B. van Leeuwen, Gorinchem/NL, C. Schaekens, Gorinchem/NL, P. Cordfunke, Gorinchem/NL	66
15:50 3.7	**New generation of cobalt-free alkyd emulsion paints with non-oxidative drying mechanism** A. Romand, Grasse/FR, B. Chorein, Lyon/FR, O. Choulet, Grasse/FR	67
16:20 3.8	**Sustainability – a special challenge for a medium-sized binder manufacturer** T. Adebahr, Hamburg/DE, D. Chmielewski, Hamburg/DE	68
18:30	BREAK	

19:30	**GET-TOGETHER** FARBEUNDLACK // PREIS 2014 by Vincentz Network Get-together, sponsored by BASF SE and Bayer MaterialScience	Brauhaus Sion

THURSDAY, 4 SEPTEMBER 2014

Großer Saal

	FUNCTIONAL COATINGS	Page
08:30 1.9	**Self-replenishing functional coatings: Repairing surfaces** C. Esteves, Eindhoven/NL	31
09:00 1.10	**Functional coatings for improving indoor air quality** P. Doll, Collegeville/US, F. Huby, Collegeville/US, S. Balijepalli, Collegeville/US, A. Maurice, Collegeville/US	33
09:30 1.11	**Anti-freeze coatings – the next generation of anti-ice coatings** P. Uhlmann, Dresden/DE, S. Höhne, R. Winkler, R. Frenzel, Dresden/DE	34
10:00 1.12	**Enzymatically triggered protein coatings** O. I. Strube, Paderborn/DE	35
10:30	COFFEE BREAK	
11:00 1.13	**Novel colour stabilization concepts for decorative surfaces made of dark wood and TMT** J. Prieto, Lünen/DE, M. Beyer, Dresden/DE, L. Passauer, Dresden/DE	36
11:30 1.14	**Degradation of a polyurethane coating in aggressive media** V. Reuscher, Schwieberdingen/DE, R. Bauer, Schwieberdingen/DE, G. Patzelt, Bremen/DE, M. Guyenot, Schwieberdingen/DE, B. Mayer, Bremen/DE	38
12:00 1.15	**Colour retention in architectural paints** N. Tissier, Ludwigshafen/DE, I. Cabrera, Ludwigshafen/DE	40
12:30	LUNCH BREAK **POSTER SESSION** Kleiner Saal, Empore	
14:00 1.16	**Dose-response functions for prediction of easy-to-clean performance of coil-coated materials** T. Prosek, Brest/FR, A. Trabelsi, Paris/FR, D. Thierry, Brest/FR	41
14:30 1.17	**Photochemical attachment of water-absorbing hydrogel coatings to polystyrene to avoid turbidity in cold environments** S. Grube, Winterthur/CH, K. Siegmann, Winterthur/CH, M. Hirayama, Winterthur/CH	42
15:00 1.18	**Development and characterization of functional coatings with dedicated thermo-optical properties for solar energy-related applications** T. Aerts, Limelette/BE, N. Taminiaux, M. Wenkin, C. de Lame, Limelette/BE, K. Fleury-Frenette, T. Thibert, F. Rabecki, Angleur/BE, D. Leboutte, A. Dethier, Seraing/BE	43
15:30	COFFEE BREAK	
	POLYMERS, PIGMENTS AND OTHER RAW MATERIALS	
16:00 1.19	**Sustainable developments in the pigment industry** C. Kujat, Ludwigshafen/DE, E. Korona, Ludwigshafen/DE, G. Döring, Ludwigshafen/DE	71
16:30 1.20	**Impact of new EU-regulation on the usage of biocides** P. Clegg, Manchester/GB, H. Peters, Köln/DE	72
17:00 1.21	**Application of ionic liquids in synthesis of polymeric binders for coatings** V. Strehmel, Krefeld/DE, S. Berdzinski, Krefeld/DE, A. Wenda, Krefeld/DE	73
17:30 1.22	**Benzoate Technology for Coatings Applications** W. D. Arendt, Washington/US, E. L. McBride, Washington/US, M. A. Conner, Geleen/NL	74
18:00	BREAK	
19:00	**SOCIAL EVENING** (River Dream party) Ship River Dream	

Kleiner Saal

CORROSION PROTECTION

		Page
08:30 2.9	**Surface modification of mesoporous silica for improvement of compatibility with anti-corrosion coatings** J. Carneiro, Aveiro/PT, F. Maia, J. Tedim, M. L. Zheludkevich, M. G. S. Ferreira, Aveiro/PT	56

ADVANCES IN COATINGS AND INKS SCIENCES

09:00 2.10	**Carbon fibre reinforced plastics – a challenge for surface treatment and painting** V. Stenzel, Bremen/DE, Y. Wilke, A. Zockoll, K. Brune, G. Patzelt, Bremen/DE	89
09:30 2.11	**Some surface phenomena at formation of coatings** E. Indeikin, Yaroslavl/RU	91
10:00 2.12	**Innovative technologies and techniques for enhancing the application of architectural coatings** T. L. Conley, Collegeville/US, D. M. Fasano, Collegeville/US	92
10:30	COFFEE BREAK	
11:00 2.13	KEYNOTE LECTURE **Silicone ceramizable rubbers: New solution for the emerging coatings** M. Zielecka, Warsaw/PL	93
11:30 2.14	**Sustainable UV-protection of coating layers using nanoscale organic and inorganic components** M. Entenmann, Stuttgart/DE, D. Koch, Stuttgart/DE, H. W. Greisiger, Stuttgart/DE	94
12:00 2.15	**Automotive application processes: A focus on molecular migration** A. Andersen, Münster/DE	95
12:30	LUNCH BREAK **POSTER SESSION** Kleiner Saal, Empore	
14:00 2.16	**Advanced rheology for waterborne paints, the key to good flow and application properties** J. M. Akkerman, Bergen op Zoom/NL, R. Adolphs, R. van Egmond, J. Goossen, Bergen op Zoom/NL, A. Roelofs, Wageningen/NL, R. van der Horst, Wageningen/NL, M. Bosma, Wageningen/NL, D. Mestach, Bergen op Zoom/NL	96
14:30 2.17	**Influence of matting on the properties of powder epoxy-polyester coatings** D. S. Kotova, Yaroslavl/RU, E. A. Indeikin, Yaroslavl/RU	97
15:00 2.18	**Hyper-branched structures for new functional additives** P. Lenz, Wesel/DE	98
15:30	COFFEE BREAK	
16:00 2.19	KEYNOTE LECTURE **Photoinitiated cationic polymerization: Current developments and future prospects for coatings** J. V. Crivello, Troy/US	99
16:30 2.20	**Efficiency of near infrared curable coating systems via radical photopolymerization** C. Schmitz, Krefeld/DE, A. Halbhuber, Krefeld/DE, B. Strehmel, Krefeld/DE	101
17:00 2.21	**Tuning the mechanical performance of polyurethane UV cured coatings: modifying the composition of reactive diluents** I. Zvonkina, Stuttgart/DE, M. Hilt, Stuttgart/DE	103
17:30 2.22	**Improving the efficiency of photocatalysts** H.-C. Krempels, Leverkusen/DE, C. Scheidt, B. Vielhaber-Kirsch, Leverkusen/DE	104
18:00	BREAK	
19:00	**SOCIAL EVENING** (River Dream party) Ship River Dream	

Isabellensaal

	PROGRESS IN PRODUCTION, APPLICATION AND PROCESSES	Page
08:30 3.9	**Extensional rheology as related to paint atomization** M. R. Koerner, Mt.Clemens, MI/US, E. C. Houze, J. R. Moore, Wilmington, DE/US, G. H. McKinley, B. Keshavarz, Cambridge, MA/US	115
09:00 3.10	**Process optimization and simulation in the coatings industry** M. Breucker, Waltrop/DE	116
09:30 3.11	**Selective and overspray free painting technology** O. Tiedje, Stuttgart/DE, W. Niemeier, Stuttgart/DE	117
10:00 3.12	**Air entrapment in droplets impacting the surface** Q. Ye, Stuttgart/DE, O. Tiedje, Stuttgart/DE	118
10:30	COFFEE BREAK	
11:00 3.13	**Improving efficiency and quality by high throughput technologies in development of coatings** T. Brinz, Waiblingen/DE, R. Emmerich, Waiblingen/DE, T. Burk, Waiblingen/DE	120
	MEASURING AND TESTING	
11:30 3.14	**Towards a durable, water-based coating for wood-based composites** C. Bellmann, Dresden/DE, A. Calvimontes, Dresden/DE, A. Caspari, Dresden/DE, C. Schirp, Braunschweig/DE, A. Schirp, Braunschweig/DE	123
12:00 3.15	**Early recognition of weathering defects: Evaluation of two newly elaborated methods for detecting coating degradation** M. Wanner, Stuttgart/DE, U. Christ, Stuttgart/DE	124
12:30	LUNCH BREAK **POSTER SESSION** Kleiner Saal, Empore	
14:00 3.16	KEYNOTE LECTURE **Film formation and subsequent environmental degradation of crosslinking polymers: Exploration using computer simulations** S. Croll, Fargo/US, A. Feickert, Fargo/US, D. Kroll, Fargo/US	125
14:30 3.17	**A multi-method approach for the prediction of weather-related ageing of wood coatings** L. Passauer, Dresden/DE, M. Beyer, Dresden/DE, M. Freese, Tharandt/DE, S. Fischer, Tharandt/DE, J. Peters, Tharandt/DE	126
15:00 3.18	**Measuring and optimizing the efficiency of titanium dioxide in paint** J. Rommens, Mechelen/BE, S. De Backer, Mechelen/BE	128
15:30	COFFEE BREAK	
16:00 3.19	**Simulation of temperatures on surfaces exposed to solar radiation** A. Schönlein, Linsengericht/DE, S. Senff, Linsengericht/DE	129
16:30 3.20	**Water in coatings** S. J. F. Erich, Eindhoven/NL, H. P. Huinink, Eindhoven/NL, V. Baukh, Eindhoven/NL, L. van der Ven, Sassenheim/NL, O. C. G. Adan, Eindhoven/NL	131
17:00 3.21	**Seeing clearly through the mist** B. Neumann, Magdeburg/DE	133
17:30	**Farbe und Lack Preisverleihung**	
18:00	BREAK	
19:00	**SOCIAL EVENING** (River Dream party) Ship River Dream	

Großer Saal

	POLYMERS, PIGMENTS AND OTHER RAW MATERIALS	Page
08:30 1.23	**Hyperbranched polyesterols in coating applications** H. Schäfer, Ludwigshafen/DE, D. Türp, Ludwigshafen/DE, R. Erhardt, Ludwigshafen/DE	75
09:00 1.24	**Rational design of new pigment dispersants by understanding polymer-pigment interactions** M. Maier, Ludwigshafen/DE, S. Onclin, Ludwigshafen/DE, J. Mikhael, Ludwigshafen/DE, C. Auschra, Ludwigshafen/DE	76
09:30 1.25	**Outstanding advantages of ultra-low viscosity hydrophobic poly-isocyanate: Duranate™ TUL-100** M. Yamauchi, Kawasaki/JP, M. Meiss, Brussels/BE, K. Takeno, Kawasaki/JP	77
10:00	COFFEE BREAK	
10:30 1.26	**UV-crosslinkable polymer coatings** Z. Czech, Szczecin/PL, P. Raganska, Szczecin/PL, A. Kowalczyk, Szczecin/PL	78
11:00 1.27	**Chrome-like appearance and optical properties of polymer layers including vacuum metallized pigments, VMPs** F. J. Maile, Roth/DE, M. R. F. Kuntz, Roth/DE	79
11:30 1.28	**Thermal resistance of silicone-based coating systems** D. Pierre, Seneffe/BE, P. Léger, Seneffe/BE	80
12:00	BREAK	
12:15	**AWARDS AND CLOSING CEREMONY** Großer Saal	

Kleiner Saal

	ADVANCES IN COATINGS AND INKS SCIENCES	Page
08:30 2.23	**Iodonium salts comprising different cations and anions: Effect of solubility in coatings, reactivity in NIR-photopolymers and toxicological aspects** T. Brömme, Krefeld/DE, A. Halbhuber, Krefeld/DE, E. Dopp, Mülheim/DE, B. Strehmel, Krefeld/DE	106
09:00 2.24	**New catalyst developments and their significance for polyurethane coatings** M. Grahl, Leverkusen/DE, F. U. Richter, Leverkusen/DE, J. Weikard, Leverkusen/DE, V. Abejavarathan, Dortmund/DE, L. Iovkova-Berends, Dortmund/DE, G. Bradtmöller, Dortmund/DE, T. Zöller, Dortmund/DE, K. Jurkschat, Dortmund/DE	108
09:30 2.25	**Cross-linking systems using cyclic-carbonate for coatings applications** F. Camara, Montpellier/FR, B. Boutevin, Montpellier/FR, S. Caillol, Montpellier/FR, R. Auvergne, Montpellier/FR	109
10:00	COFFEE BREAK	
10:30 2.26	**Antistatic coatings for wood-floorings by imidazolium salt-based ionic liquids** A. Rössler, Schwaz/AT, H. Schottenberger, Innsbruck/AT	110
11:00 2.27	**Bringing polyaspartic technology to the next level: Low viscous solvent-free floor coatings** M. Wintermantel, Leverkusen/DE, T. Schüttler, Leverkusen/DE, K.-H. Wührer, Leverkusen/DE	111
11:30 2.28	**Sustainable solutions for coatings and the role of renewable raw materials** G. Behnken, Leverkusen/DE, C. Eggert, Leverkusen/DE, H.-G. Grablowitz, Leverkusen/DE, R. Halpaap, Leverkusen/DE, H.-W. Lucas, Leverkusen/DE, P. Nazaran, Leverkusen/DE	112
12:00	BREAK	
12:15	**AWARDS AND CLOSING CEREMONY** Großer Saal	

Isabellensaal

	MEASURING AND TESTING	Page
08:30 3.22	**The effect of coating thickness on pendulum hardness** M. Bosma, Wageningen/NL, E. R. Rensen, Wageningen/NL	135
09:00 3.23	**Limit values for VOC emissions from decorative products around the globe** M. Augustin, Galten/DK, R. C. Oppl, Galten/DK, S. I. Manson, Folsom/US, C. Laffargue, Galten/DK	136
	POLYMERS, PIGMENTS AND OTHER RAW MATERIALS	
09:30 3.24	**Novel high efficient NISAT thickeners** C. Feito Fraile, Cologne/DE	81
10:00	COFFEE BREAK	
10:30 3.25	**Socal® UP: An innovative high performance precipitated calcium carbonate to reduce TiO_2 content in emulsion paints** P. Fritzen, Rheinberg/DE, O. Persyn, Salin de Giraud/FR	82
11:00 3.26	**Next generation silicone antifoams: Structure property relationships in low VOC binder systems** J. C. Corcuera, Seneffe/BE, B. Lenoble, Seneffe/BE, G. Witucki, Midland/US	84
11:30 3.27	**Life after pyrrolidones – achieving hard coatings without increasing VOCs** C. Evans, Preston/GB, I. Martin, Preston/GB, C. Smart, Preston/GB	85
12:00	BREAK	
12:15	**AWARDS AND CLOSING CEREMONY** Großer Saal	

Page

P01 **Selectively functionalized mesoporous silica for pH-controlled delivery of aromatic amino acids** 139
N. V. Roik, Kiev/UA, L. A. Belyakova, Kiev/UA, M. O. Dziazko, Kiev/UA

P02 **TEXSHIELD – Environmental friendly and Durable Oil and Water Repellence Finish on Technical Textiles** 140
I. Garez, Gent/BE

P03 **New generation of synthesis nanocrystalline biomaterials for coating on Ti-6Al-4V Implant with EPD technique** 141
A. Khandan, Isfahan/IR, E. Karamian, Isfahan/IR, H. Mirmohammadi, Isfahan/IR, M. Bonakdarchian, Isfahan/IR, M. Kalantar Motamedi, Isfahan/IR, P. Soltani, Isfahan/IR

cancelled

P04 **Reduced fluorine content oil and water repellent treatments for technical textiles** 142
S. Sundaram, Cambridge/GB, A. Taylor, Cambridge/GB

P05 **Practical application of easy-to-clean coatings** 143
H. Van den Rul, Diepenbeek/BE, D. Dewulf, Diepenbeek/BE, J. Bosmans, Diepenbeek/BE

P06 **How key variables affect hot tack of emulsion polymers** 144
G. Metselaar, Heerenveen/NL, J. Renema, Heerenveen/NL, C. van Sluijs, Heerenveen/NL, A. van Meer, Heerenveen/NL

P07 **Patterned Hydrophilic/Hydrophobic Recycled Paper Modified by Tuned Graphene Oxide Reduction** 145
S. Sabury, Tehran/IR, H. Mianehrow, Tehran/IR, S. M. Kassiriha, Tehran/IR, F. Sharif, Tehran/IR

P08 **Alternative Strategies for Permanent Easy-to-clean Effects in Exterior Coatings** 147
C. Deschamps, Langenfeld/DE, N. Simpson, Langenfeld/DE, H. Gibbs, Langenfeld/DE

P09 **Producing a piano-black design with plastics –Comparison of coating and alternative technologies** 148
J. Guenther, Lüdenscheid/DE, R. Zahradnik, Lüdenscheid/DE

P10 **Novel Non-Tin Catalysts for Polyurethane and Organosilane Applications** 150
M. Groenewoud, Waddinxveen/NL, J. Florio, Norwalk/US, E. Beketow, Düsseldorf/DE

P11 **Body and Gloss - Precipitated Calcium Carbonate supports sustainable coating performance** 151
H. N. Emmerich, Köln/DE, B. Schmid, Oftringen/CH, G. Bender, Köln/DE

P12 **New driers for high solids alkyds paint** 152
J. Nasadova, Pardubice/CZ

P14 **Develop your “Green” Waterbased DTM Coatings with Nubirox 300** 153
F. Requeijo, Barcelona/ES, P. Pérez, Barcelona/ES

P15 **Effect of conductive polymers and amorphous chalcogenides on mechanical and corrosion properties of organic coatings with high metallic zinc particle contents** 155
M. Hejdová, Pardubice/CZ, A. Kalendová, Pardubice/CZ, P. Nemec, Pardubice/CZ, M. Kohl, Pardubice/CZ

Page

P16 **Synthesis and examination of properties of tungstate and molybdate based anticorrosion pigments in paints** 156
T. Hájková, Pardubice/CZ, A. Kalendová, Pardubice/CZ

P17 **High-Temperature Corrosion of Aluminized and Chromized Fe-25.8%Cr-19.5%Ni Alloys in $N_2/H_2S/H_2O$-mixed Gases** 157
M. J. Kim, Suwon/KR, D. B. Lee, Suwon/KR

P18 **Inhibispheres™ as Alternative to Chromates for Corrosion Protective Coatings in Aerospace** 158
E. Campazzi, Suresnes/FR, C. Barbe, Gladesville/AU, M. Villatte, Suresnes/FR, P. Lathiere, Pamiers/FR, P. Cote, Pamiers/FR, N. Pebere, Toulouse/FR, C. Da Silva, Toulouse/FR

P19 **Characterization of the fatigue behavior of reactive resin-bound concrete protection systems under load** 159
D. Mikautsch, Aurich/DE, M. Sohn, Emden/DE, E. Kunst, Aurich/DE

P20 **Measurement of Sparkle & Graininess** 160
H. Folkerts, Geretsried/DE

P21 **Rotational and oscillatory methods for determining the rheological behaviour of coatings, paints and inks** 162
O. Arnolds, Ostfildern/DE, O. Sack, Ostfildern/DE

P22 **New measurement systems to drive process innovation** 163
H. Hustert, Dortmund/DE, R. Wörheide, Wuppertal/DE

P23 **Improving the properties of biobased PLA matrices by addition of surface treated nano- and microscale particles** 164
M. Wanner, Stuttgart/DE, M. Entenmann, Stuttgart/DE, K. Krawczyk, Stuttgart/DE, P. Keller, Stuttgart/DE, H. Greisiger, Stuttgart/DE, K. Er, Stuttgart/DE, T. Schauer, Stuttgart/DE

P24 **Evaluation of bio-based additives in architectural paints** 165
M. Wenkin, Limelette/BE, M. H. Delvaux, Limelette/BE, A. Lourtie, Limelette/BE, A. Pirmez, Limelette/BE, A. Richel, Gembloux/BE, G. Olive, Gembloux/BE

P25 **Electrodeposition of nano-aluminium coatings from aromatic cation based ionic liquids** 166
A. S. Ismail, Salmabad/BH

P26 **Nano modified coatings with high durability of various supports from the outside environments** 167
A. Pica, Bucharest/RO, C. Guran, Bucharest/RO, D. Ficai, Bucharest/RO, A. Ficai, Bucharest/RO, O. Oprea, Bucharest/RO, F. Serban, Bucharest/RO

P27 **NIR-Reflective Pigment Formulations** 169
B. Neumann, Magdeburg/DE, M. Piorkowska, Magdeburg/DE, C. Dreyer, Magdeburg/DE

P28 **New catalysts for ROP of ε-caprolactone** 171
P. Vlasak, Pardubice/CZ, A. Ruzicka, Pardubice/CZ, T. Chlupaty, Pardubice/CZ

Page

P29 **Investigation of influence of atomizing assisting gases on the coating process** 172
B. Shen, Stuttgart/DE, Q. Ye, Stuttgart/DE, O. Tiedje, Stuttgart/DE

P31 **Synchronization of a DSC with NIR-LEDs: a Simple Way to Photo-DSC** 174
T. Brömme, Krefeld/DE, D. Matthesius, Berlin/DE, B. Strehmel, Krefeld/DE

P32 **New methods of specimen preparation of pigment particles for investigations in transmission electron microscopy** 176
L. Berthold, Halle/DE, M. Krause, Halle/DE, M. Ebert, Halle/DE, T. Hoeche, Halle/DE

P33 **COLOUR BLACK FW 255 – a high jet Carbon Black Pigment for solvent-, water-borne and high solid coating systems** 178
K. Krauß, Frankfurt/DE, A. Hermes, Frankfurt/DE, A. Vulcano, Frankfurt/DE, Y. Wolf, Frankfurt/DE

P34 **The alcaline depolimerization as a recovery source of poly (ethylene terephtalate)** 179
M. Pysz, Gliwice/PL, M. Bodzek-Kochel, Gliwice/PL, B. Soltysik, Gliwice/PL

P35 **Strategies for Chemical Curing of Coatings by the Use of Sunlight** 180
A. Halbhuber, Krefeld/DE, K. Möller, Krefeld/DE, S. Overmeyer, Krefeld/DE, M. Oelgemöller, Townsville/AU, B. Strehmel, Krefeld/DE

P36 **Impact of IR-irradiation as powerful curing method to obtain crack free coating for sol-gel derived coating materials** 181
S. Pfeifer, Freiberg/DE, E. Kroke, Freiberg/DE

P37 **Functionalization of Textile Substrates by NIR Initiated Photopolymerization of Multi-Functional Acrylic Esters** 182
F. Terzioglu, Mönchengladbach/DE, E. Rohleder, Mönchengladbach/DE, M. Rabe, Mönchengladbach/DE, T. Brömme, Krefeld/DE, C. Schmitz, Krefeld/DE, B. Strehmel, Krefeld/DE

P38 **Design-Strategies for highly-sensitive photopolymers** 184
M. Schläpfer, Krefeld/DE, B. Strehmel, Krefeld/DE

P39 **Effects of different nano-sized TiO_2 additives on their UV protective performance in transparent polymer coatings** 186
E. Drotar, Budapest/HU, G. Tolnai, Budapest/HU, L. Molnar-Nagy, Budapest/HU, J. Bognar, Budapest/HU

Plenary Lectures

Smart and Functional Materials

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Abstract

Smart coatings are no longer farfetched ideas! The products are being used in modern societies globally, although an average user would not term them as “smart materials or smart coatings.” Typical polymers, pigments and additives used in coatings are normally un-responsive to external stimuli and with defined structures and properties behave statically. Some multi-functional materials on the other hand respond to external stimulus and render novel functions in addition to traditional properties. Types of materials that sense inflammation in human body and dispense appropriate dose of a drug precisely where is needed, and those that change color as a function of environmental condition, molecular mechanics, and certain military coatings as well as those that enable touch screen performance are among such products. With increased demands for coatings that can sense their environment, perform multifunctional tasks and at the same time be produced economically and safely has emerged a new class of materials that are key components of novel materials. In this presentation we will discuss the science and technology of smart and multifunctional materials, present pathways and examples of such products and highlight current global research and development trends.

Strategies for a More Sustainable Coatings Industry

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Dow Chemical Company, Collegeville PA, USA and Valbonne FR.

The key business drivers of any successful company need to encompass sustainable development criteria during technology and product design. Such criteria put a focus on sustainable competitive advantage leading to sustainable earnings power. Sustainability as a concept becomes a founding principle for continuous improvement, potentially leading to both evolutionary and revolutionary innovations.

Adopting a sustainability strategy can be more than just an answer to questions on how to manage environmental or resource availability issues. Such a strategy can be an excellent way to guide a business in a challenging economic environment and can help to identify the right trends and find the right practical solutions to satisfy the long-term market needs.

A part of this presentation will focus on the mega-trends of Health & Nutrition, Energy, Transportation & Infrastructure and Consumerism as the key drivers for designing a sustainable coatings industry.

In the other part the Sustainability progress in the coatings industry through product design (RP3: Right Planning, Right Process and Right Product) will be presented including:

- Smart solutions for today “Technologies which enable our customers to develop more sustainable products”
- Innovations for Tomorrow “Contributing to the sustainability of our society and our planet”
- Partner for Change “Collaborating with customers, suppliers, communities, civil society and governments on all aspects of sustainability”
- Responsible Operations “Best infrastructure and operation model wherever we operate”
- Awareness and Innovation should help the Right Planning, Right Process and Right Product design to satisfy today and tomorrow growth.

Key words:
Sustainability, Mega trends, Growth, Shortages, R&D, Coatings, Consumers, Energy, Innovation, Partner, Operations, Life Cycle, Market, Planning, Process, Product.

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Lectures

Functional coatings/Nano technology

Ordered Liquids from Molecular Mess: Self-Assembly of Novel Bola-Amphiphiles

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Organic coatings for large scale industrial applications like coil or automotive coatings usually are formulated on the basis of ill-defined technical grade polymers and yield isotropic film morphologies unless tedious application methods (e.g. LbL) or external directional forces are applied and / or large anisotropic particles like aluminium flakes are involved. However attractive property profiles with regard to energy dissipation, diffusion barrier and pigment orientation can be anticipated from ordered structures like lamellar assemblies or nano composites, as we have recently reported for layered double hydroxide (LDH) based stone chip resistant coatings obtained via an aqueous lyotropic mesophase of polymer stabilized LDH platelets [1].

Besides entropy driven ordering of extended 1D or 2D particles amphiphiles are well known to form lyotropic aqueous mesophases. Their structural features vary with the volume fraction and the molecular properties of the amphiphile, e.g. HLB value and shape. With regard to the ordering in coating layers we describe an approach to obtain extended layered assemblies, mimicking robust lipid membranes of archaea which are based on bola-amphiphiles [2]. These consist of hydrophilic head groups attached to a hydrophobic spacer.

Contrary to most of the reported synthetic bola-amphiphilic systems [3] we were aiming at polymeric mesogenes that are based on established raw materials and large scale synthesis processes in order to keep the hydrophilic portion and the manufacturing costs as low as possible. Thus dimer fatty acid based polycondensation products have been found to assemble into ordered aqueous dispersions despite their structural diversity of different building blocks with regard to the ill-defined diacid as well as the high polymer dispersive index. Additionally novel bola-amphiphilic structures have been realized by the addition of alkenyl succinic end groups. The role of such terminal hydrophobic side groups in the self-assembly as well as their impact on the resulting mesophase have been studied and simulated in detail using monomeric model systems going from bola-amphiphiles over bola-electrolytes or gemini surfactants to the ordinary surfactant species, i.e. the alkenyl succinic acid.

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Ionic Liquids as Conductivity Promoters in Coatings Applications

A. Eichfelder BASF SE, S. Shah BASF Corporation,
J. Zuurveld BASF Nederland BV

Zero accident mind-set requires us to think about how we can develop coatings systems that can safely discharge static build-up. More plastic and polymer materials are used for light weight constructions, flexible floorings and membranes, surface finishes, adhesives etc. where static build-up can be expected due to friction between different materials which can result in an uncontrolled discharge. Such events can also damage or cause malfunction in microelectronic appliances. Quaternary salts, humectants, carbon fibers and doped metal oxides are all employed to address these problems.

This paper will give an overview of electricity flow mechanisms in polymers. It also covers efficient ways to prevent charge build-up or to realize electrostatic decay by employing a new class of conductivity aids that are organic ionic liquids. A selection of applications of these novel compounds will be discussed.

Ionic Liquids as Innovative Materials for the Stabilization of Multifunctional Nanofluids

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Ionic liquids (ILs) are pure molten salts that are liquid at temperatures below 100°C and provide a set of unique physical and chemical properties.[1] Their low vapor pressure and non-flammability, large (electro-)chemical and thermal stability as well as excellent electrical and thermal conductivity makes them promising candidates for numerous industrial applications. A few examples are utilizations as electrolytes, lubricants or media for harsh operation conditions. Furthermore, an estimated number of 10^9 to 10^{18} possible combinations of selectively producible ions enable the preparation of customized materials as additives for different functional finishes.[2]

Many beneficial properties like e.g. an improved scratch resistance, an incorporated conductivity or easy-to-clean respective self-cleaning characteristics can be gained through the application of nanomaterials in coatings. The use of ILs, providing tunable qualities and a surface active character for the stabilization of well dispersed nanoparticles, is subject of detailed evaluations and has lead to an increased demand for this kind of material.[3] The preparation of stable nanofluids is becoming more and more important in terms of an easy processability and a safe handling of these materials. This is particularly true, since uncertainties concerning the specific toxicity of certain nanoparticles are intensively discussed at the moment.[4]

We will give an introduction into the field of ILs and an overview of the application of ionic liquids in the area of coating technologies. Furthermore, the preparation and stability analysis of dispersions containing nanomaterials, such as CNTs, graphene, silicon oxide, titanium oxide and so on, using ILs as stabilizing agents will be presented. We will report on first applications, like ink-jet printing of conductive dispersions to enable surface conductivity of paper sheets or the incorporation of nanoparticles for thermally and electrically conductive pastes. Finally, results of performed stability test via PCCS (Nanophox®) will be presented.

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Nanofibrillated Cellulose in Wood Coatings – A Feasibility Study

***Tina Künniger*, Franziska Grüneberger, Tanja Zimmermann, Martin Arnold**

Empa, Swiss Federal Laboratories for Materials Science and Technology,
Applied Wood Materials, Dübendorf, Switzerland

The biomaterial wood is a popular construction material for outdoor application. To protect the wood surface against weathering effects and microorganisms and avoid related degradation processes, protective coatings are necessary.

Various organic and inorganic additives are introduced to such coating systems, tailored to give special functionalities, to achieve a better performance and obtain a longer durability.

Nanofibrillated cellulose (NFC) is considered as a new multifunctional organic component to enhance coating performance and durability. NFC, isolated from the wood cell wall, consists of a network of interconnected cellulose microfibril aggregates, with high specific strength and modulus. It can possibly act as rheology modifier, mechanically reinforcing component and as carrier substance for functional agents such as UV absorbers or biocides.

A feasibility study was conducted to investigate the suitability of NFC as component in exterior wood coatings. Waterborne acrylic polymer emulsions were selected as typical wood coating binders and processed with NFC.

The NFC was produced at laboratory scale from wood pulp, through a two-step mechanical disintegration process [1], [2].

The viscosity of the polymer-NFC suspensions was measured depending on NFC-concentration and could be fine-tuned by NFC addition. Accelerated storage experiments at elevated temperatures were done to estimate long time storage of such suspensions by monitored changes in viscosity.

Free nanocomposite films were prepared from polymer-NFC suspensions via bar coating. Mechanical properties of free films were determined by tensile tests and visco-elastic properties were investigated by Dynamic Mechanical Analysis (DMA). Weathering tests on coated wooden specimens are under progress.

First results about properties and possible improvements will be presented.

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1.5

The use of functionalized nanoparticles for surface properties enhancement of coatings for wind energy and aerospace.

Géraldine G. Durand, Alan Taylor, Damaso D. Bono

TWI Ltd, Speciality materials and joining (United Kingdom)

New coatings and surface treatments with nano-structured materials are generally believed to offer the potential to reduce erosion rates, fouling and icing [1].. Therefore they are expected to have significant beneficial impacts on performance and efficiency in sectors such as aerospace and wind energy leading to reduced carbon emissions.

Such advantages of nano-coatings come from both their ability to tailor roughness levels, enhance mechanical and chemical durability, and more importantly to tailor the surface energy [2].

TWI has been investigating sol-gel chemistry as a route to developing new materials and their incorporation into acrylate, epoxy and polyurethane based resin for various applications in order to enhance the retention of the surface properties with time and abrasion [3]. The key innovative aspects of the approach are the fabrication of the silica additives and the routes to achieve their specific and tailorable functionalization that allow high silica nanoparticles loading (above 50%) into resins.

This paper will illustrate the work that is being carried out by TWI in order to create hybrid coatings that exhibit low energy surface and durability. The TWI approach pulls together a number of diverse fields to create a new platform technology. The lack of durable highly repellent coatings industrially or at the research level, figure 1, illustrates the need for a new approach. The retention of contact angle after abrasion cycle of class leading hydrophobic coatings and the novel additive coatings were compared to highlight the performance of the novels additives.

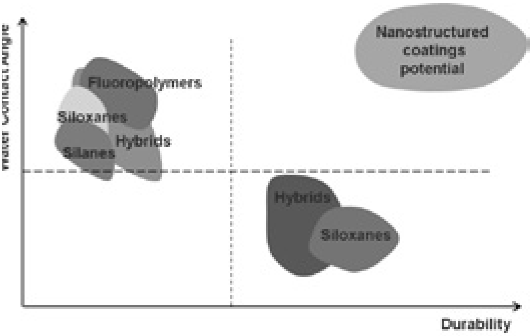

Figure 1. Illustration of the need for nanostructured coating with a high water contact angle and durability.

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1.6

Controlled synthesis and application of silver nanoparticles in coatings for inhibition of microbial growth and biofouling formation

T. Szabó [a], *J. Telegdi* [a,b], *L. Nyikos* [a]

[a]: *Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences 1117 Budapest, Magyar tudósok körútja 2. (Hungary),* [b]: *Óbuda University, Institute of Media technology and Light Industry, 1034 Budapest, Doberdó u. 6. (Hungary)*

The silver nanoparticles (AgNPs) have already been used in plenty of products such as in food industry, as laundry additives, on textiles as well as in different membranes and in the daily life due to their effective antimicrobial activity. The antimicrobial mechanism of the silver ion can be attributed to its interaction with the respiratory electron transport, with the outer membrane (change in the permeability) and with the membrane-bound enzymes.

Our research was focused on the synthesis, on the characterization and application of AgNPs deposited onto SiO_2 microspheres (Figure 1.) as well as embedded in inorganic or organic (Figure 2.) microsphere. In the syntheses different precursors, reductive materials and protective agents were used. The algae-growth-inhibitive activity as well as the antifouling effect of these microspheres, either alone or dispersed in coatings were tested in natural river and lake waters. The AgNPs-containing microspheres were visualized by scanning (SEM) and transmission (TEM) electronmicroscopy. The dissolution of the silver from the nanoparticles and form the coatings was followed by inductively coupled plasma optical emission spectrometry. The proliferation of algae was visually evaluated; the bio-deposition was followed by fluorescent microscope.

The AgNPs combined with silica spheres controlled the growth of algae for months. Their activity depended on the preparation technique. The organic matrix with AgNPs effectively hindered the formation of biofilm and the evolution of biofouling. Our experiments proved that the inorganic nanospheres with AgNPs are able to control the microbial growth in aqueous environment. The microbial adhesion was prevented at very low silver load in the coating; the inhibition of growth was reached at higher silver content. These properties give reason for their application in paints used on bodies submerged in natural waters.

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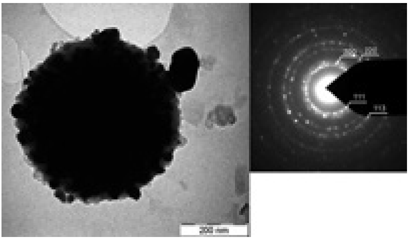

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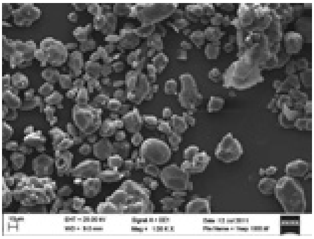

Figure 1. TEM image and electron diffraction pattern of silica particle with AgNPs.
Figure 2. SEM image of organic microcapsules containing AgNPs.

Towards More Reliable Sol-Gel Coatings by Combined Extrinsic and Intrinsic Healing

M. Abdolah Zadeh, S. van der Zwaag and S.J Garcia

Novel Aerospace Materials Group, Aerospace Engineering Faculty, Delft University of Technology, Delft, The Netherlands

Sol-gel coatings are commonly used as surface pre-treatments or thin coatings to improve the adhesion and barrier protection offered by the coating system [1]. The reliability of such coatings can be further increased by implementing self-healing concepts ensuring a longer protection of the underlying substrate. Extrinsic self-healing sol-gel coatings, i.e. coatings in which the self-healing capability is achieved by inclusion of nano- and micro-sized particles containing corrosion inhibitors [2] can provide local corrosion protection. Yet cracks in extrinsic self-healing sol-gel coating will not disappear as the matrix is permanently cross-linked and hence immobile.

In this work we present a double-layer sol-gel coating capable of mending corrosion protection as well as superficial and interfacial damage by combination of extrinsic and intrinsic healing approaches. In the developed systems, inner layer is a conventional silica-zirconia thin film loaded with both cation- and anion-exchange inhibitors for active corrosion inhibition of the metallic surface. The outer layer is a new family of intrinsic sol-gels coatings based on hybrid epoxy-alkoxysilanes containing dynamic di-sulfide bonds for healing promotion. Upon application of moderate pressures and temperatures, the new systems flow and repair (i.e. close and seal) macroscopic scratches up to an approximate width of 500 µm and restore the barrier properties [3,4].

Active corrosion protection provided by the extrinsic healing inner layer was evaluated by bulk and local electrochemical characterization techniques i.e. electrochemical impedance spectroscopy (EIS), scanning vibrating electrode technique (SVET) and scanning ion-selective electrode technique (SIET) revealing the synergic effect of cation- and anion- exchange inhibitors employed. Moreover, the new intrinsic healing sol-gel systems are thermally and mechanically characterized and their healing kinetics are evaluated as a function of composition and healing temperature. In order to get a better insight of the healing mechanism, thermo-mechanical tests are complemented by in-situ Raman spectroscopy to follow the status of the di-sulfide dynamic bonds during the healing process. The electrochemical properties of the scratched and healed coatings are determined by EIS to monitor the ability of the coatings to restore their barrier functionality.

The current systems showed promising results and may provide the basis for the first generation of single and multilayer extrinsic-intrinsic healing sol-gel based coatings.

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1.8

Scratch Resistant and Outdoor Weatherable Coatings - Applied Nanotechnology & Functional Properties

Christoph Hilgers, Andreas Haeuseler, Robert Hayes

Momentive Performance Materials GmbH, Leverkusen

The driver for using coated plastic articles like automotive headlamp lenses and body parts as well as sheets and films in different industrial areas has diversified from a focus on productivity and functionality to a focus on benefit delivery, such as scratch resistance and long-term weatherability. Momentive Performance Materials develops thermally and UV-curable coatings. In both systems nanotechnology is realized to generate high abrasion resistance.
Thermally cured, weatherable coatings technology, which is based on the hydrolysis and condensation of alkoxysilanes (fig. 1), is preferably used for automotive body part applications due to its long term outdoor stability.
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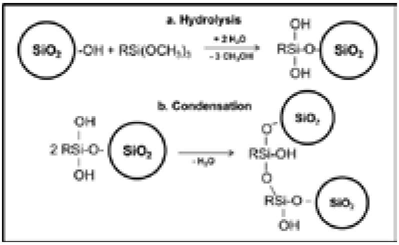

Figure 1: Schematic of siloxane hardcoat chemistry (SiO_2 = silica nanoparticles)[1]

UV-curable coatings are based on polyurethane acrylate chemistry and applied mainly on transparent substrates. The use of tailor-made UV-absorbers results in an outdoor weatherability of 3-5 years in Florida and Arizona (45°, south facing). Functionalized colloidal silica particles (FCS) are imbedded in the polyurethane matrix in order to enhance the general mechanical resistance of the coatings.

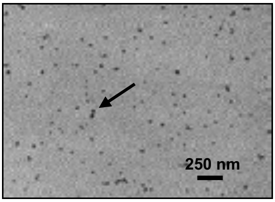

Figure 2: Transmission electron microscopic image of functionalized nanoparticles (FCS) incorporated in a UV-curable coating (arrow)

In this overview the general performance of the two coating technologies with focus on the UV-absorber and nanotechnology is summarized. Optimized UV-absorbers provide an absorbance loss of < 0.1 per 1000 kJ Xenon-lamp irradiation (340 nm).

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1.9

Self-replenishing functional coatings: repairing surfaces

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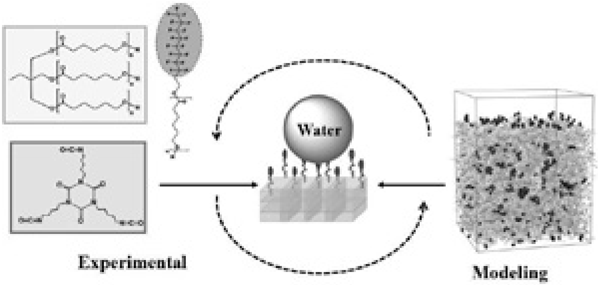
During the last decade, extensive research has been carried out on functional coatings with easy-to-clean/self-cleaning, anti-bacteria or anti-fouling properties, mainly driven by an industrial demand but also an academic interest.

Such properties are strongly related to the coatings surface characteristics. Since coatings damage can never be totally avoided, the introduction of self-repairing mechanisms is one way to repair the surface chemistry and extend their service life-time.[1,2] Moreover, it is now important to move further and make such coatings robust, durable and easy to manufacture and scale-up.

Previously, we reported self-replenishing low-adherence (*hydrophobic*) polymer coatings which “repair” damaged surfaces by replenishing it with new low surface energy groups (*e.g.* fluorinated-dangling ends).[3] Following up, we pursued a dual-approach study (*experimental and simulation*) to understand in-depth the self-healing mechanism involved and to investigate the influence of several experimental parameters (*e.g.* network constituent’s mobility) on the self-replenishing behaviour. [4,5]



Scheme: Dual experimental-simulation approach to investigate model hydrophobic self-replenishing polymer coatings [3].

Further on, we used this model self-replenishing polymer system to obtain robust and easy processing *superhydrophobic* coatings. By incorporating inorganic nanoparticles in the polymer system, we were able to design *surface-structured coatings* which can recover their low surface energy groups, partially responsible for the superhydrophobic behavior, at new structured surfaces created upon the damage. [6]

Our current studies focus on developing *hydrophobic* self-replenishing coatings with improved mechanical properties, i.e. sufficient hardness, durability and solvent resistance, hence, being more suitable for direct industrial applications. Currently, we are also investigating self-replenishing *hydrophilic* coatings targeting new application areas, such as biomedical and marine coatings.

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Functional Coatings for Improving Indoor Air Quality

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Indoor air quality (IAQ) is a topic which is becoming more important and is receiving increased awareness as architects and builders place greater emphasis on the health and wellness of occupants in buildings. In the past, the simplest route to improve IAQ was to increase ventilation in the building. However, with new regulations requiring greater energy conservation in buildings (i.e., less frequent exchange of air inside the building) alternative solutions are now needed. A variety of solutions are currently being used to address complex IAQ issues with an emphasis on low VOC emitting paints, such as the limits set by the French Decree n° 2011-321 and the German AgBB testing and evaluation scheme on emissions from paints. Some ultra low emitting paints can further make a positive contribution towards improving IAQ by adding functionality which enables them to passively abate unwanted contaminants from various sources within a room. Pollutants, their sources, testing methodologies, and reduction of formaldehyde levels by functional coatings in both laboratory and real world environments will be reviewed.

1.11

Anti-freeze coatings - The next generation of anti-ice coatings

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The reduction of ice adhesion and frost formation at surfaces is very desirable in a variety of sectors, as traffic (aircrafts, special purpose vehicles, trains), energy production (electrical and wind power plants), heat exchangers and cooling devices. Because a reduction of ice growths and frost formation can make a considerable contribution to the preservation of resources and reduction of costs, there is a big interest in the improvement of existing approaches to create anti-ice functions.
We have developed novel polymer-based active anti-freeze coatings that combine two principles known from nature: freezing point depression and mimicking of anti-freeze protein structures, which allows to decrease crystal growth, ice adhesion, and frost layer thickness. The general principle is shown in Fig. 1.

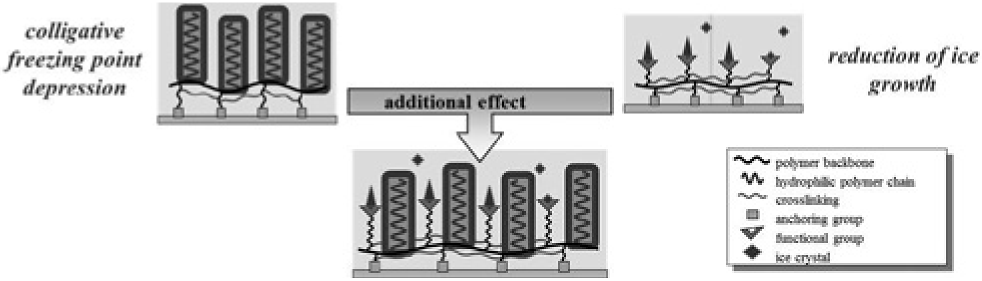

Figure 1: General principle of novel polymer based anti-freeze coatings

Our concept comprises the immobilization of self-organizing water soluble polymers (mimicking the de-icing salt effect) combined with hydrophobic moieties and functions for covalent attachment at the substrate. The aim was to preserve the flexibility of the water soluble parts of the polymers, but nevertheless to obtain a stable coating. Additionally self-assembly of polymers with hydrophilic and hydrophobic units is used to produce nano domains at the surface mimicking anti-freeze protein structures at technical surfaces.
The performance of the developed coatings concerning frost formation, unfreezing and ice adhesion was investigated and quantified. Based on the obtained results several selected coatings where applied to heat exchangers, dehumidifiers or roller blinds and tested. For test conditions relevant for heat exchangers a distinct reduction of frost formation and ice adhesion was found.

Reference:
[1] „Verwendung einer dauerhaften Beschichtung von Metall- oder Glasoberflächen zur Be- und/ oder Verhinderung des Vereisens“ German Patent DE 10 2006 060 340

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Enzymatically triggered protein coatings

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We present a novel approach for the assembly of biological coatings. For the first time, the film formation is induced by an enzymatic process. The system used in this work is the cleavage of casein with the aspartic protease chymosin, which is the same reaction that is present in the milk clotting process.

The principle of this mechanism is shown in **Figure 1**. Chymosin cleaves the hydrophilic arms of the casein micelles, which consequently precipitate, coagulate and form a coating on a given surface.

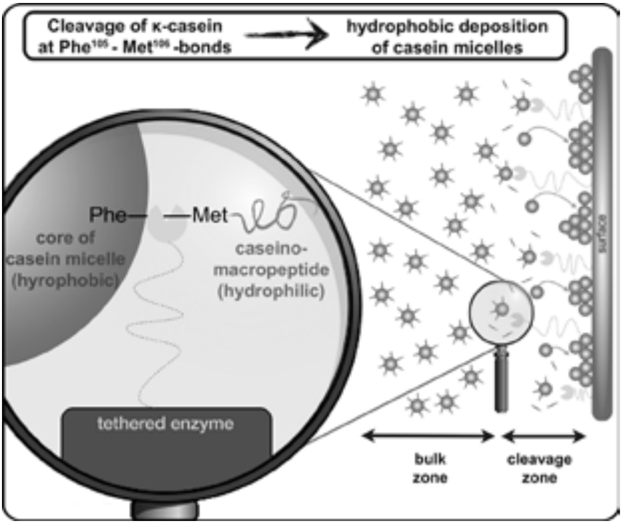

Figure 1: Mechanism of the enzymatically triggered deposition of casein.

An important point of our concept is the tethering of the enzyme onto the support material. Hence, the precipitation of casein only takes place in close proximity to the support surface, an area we call „cleavage zone“. To gain enhanced control over the film formation, different immobilization techniques are used, which leads to variations in the dimension of the cleavage zone.

Our results show that the enzyme-catalyzed deposition of casein coatings can be easily performed with adsorbed chymosin. Continuous casein films result with an enhanced water stability compared to conventionally produced casein films and a certain control over film characteristics. Covalent immobilization of chymosin offers many opportunities for well defined film characteristics, e.g. patterned casein structures, since the deposition takes only place where covalently attached enzyme molecules are present. Our concept could lead to very interesting innovations in the areas of biocompatibility, biodegradability and regenerative resources especially in combination with the coating of complex geometries.

1.13

Novel colour stabilization concepts for decorative surfaces made of dark wood and TMT

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High-value wood surfaces for exclusive furniture and interior outfittings of residences, luxury yachts, aircrafts and railway vehicles are preferentially made of dark-coloured tropical wood species. Decreasing availability, high material costs and environmental issues led to efforts to substitute those wood species by other materials, e.g., Thermally Modified Timber (TMT), possessing comparable surface properties. TMT could be made from actually bright low-grade European wood species due to thermal modification processes where different medium to dark colour tones are generated in a reproducible manner.

However, exposure to daylight often leads to brightening or greying of transparently coated dark wood or TMT surfaces (Fig. 1). The intensive light-induced discolouration of massive dark wood or veneer surfaces cannot be sufficiently stabilized by conventional light protecting systems such as UV-absorbers and radical scavengers (HALS). In some cases (e.g. spruce TMT) their addition was found to reinforce discolouration in comparison to counterparts without any stabilizing agent [1]. Similarly, nanoscaled zinc, titanium, or cerium oxide UV-absorbers which could be successfully applied on softwood and bright hardwood did not succeed for light-stabilization of dark wood surfaces [2]. A certain success was achieved with modified UV-absorbers which cover a part of the visible light spectrum [3]. Furthermore it was found that light-induced discoloration of dark wood species is not only caused by UV-induced bond cleavage of the lignin macromolecule leading to the formation of coloured low-molecular fragments. It is also a result of bleaching reactions of (Scheme 1) chromophores by VIS-light [4].

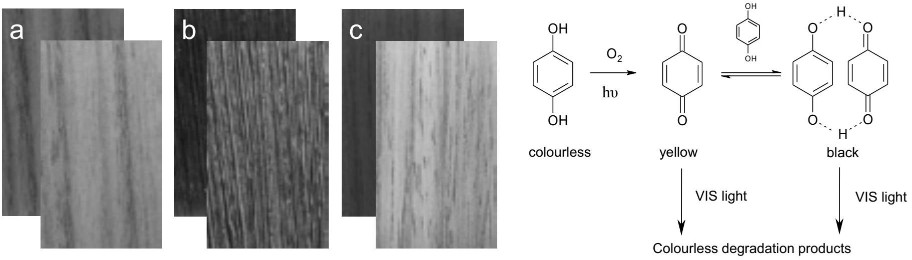

Fig.1: Light-induced discolouration of (a) American walnut (*Juglans nigra*), (b) Wengè (*Millettia laurentii*), and (c) African padouk (*Pterocarpus soyauxii*) clear-coated with 2K-PUR after outdoor-irradiation behind window glass (42 d); samples before (background) and after (front) irradiation; Scheme: UV-induced formation of coloured quinoid structures and subsequent VIS-light induced formation of colourless degradation products [4, 5]

In the current work alternative colour-stabilization concepts are presented which consider the particular discolouration behavior of dark-coloured tropical wood and TMT. Generally, these wood species contain relatively high concentrations of chromophores such as quinones and phenolic or furfuryl derivatives. Particularly quinones form dark-coloured charge-transfer complexes with hydroquinones and related compounds which may contribute to the colour of the respective wood species and which are prone to decolouration or bleaching, respectively (Reaction scheme Fig. 1).

To stabilize these highly photosensitive species, specific additives were applied in aqueous impregnation basecoats. The effects of these light-stabilizing impregnations (LSIs) on the light-induced discolouration of 2K-Hydro-PUR coated wood specimens are shown in figure 2.

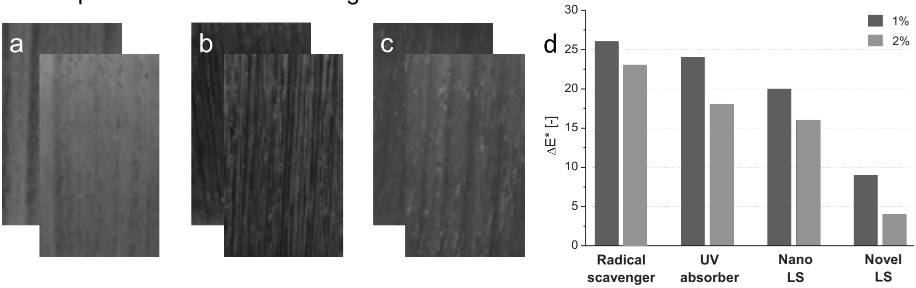

Fig. 2: Light-induced discolouration of stabilized wood species (a) Eastern black walnut (*Juglans nigra*), (b) Wengè (*Millettia laurentii*), and (c) African padouk (*Pterocarpus soyauxii*) clear-coated with 2K-PUR after outdoor irradiation behind window glass (42 d); samples before (background) and after (front) irradiation. d) ΔE values of African padouk treated with different light stabilizers (2K-PUR coating) after UV-irradiation (400 h)

The selective stabilizing effect of novel LSI is obvious for both American walnut and Wengè and also impregnation of African padouk led to good results with only minor brightening effects and low initial discolouration. Similar results were obtained for other tropical wood and TMT species such as East Indian rosewood or African mahogany and were supported by colorimetric measurements revealing colour differences down to $\Delta E^* < 5$ after 400 h Xenotest irradiation (Fig. 2d). Furthermore it was found that the effect of LSI is specific to the respective wood species (wood extractives) and could be selectively adjusted to wood-specific requirements.

Acknowledgement
The current ZIM project KF2178720CK2 is funded via the AiF by the Federal Ministry of Economic Affairs and Energy within the Central Innovation Programme SME, based on a decision of the German Parliament.

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Degradation of a polyurethane coating in aggressive media

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Current printed circuit board (PCB) protection coatings are based on acrylate, silicone, epoxy and polyurethane polymer systems [1, 2]. Due to their good electrical insulation properties, excellent adhesion, high media resistance and versability in e.g. mechanical properties, polyurethanes are common protection materials [3]. A typical ageing mechanism is the chemical degradation of the polymer matrix, with exposure to air predominantly caused by thermal oxidation [4, 5]

During this work, the degradation behavior of a polyurethane-based casting resin for electronic applications was examined in aggressive media. The polyurethane was an aluminum hydroxide filled, flexible material with low T_g. The sample preparation was carried out by coating plain, solder resist coated PCB sheets with a custom-made application mask. The material was cured for four hours in a convection oven at 60 °C and post-cured for two hours at 120 °C. The ageing was performed at 120 °C and 150 °C with exposure to air and oil up to 1000 h, respectively. Structural evolution during the course of ageing was quantified by FTIR investigations and gravimetric analysis.

The first observation after ageing was the massive chalking of the coating at 150 °C in oil, already after 250 h. This observation can be attributed to a degradation of the polyurethane matrix. The weight loss as well as the intensity decrease of IR signals, which could be ascribed to the polyurethane, supports this hypothesis. On the contrary, samples aged in air exhibited the massive matrix degradation not until 1000 h of ageing. For this reason, a strong impact of the oil on the matrix degradation can be deduced. Furthermore, from the discoloration of the PCB material in air, which is assigned to the thermal oxidation of the material, and the lack of this behavior in oil it is also concluded, that the thermal oxidation is not the predominant degradation mechanism of the coating in oil.

The matrix degradation of the coating was also observed for samples aged at 120 °C in oil, but on a longer timescale. First evaluation on the degradation kinetics exhibits a time constant of $k = 1.2 \cdot 10^6 \text{ s}^{-1}$.

In conclusion, the aggressive oil accelerates the degradation of the polyurethane compared to air, massively. It is unlikely, that thermal oxidation is the predominant degradation mechanism in oil. The degradation rate of the material is temperature dependent. Further investigations on the mechanism are ongoing.

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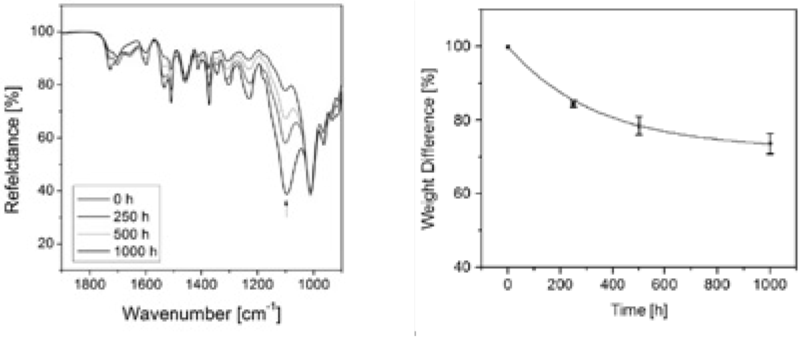

Figure 1: (Left) The ATR-IR spectra of the polyurethane after ageing at 120 °C in oil. The degradation can be traced by an ether band at 1100 cm^{-1}. The preserved prominent peak at 1020 cm^{-1} is attributed to the filler. (Right) The fitted weight loss of the material at 120 °C in oil.

1.15

Color retention in Architectural Paints

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BASF SE, Ludwigshafen (Germany)

Color is an important and powerful tool used by architects and home owners to create or enhance attractive features in a home or commercial buildings. Especially brilliant colors can provide a pleasant feeling and draw attention to architectural details. Therefore, the trend to brilliant colors in exterior paints will continue. On the other hand, once the perfect color has been chosen to paint the exterior of a home, the owner expects that color to last and not fade prematurely. This means that beyond aesthetics, the requirements concerning color fastness will become more essential.

Using the experience that BASF has gained over the years in the development of polymer dispersions for architectural coatings, a new specialized acrylic binder for paints with improved color retention has been developed (Acronal® EDGE 6295).

In the first part of our talk, we will describe and present some of the analytical tools and findings we have used to develop and understand the mechanism of color retention and further develop Acronal® EDGE 6295. Formulation latitude including the influence of additives will be the topic of the second part of the presentation.

1.16

Dose-response functions for prediction of easy-to-clean performance of coil-coated materials

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The demand for specific functional properties of coil-coated materials for building industry tends to increase rapidly. Easy-to-clean (EtC) paints are especially interesting for Asian markets due to non-negligible air pollution.

Within a large industrially funded project, 10 coil-coated EtC and reference materials selected to cover basic EtC concepts and paint chemistries were repeatedly exposed at 12 outdoor sites in Europe, China, India and South-East Asia in 3-month periods and for 1 year. Samples of 300×100 mm were bend in 2/3 of the length to angle of 95°. The upper part of the panels was exposed at angle of 5° to horizontal. It served for assessment of general EtC properties and as a dirt collector for the bottom part. The bottom part was exposed vertically to the ground and it was used for evaluation of tiger stripe formation. Dirt pick up (difference between initial lightness and lightness of a non-washed panel after field exposure), dirt retention (lightness change assessed after gentle cleaning) and tiger stripe formation were followed.

All EtC systems performed better than reference materials proving that surface modification can improve lightness stability of coil-coated materials in service conditions.

Main parameters controlling dirt pick up, dirt retention and tiger stripe formation were the initial water contact angle affecting mainly dirt removal, concentrations of sulphur dioxide (SO_2) and nitrogen dioxide (NO_2) in air correlating to dirt deposition in industrially-polluted atmospheres, mean air temperature affecting the rate of dirt build up into organic coatings and glass transition temperature (T_g) of topcoat paints connected to the surface reactivity. Paint lightness tended to change less for hydrophilic paints with higher T_g in less polluted areas with lower mean air temperature. Except of completely dry conditions leading to high dirt pick up, the effect of precipitation on dirt pick up and dirt retention was low.

Tiger stripe formation mostly followed changes in lightness at surfaces oriented at 5° to horizontal.

Semi-empirical dose-response functions for prediction of material performance in terms of general lightness changes at 5° and 90° and tiger stripe formation on vertical surfaces for white coil-coated materials applied in industrial and urban areas have been formulated. Despite a number of limitations, the models can be used for estimation of the effect of paint properties and climatic factors on the EtC performance in service environments, see the example in Figure 1. Additional long-term data will allow for incorporation of the time factor.

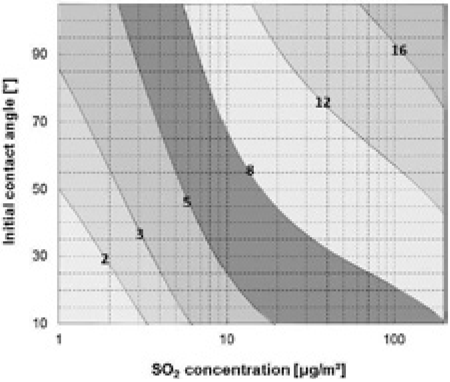

Figure 1: Predicted effect of initial contact angle and SO_2 concentration on dirt pick up (drop in lightness) of white paints at 5° to horizontal after 3 months of outdoor exposure; T_{air} = 15 °C, c(NO_2) = 15 µg/m³, T_g = 25 °C

Photochemical Attachment of Water-Absorbing Hydrogel Coatings to Polystyrene to Avoid Turbidity in Cold Environments

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If a cold surface comes into contact with humid air, water can condense onto it. Depending on humidity and temperature either water droplets or ice crystals are formed. A previously transparent substrate thus becomes opaque. This problem, for instance, is relevant for drawers or shelves in refrigerators and especially in freezers. Upon opening the door of a freezer one should be able to see what is stored in the drawers. However, due to air moisture it often happens that the surface of the drawers fogs, so that the contents can no longer be identified. The coating reported about here is supposed to prevent the fogging (Fig. 1), hopefully reducing the period of time that the freezer has to stay open before the needed product is found.

To avoid this practical but also aesthetic problem of fogging, a coating is applied to the surface of the drawers. The active substance is polyvinylpyrrolidone (PVP), a hydrophilic polymer. It absorbs the water that condenses on the surface, so that no droplets or ice crystals are formed[1]. The drawer stays clear. The efficiency of this mechanism depends on several factors such as coating thickness and cross-link density as well as temperature and atmospheric humidity. It can be shown that a higher thickness increases the efficacy of the coating since more water can be absorbed. Thus, at higher humidity the same coating will fail sooner than at lower humidity. Also, the lower the substrate temperature the sooner it will fog at constant or repeated exposure since the water can condense faster.

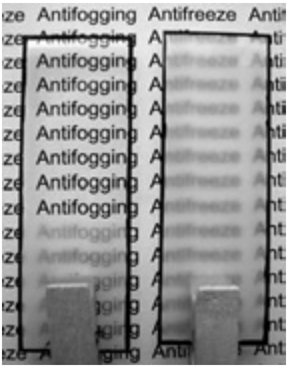

Figure 1: substrates directly after having been taken out of the freezer; right: uncoated and fully fogged; left: coating at the top prevents fogging

In this study, the substrate material is polystyrene (PS), a relatively unreactive plastic. It is frequently used for drawers in freezers as it is a clear, light and inexpensive material. Due to its relative chemical inertness it is a challenge to firmly attach a coating to the PS surface without interfering with its optical properties. For the adhesion of the hydrophilic PVP onto the rather hydrophobic PS surface the following measures are taken. Inevitably, the PS substrate has to be activated by plasma treatment, thus greatly increasing the wettability by the coating solution. UV light, supported by H_2O_2, is used to cure PVP and form a resistant coating. To enhance the adhesion of the PVP coating on the PS surface benzophenone (BP) is used. By UV irradiation it creates radicals on the PS surface[2] that can bind to the PVP chains. The adhesion improves with increasing concentration of BP and with longer irradiation times.

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Development and characterisation of functional coatings with dedicated thermo-optical properties for solar energy-related applications

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In the scope of the current concern about energy consumption and the development of new technologies for its production, the interaction between materials and solar radiation has recently known a surge in attention. Coatings can also intervene in this matter and as a result the interest in this topic has led to the development of functional coatings displaying specific interactions with the solar radiation. In this paper the development and characterisation of such functional coatings with tuned thermo-optical properties is presented. Two applications, imposing different requirements to the coatings, are considered. The first application deals with architectural coatings, designed to reflect an increased percentage of the incident solar radiation. These coatings can contribute to reduce the energy consumption for the cooling of buildings and the development of urban heat islands. The second application addressed in this paper focusses on coatings for the central tower of a central receiver solar power plant. In contrast to the aforementioned architectural coatings, this coating should be capable to absorb as much as possible of the incident solar radiation, whereas it should show a limited re-emission of heat. These requirements imply the development of a spectral selective coating, displaying a high solar absorptance in combination with a low emissivity. In addition, due to the application the coating should possess an elevated thermal resistance and stability.

For both applications pigments and charges, which can attribute the desired thermo-optical properties to the system are presented. The impact of their incorporation into the formulation on the thermo-optical properties (such as total solar reflection, absorbance, emissivity) is evaluated, in combination with other pertinent coating properties such as for example accelerated weathering resistance, mechanical properties and temperature resistance.

Lectures

Corrosion protection

In-situ analytical and electrochemical evaluation of interfacial bonding and performance of corrosion protective coatings

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The initial adhesion and resistance against delamination of organic coatings on metal surfaces highly depend on the polymer/oxide/metal interfacial chemistry. Therefore, it is crucial to control and understand the bonding mechanism originating at these interfaces in order to achieve long-term stability. While the type of bonding contributes to the strength of adhesion, the nature of the interface depends on both functionality present in the organic molecules of the coating and the nature of the oxide film e.g. hydration, hydroxyl content, oxide thickness, surface morphology and chemical composition.
Studying the bonding properties of the polymeric coating to the metal (oxide) surface is experimentally difficult, because the interface is hard to be reached by analytical techniques due to the relatively high thickness of the polymer coatings. Consequently, the interfacial bonding can be modeled through adsorption of functional group, i.e. representative interfacial adhesive molecules, on differently pretreated surfaces by means of bonding mechanism (FTIR) and affinity (XPS) studies. Furthermore, the buried interface and delamination mechanisms at this location can be studied in-situ by Scanning Kelvin Probe (SKP) measurements and a novel integrated ATR-FTIR and electrochemical impedance spectroscopy (EIS) system in a Kretschmann geometry.

In recent years the design and development of self-healing coatings have emerged as new alternatives in the protection of metallic structures against corrosion upon coating damage. With the development of these intelligent materials a new challenge arises for the evaluation of the efficiency of these systems as the healing processes take place at microscopic level. In general, conventional electrochemical methods only provide averaged information on the protective properties of the coating independently of the dimension range of the processes occurring in the coated system. For this reason, it is necessary to introduce local electrochemical techniques as complementary methods which allow in-situ monitoring of the repairing processes occurring directly at the damaged area with high spatial resolution. In general, these techniques are based on near-surface scanning by a probe (microelectrode) and provide valuable information about the electrochemical activity on the studied system and its recovery resulting from the healing process. In recent times, the scanning vibrating electrode technique (SVET) and scanning electrochemical microscopy (SECM) have proven to be very powerful local techniques in the study of a wide variety of corroding and corrosion protective systems. In our work local techniques are introduced to evaluate various self-healing anticorrosive organic coatings based on inhibitor, healing agent release or thermo-reversible polymer healing concepts.

The focus of the presentation will not be on the development of new coating systems, but on the introduction of novel analytical and (local) electrochemical techniques for the evaluation of interfacial bonding and corrosion performance of coated metals as such.

New Substrates influencing the pretreatment process

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Henkel AG & Co KGaA, Düsseldorf (Germany)

Lightweighting is the buzzword of the automotive world today, and lightweighting has dramatic consequences on substrates used for car body construction today and in the future. The change in the metal mix forces adaptations and innovations in the metal pretreatment process to guarantee the expected high performance- and quality level.

Hot stamped high strength steel started to gain market share in Europe, and swaps now into North America and Asia. To prevent scaling of the surfaces and to avoid any blasting process of formed parts, different surface coatings are in use. The presentations will discuss the different coatings with their pros and cons, and dives deeper into new coating technologies.
Depending on the composition of these coatings, the pretreatment chemistry has to be adapted.

New galvanized coatings, most prominently zinc magnesium, are causing improved corrosion protection mainly on cut edges, in combination with a reduced zinc coating weight. The whole pretreatment strategy has to be adapted to the new substrates. Special challenges are in the area of adhesive bonding properties. A new type of coil pretreatment is improving those properties significantly.

Aluminum is no more an alloy fort the premium segment, but is found in more and more mid range models as well. The challenge of Aluminum pretreatment in a mixed metal car body environment is solved by the new global standard, the two step process.
The thin film technologies are making progress in the area of multi substrate performance. A global update will be presented.
Preparing stamped Aluminum parts or castings for the body shop, for welding and adhesive bonding operations, can be a challenge. State of the art is an etch passivation process to generate a uniform, reproducible surface composition.

Chrome – free pretreatment for Aluminum and even Magnesium was introduced many years ago already. But the use of Magnesium for outer skin applications was until now not possible, due to the extreme corrosion sensitivity of Magnesium. A new, innovative plasma technology boosts now the corrosion protection for Magnesium to a whole new level.

2.3

What happens during the swelling of a coating?

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University of Applied Sciences, Krefeld, Germany

The first topic in this work is the diffusion of Ions inside the coating during the swelling process with an electrolyte. The challenge was to measure the small effect of the change of the Ion concentration in the electrolyte during the swelling process. A coated wire mesh was immersed in a small amount of the electrolyte to get an optimized ratio between surface area and the volume of the electrolyte. From these solution samples have been analyzed by means of UV-VIS spectroscopy.

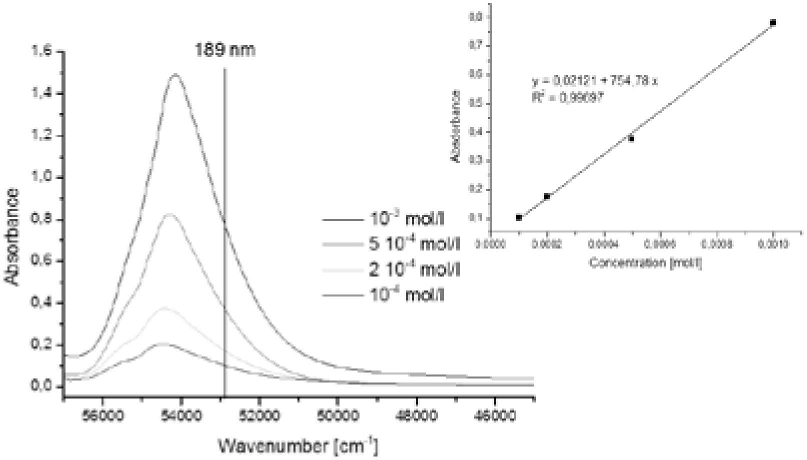

Fig 1: UV-VIS spectra (Nitrogen Atmosphere) of Sodium Chloride solution in Water and the correlation of absorbance and concentration at 189 nm.

The absorbance of the solution at 189 nm correlates with the Ion concentration (see fig. 1) and could be measured without a nitrogen atmosphere in the device. The resolution of this method is adequate for the small concentration changes.
The main result with the used samples is, that at the beginning of the swelling of a Water based coating only water diffuses inside the coating.
There are some hints that after two weeks Ions could diffuse inside the coating, too.
If Ions diffuse inside the coating or only water, the corrosion behavior of the coating will be complete different. Therefore allows this method the measurement of the Ion barrier of a coating.

The second topic in this work is the comparable description of the swelling behavior of coatings by means of electrochemical impedance spectroscopy (EIS). The swelling behavior of coatings could be measured but the EIS spectra normally analyzed with an equivalent circuit to interpret the data. Because of the fact, that different coatings need different equivalent circuits the EIS data could often hardly compared.
In this work a new analysis of such data has been developed. The Nyquist spectra of the EIS spectra are interpret by mean of different phases (fig. 2). The phases separate diffusion or swelling processes from corrosion processes. Therefore a

comparison of different coatings is possible and the corrosion protective performance of coatings in different media (Sodium Chloride concentration) could be analyzed.

For example a small Sodium Chloride concentration causes only a swelling of an Acrylate clear coat and with increase the salt concentration corrosion starts but could be inhibited by a passivation reaction and only at high salt concentration corrosion could not be stopped.

With these methods the analysis of the corrosion behavior from coatings under high humidity or under salt content humid atmosphere could be interpret on a physicochemical basis.

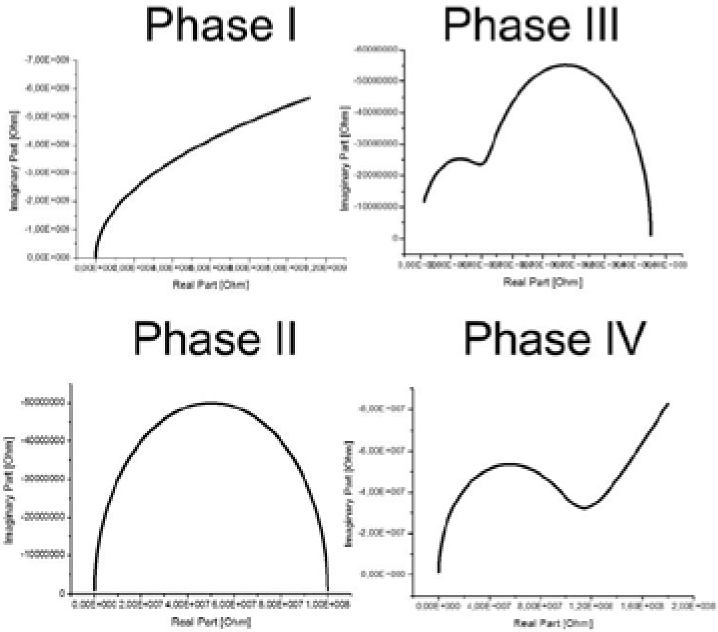

Fig.2: Possible "Phases" of a Nyquist Diagram during the swelling process of a coating with an electrolyte.

New aspects in corrosion protection with polymer dispersions

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Organic coatings play a prominent economical role for protection of steel against corrosion. The driving forces for the development and application of water based coatings for corrosion protection are the challenges of increasing environmental requirements and the compliance with legislative regulations.

In terms of these requirements, anti-corrosive coatings, based on polymer dispersions, e.g. acrylates and acrylate co-polymers, may offer best preconditions since they have further advantages concerning toxicity and work hygiene.

Up to now polymer dispersions show intrinsic weaknesses in anti-corrosive behaviour. Especially in contrast to coatings, based on two-pack EP binders, coatings with polymer dispersions reveal low performance under salt spray conditions, according to corrosivity categories greater than or equal to C3.

One objective of this study is the search for the causes of these weaknesses, in order to find out principles or criteria for selecting polymer dispersions with a high anticorrosive potential for coatings.

The other approach is to study specific contributions and synergies of fillers and anticorrosive pigments. Functional additives and their structure/property-relationships with polymer dispersions for significantly improving the barrier properties of coatings are studied as well.

Derived from the frequently occurring failure modes, i.e. blistering and undercreepage due to cathodic delamination, another focus of this work is on the question, how to block the pathways for water, electrolytes and oxygen through the coating film and along the interface between coating film and steel surface, to improve the lateral barrier against cathodic delamination. This could be done via means of better modelling of the polymer to/on the steel surface topography. Also under consideration is the role of electrolytes, trapped as traces in polymer films, as an inherent weakness of polymer dispersions, originating from the polymerization process.

Within this work a screening with over ten different polymer dispersions, based on styrene acrylates, formulated in three variants, is performed. The formulated coatings are applied to blasted steel surfaces. After standardized drying, the coated samples are tested with standard short-time corrosion tests, under salt spray and condensation-water atmosphere. The undercreepage on defined scribes, respectively the extent of blistering on the coating surface, were evaluated as a function of polymer dispersion type, pigmentation, anticorrosion pigment, film thickness, and single or two layer systems.

Studies of water and electrolyte penetration through the polymer film to and along the interfaces between steel and organic coating with EIS, SKP and sorption kinetics measurements will give insights into the start, progress and extent of the corrosion process and are a measure for the estimation of the corrosion protection performance of the system.

These results can help to identify the main factors of polymer dispersions influencing the anti-corrosion properties of coatings, and, in addition, important indications for paint producers and suppliers of polymer dispersions can be derived.

New 2-layer Epoxy Coating System achieving excellent corrosion protection and UV-stability

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For decades 2K-Epoxy systems using amine hardeners (mainly polyamidoamine type curatives) for crosslinking are setting the standards with respect to anticorrosion protection on metal surfaces and are state of the art in industrial coating processes as anticorrosion primers.

Requirements for this primer technology have changed and increased significantly over the last ten years by changing to High Solids or even solvent-free systems as a consequence of VOC-regulation in Europe on one side and the recent introduction of other EHS standards like creation of low emission products and outphasing of SVHCs (Substances of Very High Concern) linked with REACH-legislation.

Although epoxy systems are the preferred choice for industrial anticorrosion primers, their use as industrial top coats was completely prohibited by their extremely poor UV-resistance resulting in very fast drop of gloss by heavy chalking associated with strong yellowing tendencies. The only exception so far are direct to metal coatings (single coats) where focus is on corrosion protection with only a minimum of aesthetic properties like for ACE (Agricultural and Construction Equipment) applications.

This paper will summarize our results on anticorrosion performance data for High Solids Systems of different generations (standard high solids PAA-hardener, SVHC-free accelerated version, total reactive PAA-hardener being free of benzyl alcohol and therefore low emission type) versus a traditional solventborne epoxy coating PAA-Standard with type1 Solid Epoxy Resin solution as epoxy component.

To be able to benefit from the well-known and excellent mechanical and chemical resistance properties of epoxy technology for top coat applications a new non-aromatic epoxy system will be presented to be used as a top coat providing excellent gloss retention and minimal discoloration (yellowing) at the same time together with the known positive features mentioned before.

This allows for a complete paint system (primer and top coat) based on epoxy technology providing the well-known anticorrosion performance of the primer with the new feature of a UV-stable, non-yellowing epoxy top coat for significantly improved aesthetics in industrial coating applications being compliant with latest regulations for VOC and other EHS requirements comprising a completely BisphenolA-free top coat.

Effective sol-gel derived protective coatings to prevent the corrosion of steel in marine environment

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Alkoxysilanes are useful precursors for the development of sol-gel derived coatings and hybrid materials. These coatings are in strong competition to organic paints which are well known and used in many fields of application since several decades. In recent studies sol-gel materials draw increasing interest due to many promising properties.

In this study we focus on sol-gel derived coatings that can be used to prevent the corrosion of construction steel. Different single source precursors which have been used include commercially available, e.g. monosilanes like methyltriethoxysilane (MTEOS) as well as aminosilane based bridged compounds.

The sol formation and the impact of the hydrolysis and condensation states after sol formation will be discussed based on ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy data. In addition to the synthesis and formulation of a suitable coating system the curing methods are of importance and have a high impact on the obtained quality of the coatings. Therefore different curing techniques like convection heat as well as IR-irradiation will be compared.

The potential of the coatings to protect construction steel against corrosion was verified using electrical impedance spectroscopy (EIS). In addition to the determination of the coating resistance the water uptake was calculated. The Coating morphology was investigated by scanning electron microscopy (SEM).

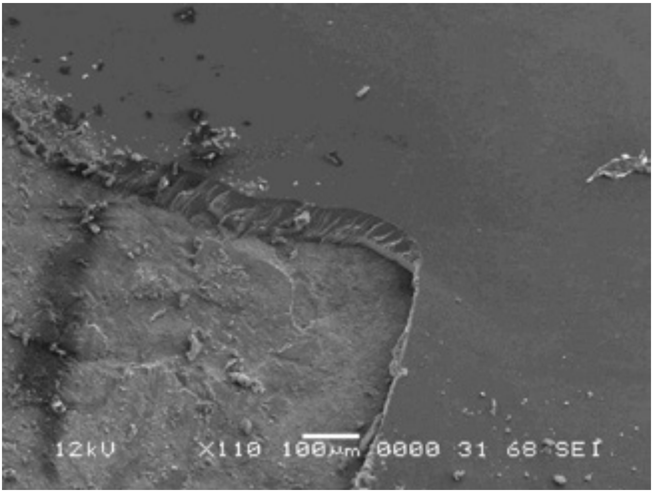

Figure 1: Sol-gel derived protective coating on construction steel.

A Wishing Well- DTM coatings with anticorrosive pigments

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The annual cost of corrosion repair and inhibition amounts to app. 4% of the Gross National Product of a Western Industrial Nation. Today, the pressure on coating formulators to develop new and cost-effective materials for corrosion protection is immense. On the other hand, environmental regulations are the driving force to re-evaluate products and re-formulate with non-hazardous alternatives.

Monocoat applications, so called direct to metal (DTM) coatings, are among the major trends in today's protective coatings industry. DTM coatings are attractive due to the reduction of application steps (no surface preparation and only one applied coating) and the reduction of raw material costs (one coat versus many). Waterborne coatings based on acrylic dispersions are suitable for one coat applications. However, the requirements represent a tough compromise between high-gloss at low VOC level while providing light to medium duty, cost-effective anticorrosive properties. This has been the most challenging goals for resin suppliers but also anticorrosive pigment producers in the past. This lecture will demonstrate the positive influence of corrosion inhibitors on the performance properties of various DTM formulations.

Electrochemical stability of the metal/paint interface: A combined Impedance Spectroscopy and Scanning Kelvin Probe study

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Paints and organic coatings are applied on metallic substrates to protect them from environmental deterioration and for aesthetic reasons. The coatings used these days range from simple single layer to very complex coating systems. With respect to the coating functionality the uptake of water is an important factor for the long term stability of coatings, e.g. the corrosive attack of the underlying metallic substrate. Organic coatings are often analysed by means of Electrochemical Impedance Spectroscopy (EIS). The final purpose of the EIS characterisation of protecting organic coatings is to obtain information about the system properties such as the presence of defects, reactivity of the interface, adhesion and barrier properties to water [1-2]. Many EIS studies correlate the data with accelerated corrosion tests such as the neutral salt spray test [3] or use aggressive conditions like varied / elevated temperatures for the prediction of service time of coating systems. The transport of hydrated ions along a coating/metal substrate interface is verifiable in humid air when a coating defect is covered with an electrolyte. The process of cathodic delamination is usually dominant on iron, steel and zinc substrates in such environments [2,4] and can be monitored by a Scanning Kelvin Probe (SKP), which is a suited method for non-destructive measurements of electrode potentials at buried coating/metal interfaces [4].

The kinetics of interfacial and vertical ion transport processes can be dependent on the structure of the polymer network as well as additives and (functional) pigments in the paint. Especially the addition of active anti-corrosive pigments has a direct influence on the stability of the polymer/substrate interface during the corrosive delamination. From the nature of the measurement techniques, EIS and SKP data provide complementary information, namely the vertical and lateral ion transport, respectively. Therefore, the prediction of the polymer/substrate interface stability based just on an EIS analysis of the polymer barrier properties could lead to an insufficient forecast. Correlations with SKP studies are rather uncommon, especially for technical coating systems containing active corrosion protection pigments.

A systematic study of the stability of the paint/metal interface against cathodic delamination of technical coating systems for automotive, refinish and coil coating applications based on EIS and SKP amongst other analysis techniques will be presented. This study consequently focuses on the evaluation of electrochemical conditions at the interface of different coating systems on steel and galvanized steel specimen, with the focus on the influence of parameters like cross-link density, nature of pre-treatment, anticorrosive pigments or contaminants. Based on the results the stability of the metal/paint interface of technical coating systems against cathodic delamination and corrosion will be discussed and evaluated as a function of the stated influencing factors.

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Surface modification of mesoporous silica for improvement of compatibility with anti-corrosion coatings

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Corrosion is a major issue in industrialized countries. The main approach to prevent corrosion consists of application of coating layers loaded with corrosion inhibitors.

However, the direct addition of inhibitor to a coating formulation can lead to the loss of inhibitor efficiency due to reactions between inhibitor and coating matrix. Also, this interaction tends to lead to a decrease in barrier properties. The inhibitor incorporation in capsules prevents the first problem, but still can disrupt coating barrier properties. A solution to circumvent this problem is the surface modification of the capsules with functional groups that may improve coating/capsule interaction and consequently improve coating barrier properties.

The use of modified mesoporous silica has been reported in literature in particular for drug delivery approaches, aiming to a control release of the active agent and also to improve particle compatibility with the medium [1, 2]. At the same time, mesoporous silica has been used successfully as a capsule for corrosion inhibitor in different types of coatings [3]. But despite improvements in coating barrier properties when compared with the direct addition of inhibitor, still some compatibility issues with the coating matrix remain.

The aim of this work is the surface modification of the mesoporous silica, loaded with a corrosion inhibitor in order to tune compatibility with hybrid sol-gel and polyurethane based coatings. The modified particles were characterized by different techniques including FTIR, zeta potential, particle size and SEM. The resulting coating formulations were applied in aluminum alloy 2024 and the coated samples tested by Electrochemical Impedance Spectroscopy (EIS) and Scanning Vibrating Electrode Technique (SVET).

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Lectures

Sustainability in the coatings field/ Saving resources/Biobased coatings

Feedstock in Transition – A Manufacturer's Perspective on Petrochemical Trends and the Downstream Impact to the Coatings Market

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Over the past decades the petrochemical industry was fuelled by crude oil. However, with persistent high oil prices and with the advent of fresh petrochemical feedstocks from shale gas to coal, biomass and other carbon sources a transformation of the individual petrochemical value chains has commenced.

Petrochemicals are increasingly produced from multiple sources and feedstock diversification has become a strategic focus in the individual regions. For example the United States, driven by abundant shale gas, started to influence the market for ethylene and its derivatives. Other new feedstocks that may have future impact on the markets are coal and biomass. Feedstock diversification will increasingly influence how refineries and the adjacent olefin crackers are operated. The output of the petrochemical building blocks can be expected to change accordingly.

In addition, environmental and market conditions are increasingly pressing issues for the petrochemical industry. Hence, the choice of the proper feedstock and the strategic orientation of the petrochemical value chain will be a key issue in the years to come.

This paper intends to give an overview about up-stream trends and drivers which impact the petrochemical building blocks and the corresponding downstream value chains.

In the middle of these ongoing changes with an almost unpredictable final outcome it seems beneficial to relay on stable elements. In this context vinyl acetate-ethylene copolymers, VAE as derived from healthy C1- and C2-value chains offer certain characteristics with the desired fundamental long term advantage. The feedstock versatility in the typical C1-chemistry gives rise to reduced price volatility and a reliable value chain combined with high carbon efficiency.

CO_2 -based Polyols: a new Polymer Backbone for Polyurethane Coatings

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The advancement in catalyst technology has enabled the development of a new generation of polyols. These polyols are based on epoxides and up to 50% of carbon dioxide (CO_2). These novel backbones are starting to find commercial applications in the coating industry with some very interesting benefits. In this presentation we will share the fundamentals behind the technology, the properties of the polyols and some of the initial results that have been achieved with these polyols in various coating applications. These applications include polyurethane dispersions, metal coatings, plastic coatings and 100% solid injected coatings. We can demonstrate that these new CO_2-based backbones have the ability to improve coating hardness whilst maintaining flexibility and also meeting and, in some cases, exceeding requirements such as weatherability, and chemical and hydrolysis resistance. In addition to the technical benefits of this technology, we will highlight sustainability aspects not only from an environmental perspective but also from an economic viewpoint.

Influence of isosorbide to polyurethane dispersions for wood coatings application

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Biobased renewables are of high interest as they may substitute petrobased chemicals in the long-term future. Many biobased, alternative monomers are already considered into account, both in scientific researches and in commercial use. They can be divided according to their chemical nature and available sources to oils and fats, saccharides, proteins and minor components. Instead of using the natural compound itself, it is also common to modify or to break down natural resources. Amongst the saccharides, isosorbide turns up to be a suitable diol for polyester synthesizes and hence for polyester-based polyurethane dispersions to use as resins in wood coatings.

Most of the vegetable oil based monomers are excellent substitutes regarding flexible and elastic properties of wood coatings. Only little natural difunctional monomers contain ring-structures which are considered to increase coating film properties like hardness and impact resilience. That's why isosorbide is supposed to be a promising monomer for coating systems. On the other hand, chemical resistance might be critical because the furane ring structure may be sensitive to hydrolysis which has to be investigated.

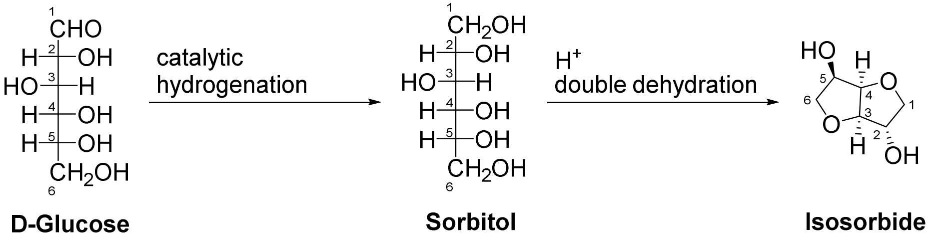

Figure 1: Two step synthesis route from D-glucose to isosorbide [1].

The two-step synthesis route from D-glucose to isosorbide is shown in Figure 1 [1]. The resulting isosorbide has two secondary hydroxyl groups with low and non-uniform reactivity caused by the steric conformation of the two-ring system. To overcome the disadvantage of non-uniform reactivity of the hydroxyl groups many derivatizations using ether bridges are described by Chatti et. al. [2]. On the other hand, Kricheldorf and Weidner performed copolymers from isosorbide, L-lactid and isophthaloylchloride by combined ring opening polymerization and in-situ polymerization. They obtained high molecular mass copolymers with increased glass transition temperature [3]. In the field of coatings, only little work is described in literature. Haveren et. al. have reported about the use of isosorbide in powder coatings [4] and Xia and Larock have investigated polyurethanes using a combination of soybean-oil and isosorbide [5].

In the present work, isosorbide is directly used for standard polycondensation without using ROP technique or any modification of isosorbide before. To overcome the disadvantage of low and non-uniform reactivity a two-step polycondensation was carried out to ensure that the isosorbide is integrated into the polyester chain. The polyester is than converted to a polyurethane polymer and dispersed in water to finally get an isosorbide-based polyurethane dispersion. In addition, a reference was synthezised using equimolar amounts of neopentylglycol. The polyurethane dispersions were characterized and the resulting binder film properties were compared. To investigate the resin performance, pendulum hardness and glass transition temperature are measured. The results are discussed related to the chemical composition of the polyurethane especially in consideration of the used amounts of isosorbide and neopentylglycol. In addition, results of the tests for resistance to water and organic solvents will be shown.

The authors would like to thank the project partners INSPIRALIA (Spain), CETEM (Spain), WIC (Slovenia), BPF (UK), MFMO (Malta), HELIOS (Slovenia), ISOLACK (Spain), RIOMADER (Spain) and BOD AYRE (UK) for kind assistance.The research leading to these results has received funding from the European Union Seventh Framework Programme (FP7/2007-2013) under grant agreement n°304998.

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3.4

Investigation The cathodic Electrodeposition behavior of chitosan biopolymer in different solid contents

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Chitosan is a linear hydrophilic polysacharid obtained by deacetylation of nature chitin. It is an attractive biocompatible and nontoxic biopolymer that exhibits excellent film forming ability. Moreover, it responsive to localized electrical signals, serves as an excellent candidate for electrodepositing process. Biopolymer chitosan with some primary amino group has PKa about 6.3. At lower pH most of the amino groups are protonated making chitosan water soluble polyelectrolyte. When the pH is higher than pKa, the amino groups are deprotonated and chitosan become insoluble. This property allows the chitosan hydrogel to be electro assemble from an aqueous bulk solution onto a conductive surface in response to cathodic signal. Although there are increasing numbers of report on application of functional device or hybrid composite in which chitosan is electrodeposited, the mechanism by which an electrodeposited film is formed are not well understood. In this report, we have focused on explanation of the electrodeposition behavior of chtitosan solution by different solid contents. Chitosan solutions(1,0.5,0.25,0.12,0.06)% (w/v) used in this study were prepared by dissolving chitosan flake (Sigma-aldrich,85% deacetylation and 50000 Da as reported by supplier)in lactic acid(1% (w/v)) and de-ionized water .The chitosan dispersion were deposited on galvanized panels using rectifier at a constant voltage of 100 V and for a constant duration (180s).

Figure1,shows the variation of current density during the electro-deposition of the chitosan at different solid contents.

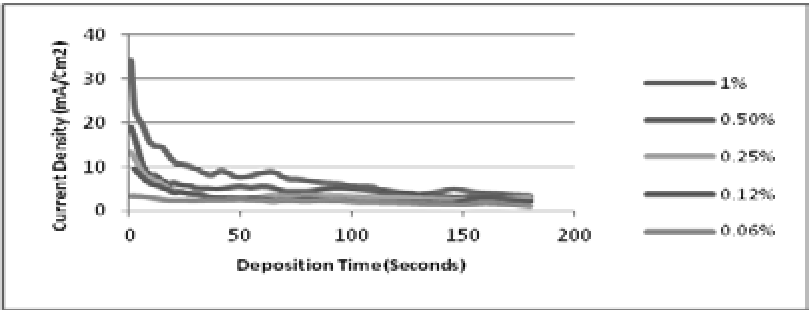
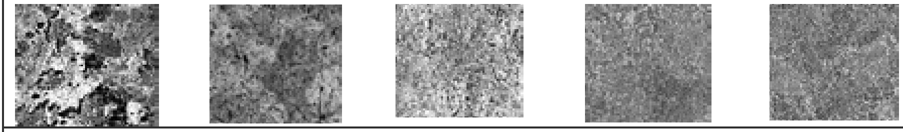


Figure 1: Variation of current density during the electrodeposition of chitosan film as a function of solid content

The current density decreases as the electro-deposition proceeds. As can be seen by increasing solid content of polyelectrolyte, both the peak current density and the residual current density increase. However, the residual current density values are so close to each other. The random coil structures of chitosan polyelectrolyte open to the rod-like form with higher concentration of charge group by increasing solid content. In dilute solution, the charged groups will be too far apart to interact. So, their migration toward cathode and the neutralization of chitosan becomes easier and a more compact film is formed .The lower residual current density confirmed this conclusions. By increasing solid content, the polymer chains entanglement and curls becomes more and causes some disruption on electrodeposition proceed .So, in this case ,a porous film is formed which let the electrical current to flow through the film. This can be seen from Fig.2. So,a higher residual current density can be assigned to this effect. It should be mentioned that in all solid contents, the pores are formed due to the evaluation of electrolyses gasses on the surface of electrodeposited film.



1% 0.5% 0.25% 0.12% 0.06%

Figure 2: Variation of the morphology of the electrodeposited films at different chitosan weight percents.

chitosan polyelectrolyte shows interesting behavior during electrodeposition process. It was found that the electrodeposition behavior is related to chitosan polymer structure at different solid contents. Uniform films with low thickness in dilute solution and porous film with high thickness at high solid content are formed.

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Silicone-hybrid technology for modern and resource efficient high solid coatings

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The latest developments in the silicone-hybrid technology for economical, environmentally friendly and innovative high solid coatings will be presented.

Several types of silicone-hybrids have been developed based on the targeted chemical combination of inorganic silicone resins with different types of organic resins. Thereby the advantages of the inorganic silicone resins and the organic resins are combined and the excellent properties of the silicone-hybrids can be achieved.

Silicone-hybrids have been designed for different curing mechanisms like the much applied isocyanate curing and isocyanate-free crosslinking based on a hydrolysis-condensation reaction.

Due to the low viscosity at high solid content of the silicone-hybrids coatings with a VOC content markedly lower than 250 g/L or even lower than 100 g/L can be realized thus complying with new and future VOC legislation.

The silicone-hybrid technology can be utilized for industrial topcoat applications to generate effects for functional coatings like outstanding anti-corrosion protection, excellent weather stability, long term durability of the coating, easy-to-clean properties combined with high mechanical and high chemical resistance of the coating.

Beside the actual status quo of the silicone-hybrids also the potential next steps in this fascinating and promising technology will be presented.

Lactide-modified polyester resins with enhanced resin- and coating performance

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Saturated polyester- and alkyd resins have been used for many years to produce high-performance materials, such as industrial- and architectural coatings (solvent- & waterborne). Over time, priorities have changed towards the preferred use of reduced Volatile Organic Compounds (VOC) products. The current industry challenge is to reduce the carbon footprint of coating systems.

Possibilities for the reduction in carbon footprint can be provided by using materials from renewable resources. These raw materials should not only contribute to a reduction of carbon footprint over the life cycle of the coating, but should also be cost-efficient and provide equal, or better, coating performance than their petrochemical alternatives. Corbion Purac has developed a new biobased building block that offers opportunities to reduce carbon footprint, Lactide. This sustainable product can be used as a chemical building block to create saturated polyester- and alkyd resins for different kind of coating applications, such as decorative paints, and can-, wood- and powder coatings.

Lactide has a low carbon footprint and when incorporated into these resins, it helps achieve CO_2 reduction. Furthermore, Lactide provides a significant lower polyester resin viscosity without compromising coating performance. Additionally, the derived saturated polyester- and alkyd coatings show enhanced hardness, with maintained, or improved flexibility and other enhanced coating properties.

In conclusion, Lactide is a versatile, biobased building block that can be easily incorporated into saturated polyester- and alkyd resins for different industrial- and architectural coating applications. The use of Lactide improves the sustainability of the coating, and concurrently enhances performance of both resin and coating.

New generation of cobalt-free alkyd emulsion paints with non-oxidative drying mechanism

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ITECH Lyon[(a)], Ecully (France), ECOAT[(b)], Grasse (France)

Paints and coatings occupy a prominent place in the cultural history of mankind. People have always been fascinated by colors and used paints to decorate and beautify themselves and their environment. Nevertheless, these products bring a lot of problems. For instance, some paints still contain organic solvents, which have negative impacts on the environment and human health. Due to environmental legislations and the need to reduce VOCs emission (volatile organic compounds), water-based paints have become increasingly popular.

Alkyd resins have been introduced in the 1930s and still continue to be the most widely used binder.[1] They are polyesters, synthetized by polycondensation reactions between polybasic acids and polyols, modified with fatty acids and monobasic acids. In the 1990s, critical developments in the surfactants world enable the design of water-based alkyd emulsions. They are less toxic, have low VOCs level and have also good performances. However, the fast drying of these binders requires the use of oxidative catalysts such as cobalt salts.[2]

Nowadays, within a growing bio-based chemistry market, Ecoat, an innovating chemical company, is developing the next generation of alkyd emulsions using renewable raw materials for the coatings industry. The company has already commercialized its first generation of bio-based alkyd emulsions with bio-based content up to 99 wt. %. These binders are competitive with conventional alkyd and acrylic binders, which are commonly used in paints.

With increasing governmental regulations such as REACH, some products will be forbidden due to their toxicity.[3] In the coating industry, for example, it is the case of the cobalt salts used as oxidative drying catalysts. After its success with its first generation of biobased alkyd emulsions, Ecoat decided to develop a fast chemical drying mechanism for alkyd resins without using any cobalt salt. As a result, a new non-oxidative crosslinking mechanism, working at room temperature and without any catalyst, was developed. This second generation of bio-based alkyd was launched on the market in early 2014 under the brand name Leaf Tech®. Binders with this technology no longer require the use of cobalt salts to dry and reach high film hardness in a few hours only.

In this talk, I will present to you different results showing the promising performances of these new Leaf Tech® alkyd emulsions in comparison with conventional acrylic and alkyd binders.

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Sustainability – a spezial challenge for medium-sized Resin Manufacturer

Dr. Thorsten Adebahr, Dr. Dietmar Chmielewski.

Worlée-Chemie, Hamburg (Germany)

What sustainability means to coating and resin manufactures and their products and services has not been answered finally and absolutely not uniformly.
There are many definitions, key words and concepts. Aspects such as Carbon Footprint, resins from renewable raw materials, Cradle to Cradle, biological degradability or life-cycle considerations of paints and a lot more definitions are used to indicate the sustainability of a product.
Which approach fits best to a company is obviously related to an individual definition and also still an open question. Today no general answer is possible.
How can a resin manufacturer cope with so many different aspects and definitions of sustainability?

Exemplarily three classes of binders are compared regarding various aspects of sustainability and evaluated in a matrix. In addition, the performance profiles of binder systems have been evaluated and compared to common market standards.

A special focus is set on the question, to what extend resins can be produced entirely from renewable sustainable produced raw materials.
For alkyd resins this is already possible without any kind of performance limitations. For polyacrylates and polyesters the development is still at the beginning.

A promising outlook is shown how to get high performing and affordable products sustainable and 100 percent out of renewable raw materials.

Lectures

Polymers, pigments and other raw materials

Sustainable Developments in the Pigment Industry

Dr. Christof Kujat, Dr. Eckhard Korona, Georg Döring

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In recent years sustainability has become a major driver for pigment innovations. Toxic pigments will be abandoned from the market or will stay only for niche application in the future. The substitution of lead chromates is the most prominent one and technical alternatives at reasonable costs are one big challenge. Therefore the search for highly durable and opaque pigments in the chromatic red and yellow color area is one focus at the moment to fill this gap, either by developing new or improved pigments or by designing smart blends of inorganic pigments (for opacity) and organic pigments (for chroma and color strength). However a 1 to 1 substitute for lead containing pigments does not exist.

New environmental regulations (e.g. REACH) further enhance the need for more sustainable pigments. On the other hand eco labels (e.g. The Blue Angel[1], The EU Ecolabel[2], …) with even more demanding requirements become more and more important in our society and the industry has to develop new solutions to fulfil these requirements. Another impact are new analytical or toxicological results of existing products which result in the development of new pigments or pigments with higher purity (e.g. lower amount of soluble heavy metals) or less toxic impurities.

In addition sustainability is not only related to the chemistry of the pigments, but also on improved secondary properties like higher NIR-reflectivity for heat management solutions resulting in less heat build-up and therefore in less energy consumption for cooling and longer lifetimes for coatings.

Therefore sustainability is a big chance and opportunity to develop new technical solutions for the future and to show the innovativeness of this industry.

This presentation will give an overview on the major trends in the pigment industry for new developments of sustainable pigments and will show some typical examples from the recent years.

References:

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[2] http://ec.europa.eu/environment/ecolabel/

Impact of New EU-Regulation on the Usage of Biocides

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The United Nations has recently developed a system to globally align the hazard communication for chemicals; this is the GHS (Global Harmonised System). GHS also aligns hazard criteria with the established international regulations on the transportation of Dangerous Goods. In the EU, GHS has been implemented by the CLP Regulation (EC/1272/2008), CLP stands for Classification, Labelling, and Packaging. Although CLP was introduced in 2008 it had to be applied to substances after December 2010; mixtures have to follow from June 2015. The GHS system is constantly developing and the UN issues updated versions of the model regulation every second year. As a consequence the EU will also regularly update the CLP Regulation by ATPs (Adaptation to Technical Progress).

A recent key change in labelling was introduced in the second ATP to the CLP Regulation (published in 2011)[1] which contains changes in the classification and labelling criteria for substances and mixtures regarding skin sensitisation.
The revised CLP introduced a differentiation for substance classification between "strong sensitisers" and "other sensitisers". The concentration threshold for the classification and labelling of mixtures as sensitising has been lowered to >= 0.1 % for strong sensitisers (other sensitisers stay at 1%). In addition the concentration threshold for elicitation labelling (the Allergen Phrase) has been lowered to 0.01 % for strong sensitisers. For any a sensitising substance with a specific concentration limit (SCL) of less than 0.1 % the limit has been set to one tenth (1/10) of the SCL. Under CLP the Allergen Phrase is referred to as EUH208.

As a consequence of the above changes, more mixtures within the EU will need to carry the Allergen Phrase "Contains (name of sensitising substance). May produce an allergic reaction" on their labels in the future. The new limits for sensitiser hazard phrases are not applicable for existing DPD labelling and are only required for CLP labelling which becomes mandatory at the latest as of June 2015.

As a responsible supplier of Biocidal Products, Lonza Industrial Solutions has monitored this new regulation closely. In order to cope with this challenge Lonza Industrial Solutions offers a product called Proxel BZ Plus which in addition to being efficacious is designed to eliminate any requirement for labelling of final products with the Allergen Phrase.

References:

[1] Official Journal of the European Union *Commission Regulation (EU) No 286/2011.*

Application of Ionic Liquids in Synthesis of Polymeric Binders for Coatings

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Institute for Coatings and Surface Chemistry

Ionic liquids have received increased interest for polymeric binder synthesis because they can function as solvents or as starting materials if they are substituted with a polymerizable functional group. Low vapour pressure, high thermal stability, and a broad variability of the structure of both the cation and the anion of ionic liquids makes them interesting for synthesis of polymers [1-4]. Variation of the alkyl substituent at the cation of ionic liquids results in changes of both their viscosity and their micropolarity [5].

Application of ionic liquids in radical polymerization and group transfer polymerization results in high yields on polymers. Furthermore, molecular weight of the polymers obtained is higher if ionic liquids are used than traditional solvents. The higher molecular weight results in higher glass transition temperatures of the polymers. This fact is important for application of polymers as binders.

Furthermore, differences exist regarding the glass transition temperature of polymerized methacrylates, which were made by using free radical mechanism or group transfer polymerization mechanism. The glass transition temperature of the polymers strongly affects their application temperature.

Initiation of polymerization can be also carried out with light in the case of thin transparent films containing monomer. As a result, a high yield on polymer was obtained in a relative short time interval using photoinitiated polymerization.

Moreover, ionic liquids are useful for manufacture of copolymers. The copolymers can be either statistically [3], alternating or block copolymers depending on the monomers and the ionic liquids chosen. Furthermore, group transfer polymerization in ionic liquids is a useful tool for synthesis of block-copolymers bearing charged and non-charged blocks that may be interesting for application in coatings as well.

References:

[1] Strehmel, V., Laschewsky, A., Wetzel, H., Görnitz, E. (2006). Free Radical Polymerization of *n*-Butyl Methacrylate in Ionic Liquids. *Macromolecules* 39, 923-930.

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Benzoate Technology for Coatings Applications

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Geleen, Netherlands

Benzoate esters have been used as plasticizers in coatings applications for decades. In more recent years there has been a focus on the development of benzoates and dibenzoates as low VOC coalescents for waterborne paint. A low VOC triblend of dibenzoates and a low VOC grade of a diethylene glycol dibenzoate, dipropylene glycol dibenzoate and propylene glycol dibenzoate blend were introduced for use in interior latex architectural paint. In addition a new diblend of dipropylene and diethylene glycol dibenzoates with mostly diethylene glycol dibenzoate was developed for latex coatings and other latex applications in particular. A monobenzoate, 3-phenyl propyl benzoate which is listed on the Register of Flavouring Substances, was evaluated as a coalescent in graphic arts applications and was effective. As benzoate esters have been developed different needs have appeared. An even lower VOC dibenzoate product was needed and to answer that need a classic blend of DPGDB and DEGDB was used as the model and a low VOC version was developed and evaluated. In testing 3-phenyl propyl benzoate were also found to be effective as lower VOC coalescents for latex coatings. The results of testing in interior and exterior architectural paint will be presented to demonstrate the utility of the new products.

Hyperbranched Polyesterols in Coating Applications

Harald Schäfer, David Türp, Rainer Erhardt

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In high solid 2K solvent borne polyurethane coatings there is continuous demand for higher curing speeds and improved application property profiles with seemingly conflicting coating properties such as scratch and chemical resistance.

One approach to solve this conflict is the use of (hyper)branched coating components. Hyperbranched structures promise intrinsically lower viscosity and higher functionality at the same molecular weight with good accessibility of functional groups due to their globular shapes and reduced entanglement of chains.

There have been several trials with hyperbranched structures for improved coating properties, but still with draw-backs. Hyperbranched polyisocyanate functional prepolymers [1] showed excellent drying properties and combination of improved hardness at high elasticity but suffered from a significant reduction of solid content.

We have developed hyperbranched polyesterols with high functionality for use in combination with acrylates in 2K polyurethanes, preferably High Solid systems. We found shorter drying times in curing as well as fast cross-link and hardness development. High scratch resistance and good reflow behaviour is combined with improved chemical resistance, high end-hardness with high elasticity. Moreover, we observed improved corrosion resistance in DTM formulation. This combination of properties renders coatings containing our hyperbranched components ideal for e.g. automotive applications or ACE.

The presentation will highlight advantages and limitations of using hyperbranched polyesterols in coating formulations.

[1] Bernd Bruchmann, Hauke Malz, Hans Renz, Harald Schäfer (2004). Dendritic Polyurethanes - from Research to Application. *XXVII FATIPEC Congress, Aix-en-Provence, France*. 1, 113 – 120.

Rational Design of new Pigment Dispersants by understanding Polymer-Pigment Interactions

Matthias Maier, Steffen Onclin, Jules Mikhael, Clemens Auschra

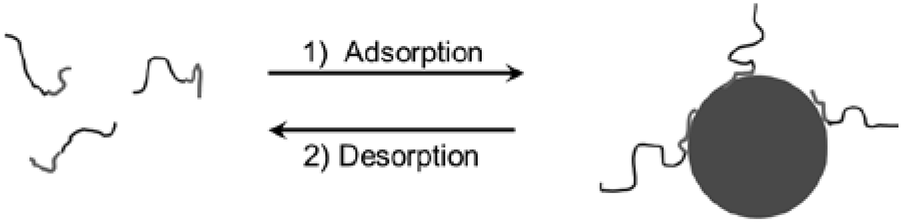
BASF SE, Ludwigshafen, Germany

The development of coatings systems with improved sustainability is a major driving force in today's coatings industry and such formulations require new or adapted raw materials. Pigment dispersants play an important role in enabling the paint manufacturer to successfully achieve this transfer. They contribute to efficient paint processing, formulation flexibility and excellent coating performance.

Especially for demanding pigments with a large specific surface area, highly efficient dispersants are necessary. Using controlled free radical polymerization (CFRP)[1,2] novel block copolymers with a precise control over the molecular structure are accessible. Improved pigment anchoring and compatibility in different resin systems can be tailor-made by the optimum design of the block copolymer. This requires an in-depth scientific understanding of the interactions of the dispersant polymers in the complex colloidal systems of pigment pastes and paints.

To enhance the understanding of the dispersant adsorption process, polymer-pigment interactions were studied. With the powerful fractionating method of the analytical ultracentrifugation (AUC),[3] the different components of a colloidal system can be well investigated. The registration of the sedimentation behavior of the unbound polymers, for instance, leads to valuable information. Not only can the micelle formation be detected but also the generation of adsorption isotherms is possible. The interplay between polymer-pigment affinity and suppression of agglomerate formation is a key criterion for an efficient dispersant.

The combination of CFRP and AUC investigations thus enables the design of new dispersants with more effective pigment anchoring groups in combination with good compatibility towards different paint systems. These dispersants perfectly meet the requirements for modern VOC-free high-quality paints, offering superior rheology and stability of pigment concentrates, with favorable coloristic properties.



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[3] Mikhael, J. (2013). Analytical ultracentrifugation of complex industrial colloids. *Separation*, 33, 25 - 27.

Outstanding advantages of ultra-low viscosity hydrophobic polyisocyanate: Duranate^{TM} TUL-100

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Nowadays emissions into the atmosphere are regulated and legislations are limiting the level of volatile organic compounds (VOC) that may be emitted during coating application. With respect to Polyurethanes based coatings there are three ways to lower the level of organic solvents emitted from coating formulations:

1. High solid coatings (non-volatile matter: > 70wt.%)
2. Waterborne coatings
3. Solvent-free systems

These days a broad portfolio of low viscous polyisocyanates adducts exists to face new legislations ordering steady reductions in VOCs. These adducts contain oligomers with very narrow molecular mass distribution (in case of isocyanurate adducts) or they consist of compounds which principally achieve low viscosity (e.g. allophanates of long chain alcohols), but these have lower functionality[1]. Moreover, the use of hydrophobic polyisocyanates in waterborne applications will lead into disadvantages in terms of appearance e.g. gloss and other optical properties because of poor compatibility.

Duranate^{TM} TUL-100 has been developed to bridge all these gaps. This innovative ultra-low viscous HDI-Isocyanurate offers a compromise about NCO-functionality and rheological properties:

Table 1: Properties of various HDI-based hardeners (average values)

HDI-Hardener	Viscosity @25˚C [mPa·s]	NCO [wt-%]	Color (Gardner)
Standard Trimer (Duranate^{TM} TKA-100)	2,600	21.7	< 1
Low Viscous Trimer (Duranate^{TM} TPA-100)	1,400	23.1	< 1
Very Low Viscous Trimer (Duranate^{TM} TLA-100)	500	23.3	< 1
Ultra Low Viscous Trimer (Duranate^{TM} TUL-100)	300	23.0	< 1
Allophanate	100 - 500	15 – 20	

Duranate^{TM} TUL-100 will give coating formulating companies the opportunity to create waterborne systems based on a hydrophobic polyisocyanate with improved optical properties and keeping good mechanical as well as chemical resistance performance of the related film. In addition, high solid coatings can be formulated easily whilst a great contribution to VOC reduction will be reached.

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UV-crosslinkable polymer coatings

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West Pomeranian University of Technology Szczecin (Poland)

UV-crosslinkable polymer coatings comprising UV-crosslinkable pressure-sensitive adhesives for self-adhesive material industry und UV-curable lacquer for car body sheet or automobile industry.

The traditional deficiencies of hotmelt pressure-sensitive adhesives are due to the use of relatively low molecular weight polymers, which result in limited heat and plasticizer resistance. Crosslinkable hotmelt PSA acrylics that are designed to be crosslinked by UV or laser radiation are now available. These products offer high processing speeds, relatively low application viscosity, high resistance to plasticizers and solvents, aggressive tack, and very high heat resistance. UV-curable HMPSA acrylics are a second technology platform being offered for solvent replacement. This method for improving the physical properties of HMPSAs introduces a crosslinking network into the polymer system. UV-acrylic hotmelts consist of acrylic copolymers with chemically built-in photoreactive groups [1]. They are free of solvents and water and are processed in the form of hotmelts. Their molecular weight range (100000 to 250000 Dalton) and viscosities are sufficiently low to make the adhesives coatable with standard hotmelt equipment at processing temperatures of 120 to 160ºC. Specific applications usually demand adhesives with a defined adhesion to cohesion ratio. With UV-acrylic hotmelts, the adhesion to cohesion ratio can be varied within wide limits by controlling the amount of radiant energy applied to the adhesive film after it has been coated. Films formed by UV-acrylic hotmelts gradually become more cohesive as more radiant energy is applied, while their adhesion and tack decrease. The UV-dose can be controlled by adjusting the power of the lamps and the speed at which the substrate is passed under the lamps in the production plant [2].

Recent developments of new UV-curable polymer systems are based on new compositions containing urethane acrylates with incorporated unsaturated copolymerizable photoinitiators into polymer chain. The kind and amount of unsaturated photoinitiators has a significant influence on automotive coatings performance [3]. The new technical standard is presented by a new cure system due to advantages of lower volume shrinkage and curing of shadow areas. The change of mar and chemical resistance depending on the amount of UV curable components in a one pack automotive clear coat is shown. The influence of temperature and distance between lamps and the painted object has been investigated by the decrease of UV curable double bonds in a given dual cure refinishing clear coat.

References:

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Chrome-like Appearance and Optical Properties of Polymer Layers incl. Vacuum Metallized Pigments, VMPs

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Within the last 5 years a clear trend towards liquid metal or chrome-mirror effects was observed in product design [1]. Simulating the appearance of "pure metal" with paint layers containing metallic pigments is still common, but is concentrated on the “chrome side”. In order to achieve the desired chrome-like appearance, the most frequently used pigments today are VMPs (vacuum metallized pigments). They allow for outstanding optical effects, replacing environmentally harmful chromium-containing technologies like galvanization [2].
Dark-chrome effects can also be achieved applying polymer layers incl. VMPs in order to result in surfaces with a dark, chrome-like appearance. In this case, the use of thinner processed VMPs is needed to influence the optical translucence of these layers.
Since the optical properties of VMPs change dramatically below ca. 50 nm thickness [3], we have investigated this behavior using pigmented polymer films incl. VMPs of different thickness by means of UV-VIS spectroscopy. Light microscopy (refer to fig. 1) already confirms, that the layer thickness of Aluminum used in VMPs significantly changes their optical properties when falling short of a critical thickness. Therefore the selection of suitable VMPs is crucial for the realisation of coatings with chrome-like appearance properties.

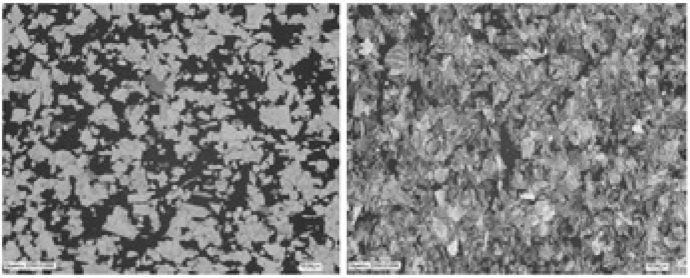

Fig 1 Light microscopy of Vacuum Metallized Pigments, VMPs, of different Aluminum-thickness in a polymer layer (PE/CAB)

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Thermal Resistance of Silicone-based Coating Systems

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Modified siloxanes are polymers presenting different advantages compared to organic materials: water repellency, weather resistance, slip surfaces, low viscosity and thermal stability. These resins can be incorporated inside coating formulation as main binder and lead to the formation of a strong and resistant film layer.
The thermal resistance of silicone-based coatings that will be discussed in that paper is a key property that produced several scientific papers.

Objectives
This paper reviews the mechanisms and parameters related to the siloxanes structures and coating formulations. 2 new binders were synthesized in our lab to fulfil actual specifications.

The effects of different components are studied:

- catalysts, and curing conditions in general,
- co-binders: long/short siloxanes, silanes, organic function,
- pigment loads and quality,
- specific additives that may even enhance the final properties of the coating with potential energy savings,

will be investigated.

TGA analyses showed that not only the final residue at temperatures >900°C is important information, but also the temperature of initial degradation, the rate of degradation.
The binders that are proposed have a positive impact on the VOC level and do act positively for environment.
That technical paper lists and evaluates different parameters in order to better understand the mechanisms of resistance.

Novel high efficient NISAT thickeners

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Elementis GmbH, Cologne, Germany

The impact of rheology modifiers on paint and coatings formulations continues to be inmeasurable. Especially in architectural coatings the choice of rheology modifier typically determines the final paint and film properties. Rheology modifiers used in architectural paints include cellulose-based watersoluble polymers (HEC), polyacrylic based (H)ASE and nonionic synthetic associative thickeners (NISAT). Paints with NISAT thickeners exhibit improved performance in sag and levellig, moisture resistance, spatter resistance and coverage. The thickening action of NISAT thickeners is predominantly determined by the interactions of the hydrophobic end-caps with the surfaces of the hydrophobic particles in a paint, forming a network structure with the latex particles mainly.

Continuously lower VOC targets for paints and coatings have forced latex manufacturers to develop low- and zero VOC latex systems. The morphology and stabilization of these newest generation of low VOC latexes however has resulted in an adverse effect on the thickening efficiency of associative thickeners. A marked increase in the level of these associative thickeners is required to achieve the targeted viscosity specifications . To this end Elementis Specialties is continuously developing associative thickeners that are unique in architecture and that provide the formulator with flexibility and solutions to thickener efficiency. This paper will present the newest generation of NISAT from Elementis Specialties that display a very significant decrease of the required amount of thickener to reach the targeted viscosity specifications, without adversely effecting the paint and coatings application properties.

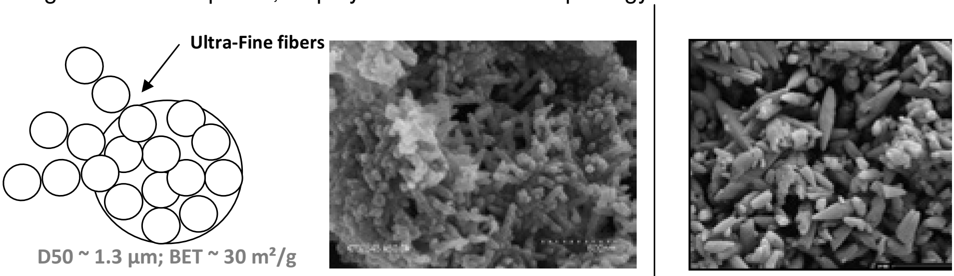
3.25

Socal® UP: an Innovative High Performance Precipitated Calcium Carbonate to reduce TiO_2 content in Emulsion Paints

Persyn, Olivia; Solvay, Salin de Giraud (France)

Paint industry is facing major challenges with the increased demand for sustainability, quality and cost savings on raw materials, especially for Titanium Dioxide (TiO_2).
For this reason, a new Ultra-Fine Precipitated Calcium Carbonate (PCC) has been developed to achieve outstanding dry opacity performances at low gloss and substitute TiO_2 in matt emulsion Paint application, providing significant costs savings and drastic reduction of carbon footprint.

This new high performance functional additive, SOCAL® UP, displays a unique morphology with Ultra-Fine fibers made of calcite pseudo-spherical shapes in a microshell structure, as shown on the following figure. In comparison, the standard PCC grades used in paints, display scalenohedral morphology.



SOCAL® UP

Standard PCC

Figure 1: SOCAL® UP morphology vs standard PCC morphology

With this innovative morphology, SOCAL® UP provides excellent performances in paint with high dry opacity at low gloss and high TiO_2 substitution level.
Based on results obtained in a broad range of paint formulations with PVC > 50 %, different TiO_2 content, filler package and type of binder; the performances of SOCAL® UP to substitute TiO_2 can be summarized as follow:

Paint formulation	TiO_2 level	% TiO_2 substitution by SOCAL® UP (same dry opacity)
Low cost paint	3 – 5 %	20 %
Medium quality paint	6 – 13 %	60 %
Premium quality paint	14 – 25 %	50 %

This high TiO_2 substitution level by SOCAL® UP can be attributed to concomitant parameters:

- Its unique morphology: the Ultra-Fine fibers bring intrinsic dry-opacity characteristics to SOCAL® UP, thanks to random orientation and high porosity in the paint.
- The extender effect: opacity is maximized thanks to the extender effect with TiO_2.

Thanks to these exceptional properties, SOCAL® UP offers significant cost savings up to 40% on filler package with substitution of 60% TiO_2 content.

Finally, SOCAL® UP will help reducing drastically (almost 80%) the carbon footprint compared to TiO_2, which is a key factor for sustainability and CO_2 footprint of paint companies.

To conclude, this innovative SOCAL® UP, with its unique morphology, offers excellent performances in emulsion paints:

- Increase of dry opacity at low gloss.
- Potential for high level of TiO_2 substitution (up to 60% for 1:1 replacement).
- Significant cost savings.
- Better sustainability with 80 % carbon footprint reduction compared to TiO_2

Next generation silicone antifoams: structure property relationships in low VOC binder systems.

Juan Carlos Corcuera, Bertrand Lenoble, Jerry Witucki.

Dow Corning Europe SA, Seneffe (Belgium)

With the reduction in VOC in waterborne binders the challenges of defoaming during production and especially application are increasing yet formulators in many (industrial) segments are hesitant to use silicone chemistry due to the history of Polydimethylsiloxane (PDMS) based systems. This study explores the structure property relationship of silicone polyether based antifoams and their ability to help defoaming performance in the journey to high performance, low VOC coatings.

Objectives:
In this study we compare the performance of silicone based antifoams with varying architectures and delivery systems for their impact on defoaming in paint production all the way to application. Comparisons are made to the traditional PDMS based materials and the benefits of high compatibility silicone polyether systems. We are intent on exploring the myths about silicones in modern coatings.

Methods:
Silicone defoamers were formulated into a range of low VOC binders, coatings and inks formulations during the various stages of paint production and diverse application conditions.

Results:
Application data shared in this paper will demonstrate how the silicone polyether based antifoam technology offers benefits over traditional PDMS based systems and traditional organic based antifoams.

Conclusion:
This study will offer the industrial and architectural formulator the chance to break out from the anti-silicone mindset and see the benefits of highly effective and yet highly compatible defoaming technology targeted at modern VOC binder and paint systems.

Life After Pyrrolidones – Achieving Hard Coatings Without Increasing VOC's.

C.Evans, I.Martin, C.Smart

Incorez Preston (England)

Pyrrolidone solvents such as NMP and NEP, have been a mainstay of the coatings industry for many years. They allow hard coatings to be prepared at low levels of VOC's without the addition of coalescing solvent. As legislation becomes increasingly restrictive on the use of these harmful solvents however, the future of the coatings industry requires ways of formulating around this change.

Currently, hard pyrrolidone free coatings are either high in VOC or require the post-addition of coalescing solvent to achieve film formation at ambient temperature or below. Although useful as a temporary means of removing pyrrolidones, this does not provide a long term solution.

In this presentation, Incorez present the knowledge needed to produce hard pyrrolidone free coatings with minimal VOC and no health hazards. This enables ambient temperature film formation with no additional cosolvent requirements. Using the information provided, formulators will be able to meet the increasingly tough performance requirements demanded of them, whilst reducing their environmental impact.

Lectures

Advances in coatings and inks sciences/ Crosslinking and hardening

Carbon Fiber Reinforced Plastic – A Challenge for Surface Treatment and Painting

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Fraunhofer Institut für Fertigungstechnik und Angewandte Materialforschung – IFAM, Bremen

Carbon-Fiber Reinforced Plastic (CFRP) is a material of growing importance in several industrial sectors like aerospace, wind energy and car manufacturing. CFRP has some unique properties, in particular the excellent toughness – weight ratio, but in terms of surface treatment and coating it turned out to raise some very specific challenges. Examples are:

- Galvanic corrosion

Fig. 1: Severe corrosion in aluminium/CFRP combinations after salt-spray test

Often CRFP is combined with metallic materials like aluminium. Direct contact of CFRP with metallic parts may negatively influence their corrosion behaviour due to the electrical conductivity, very high electrochemical potential and non-metallic surface chemistry of carbon fibers. In these cases the carbon fibers act as cathode and the metal as anode. The result is a fast degradation of the metal (figure 1). There are several approaches to tackle this problem with paint-based technologies.
In case of electric and galvanic contact, e.g. caused by small coating damages, the electrochemical corrosion system is subjected to a comprehensive modification and even the protection effect of highly efficient inhibitors like chromates may be severely impaired or completely lost [1]. Hence, new strategies are needed to overcome these problems and limitations inherent in CFRP-metal hybrid constructions under technically feasible conditions.

- Cracking and delamination

The key applicator of CFRP for components is the aviation industry. The cracking and delamination of the paint built up [2] on CFRP parts of commercial aircrafts causes serious problems. Some hypotheses describe why the conventional paint built up is stable for years on Aluminum substrates under hard environmental conditions and fail on CFRP substrates. Fraunhofer IFAM is investigating these phenomena to figure out the reasons for the occurring cracks and delamination. Besides a lab scaled test will be developed to find remedies.

- Telegraphing

Using CFRP for special applications like automotive class-A surfaces or aerodynamic airfoils with strict requirements for surface smoothness causes another challenge. Due to the different thermal expansion behaviour between carbon-fibers and resin-matrices the patterns of the fiber-fabric occur on the surface [3] (figure 2). This phenomenon is known as "Telegraphing".

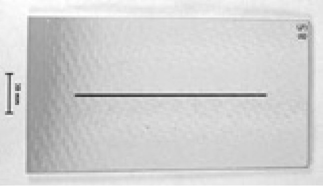

Fig. 2: "Telegraphing" on a painted CRFP sample

For the described challenges the status of current investigation projects and the proceedings to solutions will be presented.

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2.11

SOME SURFACE PHENOMENA AT FORMATION OF COATINGS

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Formation of thin polymeric layers from solutions of oligomers or polymers occurs in most cases in conditions of the unsteady surface tension on interfaces of polymer with substrate and air. Non-equilibrium of values of the surface energies is defined by a ratio of speeds of initial curing, evaporation of solvents and diffusion of the components possessing in a greater or lesser degree surface activity. Especially strongly it is shown at formation of coatings from water solutions of oligomers, water dispersions of oligomers or polymers. Non-equilibrium of the condition is shown more strongly at drawing such coatings on a polymeric substrate.

Pigmented (filled) materials and the polymeric coatings formed from them on surfaces of this or that nature, are micro and ultra heterogeneous systems with extremely high specific surface. The majority of properties of such systems is determined by physico-chemical interactions on interfaces of phases. Acid-base balance and electric charge of the surface of particles of pigments, fillers and substrate render significant influence on adsorption processes in pigmented systems. Alongside with establishment of the Hammett acidity functions distribution of the acid-basic centers and isoelectric points of a surface, use of the concept of hard and soft acids and bases by R.Pearson (HSAB theory) is useful. The knowledge of kinds and concentration of the acid and basic centers on a surface of pigments and fillers, and also on substrate, makes it possible to predict adsorption processes, both at preparation of compositions, and at formation polymer layer on substrate.

Thermodynamic quality of solvents, as a rule, combined, continuously changes during formation of polymeric coating because of various volatilities of individual components. Process of evaporation of components of solvent can be accompanied by sharp change of its thermodynamic quality on local sites of the formed coating and cause occurrence of micro inhomogenety and deformed Benard cells. At the same time change of structure of solvent simultaneously with selective adsorption of components allows to prepare self-stratifying polymeric coatings with various functions of layers.

The acid-basic properties of surfaces of a substrate, pigments and fillers are especially important for the formation of coatings using acid or basic catalysts, cross-linking agents with high reactivity, the basic or acid neutralizing agents, ionogenic surfactants. Chemisorption of chemically active components changes curing time and affects the internal stress in the coatings and surface relief. Adsorption of components on the surface of substrate not only affects the adhesion of the coating but also provides orienting action during the formation of coating.

Particles of pigments or fillers on which surface sites strongly distinguished on polarity alternate form a net in volume of the polymeric film which can create the certain relief on the coating surface.

Innovative Technologies and Techniques for Enhancing the Application of Architectural Coatings

Tara Lyn Conley and David Fasano

The Dow Chemical Company, North-East Technology Center, Collegeville, Pennsylvania, USA

Obtaining a smooth, uniform paint finish with a minimum number of coats is an ongoing consumer demand in the Do-It-Yourself (DIY) market segment of architectural paints and coatings. In the white and pastel formulation space, minimizing coats has traditionally relied on maximizing intrinsic hide in the laboratory as measured by the Contrast Ratio of a uniform draw down. Polymeric hiding technologies offer an effective route to increased intrinsic hide, while controlling the use of titanium dioxide (TiO_2). Relying on this method alone, however, overlooks the impact of rheology and application on applied hide and final appearance. Newly introduced hydrophobically modified ethylene oxide urethane (HEUR) rheology modifiers offer performance properties that can enhance applied hide. Even greater gains in the cost-efficiency and performance balance can be achieved by looking at the collective impact of polymeric hiding technologies, rheology modifier technologies and roller application. By using these raw materials and formulating techniques to maximize film thickness and uniformity, other properties can also be improved. Film characterization tools, formulation options, and quantitative demonstrations on the impact of raw material choice and film uniformity to achieve the desired hiding and performance benefits will be discussed.

KEYNOTE LECTURE 2.13

Silicone ceramizable rubbers. New solution for the emerging coatings

Maria Zielecka

Industrial Chemistry Research Institute, Warsaw, (Poland)

The state-of-the-art in the field of ceramizable silicone rubber-based composites designed for the emerging applications will be reviewed. The most important area of their application are coatings for fire resistant electrical cables with functions maintenance under fire conditions what is very important from the safety point of view for human beings and expensive electronic equipment. Materials based on silicone rubber exhibit high thermal resistance, but the problem concerns their mechanical durability under flame, maintaining circuit integrity and energy supply during fire, indispensable to secure time for evacuation. Integrity of electrical cables can be obtained by application of insulating coatings made of polymer composites ceramizing at high temperature arising during fire. The ceramic barrier should protect copper wire inside the cable against heat transfer leading to melting and against water used in sprinkler systems. Moreover, it should exhibit good mechanical strength assuring integrity of electrical circuit. Usually the coating is composed of mineral filler particles, combined with a fluxing agent. Using different crystalline additives it is possible to assure the proper course of the composite degradation and its transformation during ceramization process. The key problem to achieve the proper insulating properties is connected with the microstructure of the ceramized layer which is formed in the temperature range of 600 to 800° C when two main types of transformations are occuring: thermal degradation of silicone rubber and sintering of ceramization of inorganic fillers. Silicone rubber-based ceramizable composition should be designed to achieve low porous ceramized layer formed in the reaction between silicone rubber degradation products and inorganic fillers. During thermal degradation of silicone rubber containing chalk the following reactions are occurring:

$$\textit{Silicone rubber} \xrightarrow{\text{degradation temp.} > 500^\circ\text{C}} SiO_2 + \textit{cyclosiloxanes}$$

$$CaCO_3 \xrightarrow{\text{degradation temp.} > 600^\circ\text{C}} CaO + CO_2$$

$$CaO + SiO_2 \xrightarrow{\text{degradation temp.} > 800^\circ\text{C}} CaSiO_3 \text{ (Wollastonite)}$$

$$2CaO + SiO_2 \xrightarrow{\text{degradation temp.} > 800^\circ\text{C}} CaSiO_3 \text{ (Larnite)}$$

Calcium silicate formed during thermal decomposition containing predominantly fibrous wollastonite structure gives good mechanical properties to the ceramized layer. The effect of other fillers as well as silicone rubber crosslinking density will be presented and discussed based on the results of ceramised layer supermolecular structure examination by using SEM, AFM and high resolution SEM as well as ceramization process studied by thermal analysis, DSC and cone calorimetry.

This work has been financially supported by projects No PBS2/B4/7/2013 financed by The National Centre for Research and Development in Poland

Sustainable UV-protection of coating layers using nanoscale organic and inorganic components

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Fraunhofer Institute for Manufacturing Engineering and Automation (Germany)

It is generally accepted, that photochemical degradation processes in coating layers are initiated by the absorption of UV light.

In protective industrial and automotive coating systems, the properties of multilayer systems do not only depend on the physical and chemical properties of the single layers, but also on their sometimes complex interactions. Current automotive multilayer systems consist of an e-coat (mostly a cataphoretic coating), followed by a primer surfacer, a basecoat, and a final clear coat layer. For protective coatings on metal constructions also multilayer coating systems, consisting of a primer layer directly applied on the metal substrate, optional intermediate layers and a top coat layer on the surface are in use. In both cases of these multilayer protective coatings, it is mostly the primer or the e-coat layer, directly applied on the metallic substrate, which shows the most serious photochemical degradation effects when, the multilayer coating system is exposed to atmospheric weathering. Serious consequences like adhesion problems, peeling and finally corrosion processes of the metal substrate will be the outcome for coating systems with less sustainable and effective UV-protection properties.

Therefore, a strong need for UV-protective coatings with a high sustainability exists.

In the presented study, a combination of inorganic and organic nanoscale components was used in the top coat or clear coat formulations in order to enhance the sustainability of the UV-protection in multilayer coating systems.

The degradation experiments were performed by artificial weathering of the coated samples using a Weather-O-Meter equipment (Ci 4000, Atlas Material Testing GmbH).

For the characterization of the obtained degradation effects a confocal Raman microscope and a FT-IR microscope were used. The photooxidative degradation of e-coats in different automotive multilayer coating systems was investigated by evaluation of the photooxidation index (POI). For the photooxidation index measurements special flat cross sections of coatings were prepared and the IR-measurements were performed on the original and on the corresponding weathered multilayer systems.

With the use of Raman- and IR-spectrometric characterization methods, it could be clearly shown, that the concentration of organic UV-protection components like hindered amine light stabilizers (HALS) and conventional organic UV-absorbers in top and clear coats decrease over time by degradation and migration effects, when the protective coating layer is stressed due to artificial weathering.

As a main result of the performed investigation, it could be proofed, that an optimized combination of nanoscale inorganic and organic UV-protective components clearly increase the UV-protection properties of top and automotive clear coats by deceleration of the photochemical degradation processes as well as by inhibiting the migration of organic UV-protection components, as a direct consequence of the increased barrier properties of the nanoparticle containing coating layers.

Automotive application processes: a focus on molecular migration

Dr. A. Andersen

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In an effort to become more sustainable, the automotive market is currently drifting away from its classical paint processes to move towards more efficient, faster and eventually environment friendlier ones. In this sense, we observe today a penetration of wet-in-wet processes in the market. As a consequence, drying times become shorter or completely disappear, layer thicknesses are modified and the technology in itself is changed, as the classical primer layer is vanishing. Moreover, the trend goes also to low curing temperature processes, influencing cross-linking reactions occurring within the layers. These shifts in processes have indubitably consequences on the molecular interactions taking place within the film build.

Thus, phenomena like molecular migration or solvent exchanges through the complete film build are gaining in importance and show a stronger influence on the paint performance. It is therefore meaningful to consider the film build as an ensemble, rich in chemical and mechanical interactions, beyond the classical layers system. Understanding these interactions enables us to take the next step in coatings functionalities.

Following this mind-set, we demonstrate by means of analyses the importance of migration related to wet-on-wet and low temperature processes. We also demonstrate how it is possible to take advantage of such phenomena in order to improve macro-properties in a film build, like appearance or adhesion.

Advanced rheology for waterborne paints, the key to good flow and application properties.

J.M. Akkerman, R. Adolphs, R. van Egmond, J. Goossen, A. Roelofs, R. vd Horst, M. Bosma and D. Mestach

Nuplex Resins BV, Bergen op Zoom (the Netherlands)

Waterborne trim paints have been developed up to a level where they are essentially equal in performance to solvent based alkyd trim paints. As an additional benefit, they have fast drying and non-yellowing characteristics. Their durability is close or equal to that of super-durable alkyd paints. However, waterborne trim paints still lack the excellent application properties of solventborne alkyd paints, thus leading to a lack of flow, levelling and open time. Solutions to overcome these problems often lead to higher VOC or use of alkyd emulsion hybridization and as a consequence lead to yellowing, slower drying and softer films. The solution Nuplex developed is based on tailor made rheology control by a new class of acrylic-acrylic hybrid polymers improving flow and levelling during drying. Inferior flow, levelling and open time of waterborne trim paints with (very) low VOC is due to the adverse viscosity development during drying. In other words, the adverse rheology flow diagram with increasing solids content leads in a very early stage of drying to a steep increase of both low and high shear viscosity as a function of increasing solids content. The flow, levelling and open time can be improved substantially if this steep viscosity increase can be delayed during the drying process. In this paper this effect will be discussed from a theoretical perspective, supported by experimental results. Based on the fundamental theoretical insights obtained from these studies, a novel binder concept was developed that offers superior application properties combined with all the advantages that all-acrylic binders have to offer.

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2.17

Influence of matting on the properties of powder epoxy-polyester coatings

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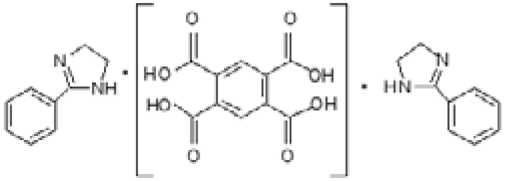
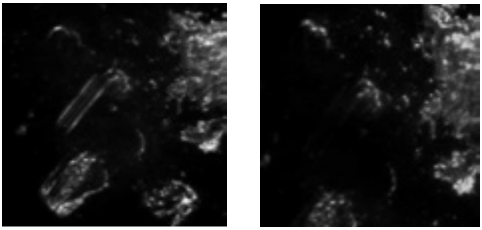
Polymer matrix of hybrid powder coatings is a mixture of epoxy oligomere and polyester. Matting agent is 4,5-dihydro-2-phenyl-1H-imidazole-1,2,4,5-benzatetracarboxylat,



which serves as an acid curing agent for the epoxy oligomere.

The rate of interaction of the crosslinking agent carboxyl groups with the epoxy is higher than the rate of interaction of the same group with polyester, since the catalytic action of the imidazole ring, having a basic character and in salt form associated with pyromellitic acid. In addition, interaction of the low-molecular acid with oligomere is higher due to greater mobility than units of high-molecular compound, which is characterized by certain acid value. Matting realizes by of advanced formation crosslinked epoxy polymer by matting agent. This polymer is incompatible with epoxy-polyester polymer formatted later. Depth curing for model systems with different content of matting agent is defined to study the effect of matting agent for curing epoxy-polyester compositions by extraction of films using Soxhlet extractor. It can be concluded that cure depth of coatings decreases with increase the content of the matting agent. It may be due to the fact that by increasing the content of the matting agent increases the proportion of linear epoxy oligomere, which can partially dissolve in acetone at Soxhlet apparatus extraction. Ultramicroscopic studies have shown that polymer aggregates, which incompatible with epoxy-polyester matrix, formed and have a crystalline structure. The crystalline nature of the formed epoxy polymer particles confirmed by matte coatings micrographs in polarized light (Figure 1). The surface topography is formed by aggregates composed of single crystals polyepoxide.



a b

Figure 1: Photomicrographs of crystal aggregates and epoxy polymer in polarized light (a) in crossed nicols (b) (3000^x).

As the amount of the resulting epoxy polymer, which incompatible with epoxy-polyester polymer, depends primarily on the amount of cross-linking agent, we studied the influence of matting agent on the optical density of unpigmented compositions. Optical density in this case is defined by scattering. Matting depends on surface topography, emerging as a result of the formation of particles of epoxy polymer - the reaction product of epoxy oligomere with matting agent. Matting agent introduction does not practically change the character of the absorption spectrum, causing only hyperchromic effect. The epoxy polymer phase formation does not alter the selective absorption of the polymer body.

Effect of matting on the physical-mechanical properties of powder materials were considered by the example of white powder paint with different content of the matting agent. Matting agent added in an amount up to 5 % leads to decrease of gloss, a further increase of its content practically unchanges gloss of coatings.

Powder paints were applied to the pretreated metallic plates by electrostatic spraying to carry out the physical-mechanical tests. It should be noted that matting has led to increase of durability and elasticity of powder coatings. This may be a consequence of increasing of proportion of linear epoxy polymer.

Hyper-branched structures for new functional additives

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Additives are an important ingredient in the formulations of coating systems.
Therefore, further development is ongoing to create increased benefits and new functions.
New highly branched and hyper-branched structures can provide properties which were not possible before. An important difference of these branched structures in comparison to linear types is a much lower viscosity which allows developing solvent-free additives for environmentally friendly systems. Higher content of functional groups leads to increased crosslinkability, no migration and long lasting effects.
Moreover, branched surface additives that are based on the macromer technology show higher mobility and orientation to the surface.

High slip and Easy-to-Clean properties are observed with additives that provide strong reduction of surface tension in liquid and low surface energy in dried coatings. However these coatings show poor intercoat adhesion to the next layer. Until now it has only been possible to either reduce the surface energy of cured coatings by adding silicone additives or to maintain its original level by adding acrylate leveling additives.
Using new branched hydrophilic molecules derived from the macromer technology it is possible to design structured additives so that the surface energy of cured coatings can now even be increased! As a result of this unique combination of structures and properties, new possibilities in terms of surface modification are opened and properties such as hydrophily, intercoat adhesion, antifogging etc. can be obtained.
Such additives increase the surface energy of cured coatings overall, especially the polarity resulting in an improvement in the wetting and intercoat adhesion to following layers such as in paints, lamination foils, adhesives, printing inks etc.. Additionally, improved leveling of the system can be observed.

Another example for the use of hyper-branched structures are wetting and dispersing additives. Pigment-affinic groups of additives which are essential to provide excellent wetting and stabilization of organic pigments are often amine-based. Due to this fact, an undesired interreaction with hardeners or catalysts could occur which might lead to shorter pot-life in 2-pack Polyurethane or gellation of Epoxy-based systems. Spherical polymers with „sterically hindered“ aminic pigment-affinic groups can be offered as solvent-free products without any influence on pot-life in 2-pack -PU or acid-catalyzed systems in comparison to linear products based on similar chemistry. A new core-shell-structured polymer with „encapsulated“ aminic pigment-affinic core is especially developed for Epoxy systems, but can be used in other solvent-borne reactive systems as well.

Further developments are ongoing for new effects with new functional additives based on hyper-branched structures.

PHOTOINITIATED CATIONIC POLYMERIZATION: CURRENT DEVELOPMENTS AND FUTURE PROSPECTS FOR COATINGS

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Photoinitiated polymerizations are of increasing interest today because they address a number of energy, economic, environmental and social issues currently of major importance to the world. These polymerizations are currently employed in many industrial coatings; adhesives and printing ink applications and can essentially eliminate air and water pollution since solvents are not required. Further, their energy requirements are only a small fraction of that required for the traditional thermally induced polymerizations that they replace. Past and present work in this laboratory has focused on the development of novel classes of photoinitiators that make it possible to carry out photoinitiated cationic polymerizations under UV and visible light irradiation. At the present time, much of the effort in this laboratory is being directed towards tailoring the structures of these photoinitiators to the specific wavelengths emitted by arc lamps, lasers and LEDs, as well as visible and solar light sources. In addition, we have undertaken the design and synthesis of several novel classes of cationically polymerizable monomer and oligomer systems which can be photopolymerized using cationic photoinitiators. The lecture will describe some of the ring-opening monomer systems that are currently under investigation in this laboratory and efforts to enhance their efficiency and utility. Of special importance are monomers and reactive oligomers derived from biorenewable sources. The use of photoinitiated cationic polymerization in a number of current commercial coating applications including 3D imaging and ink jet printing will be illustrated during this presentation.

2.20

Efficiency of Near Infrared Curable Coating Systems via Radical Photopolymerization

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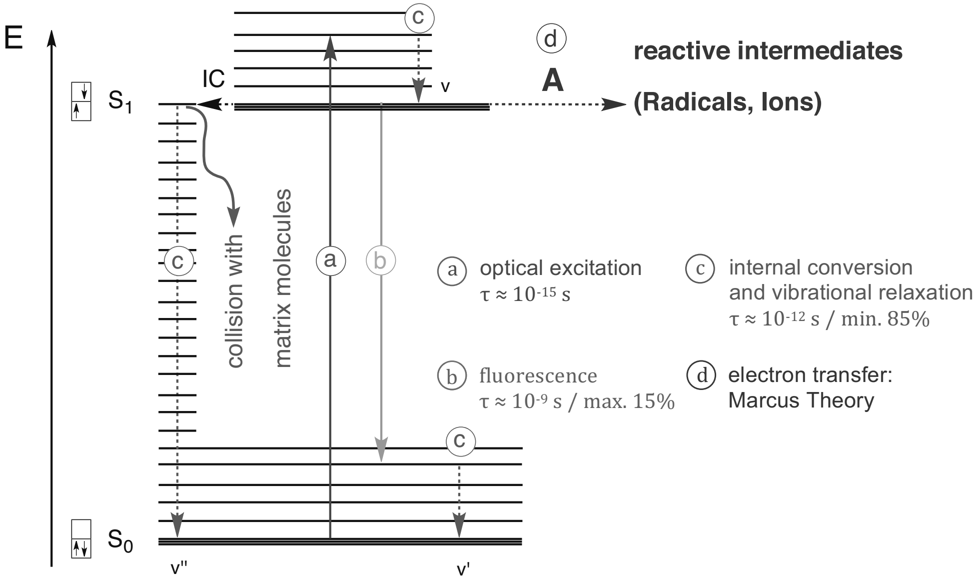
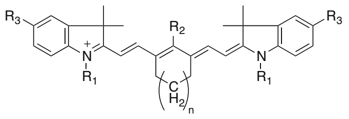
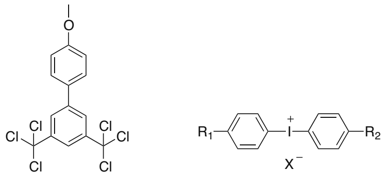
The near infrared (NIR) induced photoinitiated polymerization of reactive diluents, resins, and powder coatings was analyzed using different exposure and characterization techniques. The initiator system generates initiating radicals and cations by electron transfer from a NIR light absorbing sensitizer (**Sens**) to an acceptor (**A**) after decomposition of the products. The absorption and relaxation processes of the **Sens** and the efficiency of electron transfer influence the sensitivity of the entire initiator system. Nevertheless, radiationless deactivation can be seen as the major deactivation process. Thus, these photoinitiator systems possess a certain hybrid function; that is the photonic generation of initiating species and the generation of heat by deactivation of the excited state. **Sens** may therefore also function as an absorber. Information about reactivity and conversion of the resin are accessible by Photo-DSC and FTIR measurements.



General structure of the sensitizer (**Sens**)



General structure of the acceptor (**A**)



The photocalorimetric and FTIR measurements exhibit the efficiency of the initiators in different model resin systems. This depends on the nature of the matrix, e. g. polarity and viscosity. Furthermore, the solubility of both the sensitizer and the acceptor as well as the mobility of the dissolved molecules are highly influenced by the polarity. In matrices like molten powder coatings, initiation and polymerization are strongly controlled by the mobility of the active initiating species.
Initiator systems containing sensitizers with (thio-)barbiturate in R_2 position show a good performance. These sensitizers exhibit within the series of polymethine dyes the highest solubility in the model resins investigated. This may attributed by the fact that these dyes can be formally seen as neutral material having no charge. Nevertheless, many resonance structures are available contributing to the overall solubility and reactivity in the coating.
New light sources have been tested to maximize energy efficiency by ideal overlapping of the emission and absorption of the sensitizer. Typical light sources are NIR-LED arrays and/or NIR semiconductor lasers. The latter provides higher radiation energy for exposure, and has been named as laser sword technology. The Heidelberger Druckmaschinen AG successfully introduced this methodology in offset printing.

Acknowledgement: We thank the BMWi for financial support (ZIM cooperation project PhoREnPol; project number KF2914003BN2); Sensitizers were received from FEW Chemicals GmbH (www.few.de) as a scientific gift. We furthermore acknowledge Dr. M. Schlörholz and U. Ernst from the Heidelberger Druckmaschinen AG providing the opportunity to carry out the laser exposure measurments at 808 nm.

Tuning the mechanical performance of polyurethane UV cured coatings: modifying the composition of reactive diluents

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UV cured coatings attract considerable attention in science, technology and in industry, such as automotive, architectural and packaging. Main benefits of UV coatings compared to coatings obtained using other energy sources are their environmentally friendly nature, shorter curing time, presumably lower energy consumption, longer pot life and other [1-2]. Despite some challenges related to UV cured coatings that need further investigation and new solutions, the market of UV cured coatings is growing.

For optimisation of a composition for UV cured coatings, it is of interest to investigate the effect of reactive diluents on the structure and properties of the coatings. To tune the performance of UV cured coatings based on polyurethane oligomers, the structure and properties of the coatings were modified by altering the amount and functionality of acrylic reactive diluents, without changing the nature of oligomers. The proposed approach of modifying the coating structure affecting the mechanical properties, rheological behaviour and adhesion of the coatings has benefits due to a possibility of maintaining the advantages of the selected chemical structure of the oligomer.

The effect of a composition of two-/three-functional low-molecular weight reactive diluents on the curing kinetics, rheological behaviour, mechanical properties and adhesion of UV cured coatings applied on polymer substrates has been systematically investigated. The changes in the properties are related to alterations in the curing process and in the structure of the coatings.

Traditionally, except for only a few approaches described in the literature [3-4], monomers are used in compositions for UV coatings mainly for improvement of the technological characteristics of the coating application, related, mainly, to their rheological behaviour. New findings demonstrate, in addition to an exponential decrease in viscosity and a proportional growth of enthalpy of the exothermic photo-polymerization reaction during coating formation, alterations in other coating properties with increasing content of a reactive diluent.

Changing monomer contents leads to alterations in the coating structure, a gradual increase of the glass transition temperature and changes in elasticity and other mechanical properties of the coatings. This corresponds to a gradual improvement of coating adhesion to a polymer substrate. The relation between the rheological behaviour, mechanical properties and adhesion of coatings has been demonstrated.

Based on the results of the study, the desired properties of UV coatings can be modelled and controlled without changing the nature of a particularly selected oligomer, thus maintaining its benefits in a coating composition.

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Improving the Efficiency of Photocatalysts

Heinz-Christian Krempels Dr., Christian Scheidt, Brigitte Vielhaber-Kirsch Dr.

KRONOS INTERNATIONAL, Inc. Leverkusen (Germany)

The photocatalytic reaction is not an academic masterpiece anymore. Applications in façade paints, concrete, plasters, paper, glass and metal coating, laminates etc. are viable and economic realities in the private and public sector. [1]

Efforts were made to improve the interface photocatalytic reaction by offering the market photocatalysts with high specific surface which harvest mainly the energetic UV part of the solar spectrum. Doping the same with organic precursors (like in KRONOClean 7000) extends the effective transformation of light into chemical energy towards the visible light segment. [2]

Nonetheless there have been a series of requests concerning the activity decrease or complete deactivation when photocatalysts of each kind were incorporated in the application media. In most of the cases the deactivation was caused by either one of the two parameters:

- insufficient catalyst dispersion causing lower active surfaces hence lower catalytic activities than expected and
- shielding the catalytic surface by matrix components leading to lower performance as well

To compensate for these drawbacks, liquid forms were developed with photocatalysts in a ready made, standardised dispersion state. Special powder forms were created to increase the porosity of the application and lift the photocatalyst at the surface of the substrate, at the same time preserving the catalyst adhesion and persistence in time.

This presentation will outline the main features of photocatalytic products based on titanium dioxide TiO2, new progress made in improving the photocatalytic reaction by liquid intermediates and photocatalytic powder additives for building materials [3] (see fig. 1) as well as recommendations for their application.

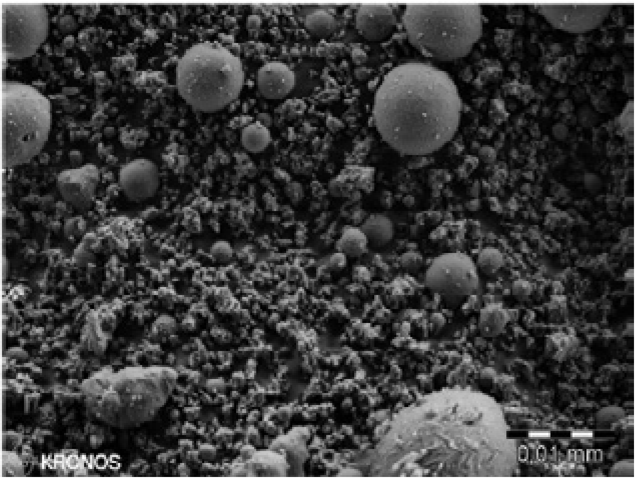

Fig. 1: Electron micrograph of the building material powder additive Photoment ®

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2.23

Iodonium Salts Comprising Different Cations and Anions: Effect of Solubility in Coatings, Reactivity in NIR-Photopolymers and Toxicological Aspects

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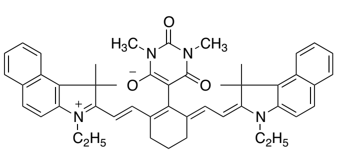
Photopolymers have received gained importance in coating sciences due to their multifunctional properties as chemical drying method resulting in a huge saving of energy. Beside the well established UV-technology, photopolymer systems using NIR radiation to initiate radical polymerization may be of interest for systems in which UV absorbers or yellow pigments are embedded. NIR-photopolymer systems have been known in the graphic industry for the use in lithographic plates for more than 15 years.

Thus, we investigate the efficiency of some NIR-photoinitiator systems comprising as sensitizer the NIR-dye (**1**) and as electron acceptor an iodonium salt (**2**). Such a combination initiates well radical polymerization in some model coatings. One major focus was also the solubility of **1** and **2** in coatings of different polarity and viscosity. Particularly, the introduction of the $[CF_3SO_2NSO_2CF_3]^-$ anion resulted in a giant solubility of the iodonium salt. Some of the iodonium salts were obtained as liquids, which were completely compatible with the resins used.

1



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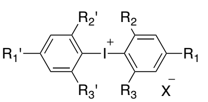

X^-: PF_6^-; SbF_6^-; NO_3^-; $B(Ph)_4^-$; $B(CN)_4^-$; $CF_3SO_3^-$; $C_4F_9SO_3^-$; $C_{12}H_{25}$-Ph-SO_3^-; CH_2=CH-Ph--SO_3^-; $(CN)_2N^-$; $(CF_3SO_2)N^-$; Benzilate; Lactate

R_1,R_1': -O-*i*-C_5H_{11}; -O-*i*-C_8H_{17}; -*i*-C_3H_7; -CH_3; -*t*-C_4H_9

$R_2;R_2'$: H; -*i*-C_3H_7; -CH_3

$R_3;R_3'$: H; -CH_3

Multifunctional model monomers were taken to study the photoinitiated crosslinking by a synchronized photo-DSC setup using an LED-array emitting at 790 nm. The monomers used were acrylates derived from poly(ethylene glycol), tri(propylene glycol), hexanediol, and trimethylpropane. The anion of **2** influences the reactivity of such photoinitiator systems. It was derived either from organic or inorganic matter resulting in a different solubility in the monomers chosen. The better the solubility the higher reactive the system. In particular, the anion $[CF_3SO_2NSO_2CF_3]^-$ with bis(4,4'-*t*-butylphenyliodonium) cation results in an unexpected high reactivity in the coatings being larger compared to tetraarylborates ($B(Ph)_4^-$), which have been widely applied in different coatings for digital imaging. This correlates well with the solubility of the iodonium salt in the acrylates, which can be several 100g/L in case of the iodonium salt comprising the $[CF_3SO_2NSO_2CF_3]^-$-anion.

The different substitution of iodonium cation does not only result in a different reactivity and solubility. It may also deeply change the physical appearance. Thus, the iodonium cation with diisopropyl-substituent comes out as an oil – while all other iodonium salts were obtained as solids after anion metathesis with the $[CF_3SO_2NSO_2CF_3]^-$-anion.

Moreover, our NIR photoinitiator system comprising **1** and selected combinations of **2** possesses the capability to obtain a curing depth of more than one centimeter in industrial coatings. This can be seen as one main benefit compared to UV-systems although the curing sensitivity is slower.

Some of our iodonium compounds are new materials with unknown toxicological properties. The cytotoxicity of some photoinitiator components was evaluated with a colorimetric assay (MTT assay) using **C**hinese **h**amster **o**vary (CHO) cells. The sensitizer **1** and **2** with either the $[CF_3SO_2NSO_2CF_3]^-$-anion or the $B(Ph)_4^-$-anion were evaluated. The cation of **2**, Bis(*t*-butyl-phenyl iodonium), was not changed. The results clearly showed a less toxic behavior of the $[CF_3SO_2NSO_2CF_3]^-$-anion compared to the $B(Ph)_4^-$-anion. According to our experiments, the latter can be seen as slightly toxic within the concentration range used in commercial photopolymerization formulations while the assay shows no cytotoxicity of an iodonium salt with $[CF_3SO_2NSO_2CF_3]^-$-anion. Exposure of the photoinitiator system showed no increase of cytotoxicity.

Acknowledgement: We thank the BMWi for financial support (ZIM cooperation project PhoREnPol; project number KF2914003BN2); Sensitizers were received from FEW Chemicals GmbH (www.few.de) as a scientific gift. We furthermore acknowledge Ivoclar Vivadent for partial financial funding of this project.

New catalyst developments and their significance for Polyurethane Coatings

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Aliphatic Polyisocyanates are superior raw materials for the generation of lightfast and versatile polyurethane coatings systems. Due to their unique profile in terms of high reactivity and low melting point / glass transition temperature, especially oligomers of hexamethylene diisocyanate (HDI) are the hardeners of choice in numerous applications.

However, sometimes this balance does not cover all needs met in practice: may it be that the viscosity for a given application is too high (and excessive use of solvent is not an option) or the reactivity at a given temperature is too low.

Catalysis is key to both “ends” of a solution to this dilemma: firstly, the tailormade manufacture of various specialties in the portfolio of HDI-polyisocyanates is only possible with precise adjustment of the catalysts used for their synthesis [1] and secondly, the NCO-OH-reaction providing for the final polyurethane coating requires a well-balanced catalyst package as well in order to proceed at the desired reaction condition with the desired speed.

Well known catalysts for the latter reaction such as organotin derivatives like dibutyltin dilaureate (DBTL) accelerate the NCO-OH reaction already at room temperature narrowing the potlife window considerably. Organotin-free catalysts developing their catalytic activity only at elevated temperatures are an interesting option to overcome this dilemma [2]. A variety of applications for the new systems will be discussed.

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Cross-linking systems using cyclic-carbonate for coatings applications

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Coating resins are used in a lot of field of applications (ex: aeronautic, automobile and marine industries, can coil, general industry… etc). For bi-component systems, according to the application and the properties envisaged, isocyanates are used as cross-linkers to allow the formation of urethane linkages. These urethane groups give high properties to the corresponding coatings as hardness, flexibility, gloss, chemical durability… etc. But isocyanates are harmful reactants for humans' health, or CMR (Carcinogenic, Mutagenic or Toxic to Reproduction) components. Thus, the development of new cross-linking systems with similar properties without the use of isocyanates is a major industrial issue.

The introduction of reactive cyclic carbonate moieties in resins and their cross-linking with polyamines is an interesting alternative to the use of isocyanates. Indeed, the ring opening reaction of cyclic carbonate with amines conducts to the formation of hydroxyurethanes (fig.1) with even better properties than classical urethanes.

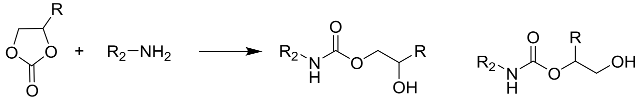

Figure 1: Hydroxyurethane formation by cyclic carbonate ring opening reaction with amines

Our laboratory is very active in the synthesis and the characterization of new polyhydroxyurethanes, notably for coating applications. The study of the thermal degradation of hydroxyurethanes was performed by our team[1] and has displayed that these compounds do not release isocyanates during thermal degradation contrary to classical urethanes. Among all unsaturated cyclic carbonates monomers[2] which can be used for the synthesis of resins, glycerin carbonate methacrylate (GCMA) is one of the more interesting to study. Its copolymerization in acrylic resins allows the introduction of reactive cyclic carbonate functions which can then react with polyamines in order to form urethane linkages. To determine the synthesis conditions of resins bearing cyclic carbonate moieties, the conventional radical polymerization of GCMA was carefully studied. First the kinetic study for the homopolymerization of GCMA allowed us to highlight the high reactivity of this monomer. Then the copolymerization study of GCMA demonstrated a very good incorporation of this monomer in copolymers. And finally we also fulfilled the study of the cross-linking reaction with amines. All these studies led us to the synthesis of cyclocarbonated resins and the formulation of new isocyanates free urethane coatings.

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ANTISTATIC COATINGS FOR WOOD-FLOORINGS BY IMIDAZOLIUM SALT-BASED IONIC LIQUIDS

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Abstract

The tendency to electrostatic charge is unfortunately typical for many floors. Ionic liquids represent a good alternative to overcome this sometimes annoying and sometimes painful property and also the disadvantages from typical state of the art antistatic agents. Ionic liquids, preferably representing salts which are liquid at room temperature (RTILs), had an exponential development in the last years [1]. They have also been reported to be effective anti-electrostatic agents on plastics [2] and wood [3].

In this study, tailor-made UV-curable methyl-imidazolium based ionic liquids have been evaluated for their potential as antistatic additives in a UV-curing coating for parquet flooring. Cross-linking the UV-active double-bond containing antistatic component with the UV-reactive binder should minimize the leaching behavior of salt based antistatic auxiliaries. 1-Allyl-3-methyllimidazolium chloride has been identified to exhibit the highest activity and a minimized leaching as well as no haze in the coating. The measured body voltage regarding EN 1815 could be realized below ≤ 2.0 kV and the resistivity regarding EN 1081 below 10^{10} Ohm. No standards are available at present in case of wood floorings. However, the measured body voltage ≤ 2.0 kV is an essential characteristic regarding EN 14041, which is a relevant standard in comparable resilient, textile and laminate floor coverings. In addition, a synergistic effect with conductive and transparent indium-tin-oxide pigment particles could be shown, which might be of interest for the economic optimization of the system. Combining the conductive pigment with the antistatic ionic liquid ends up in significant lower resistances. The effect of a particle-to-particle contact is generated by a bridging due to the ILs.

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Bringing Polyaspartic Technology to the Next Level: Low Viscous Solvent-free Floor Coatings

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The chemistry of polyaspartic coatings, first introduced in the early 1990s, is today a well-established state-of-the-art technology. It is based on the reaction of an aliphatic polyisocyanate and a polyaspartic ester, which is an aliphatic diamine.

Polyaspartic esters were initially used as reactive diluents in conventional two-component polyurethane solvent-borne coatings [1]. In our days they are the main component of the co-reactant for the reaction with a polyisocynate, allowing for the formulation of low or near-zero VOC coatings. The unique and adjustable reactivity of the polyaspartic esters enables the design of fast-curing coatings tailored to the needs of the application. The fast curing feature in combination with a high film build can provide significant money-saving productivity improvements as the total number of coating layers can be reduced [2]. In addition polyaspartic coatings technology provides low-temperature curing and excellent abrasion and corrosion resistance.

Due to their unique property profile polyaspartic coatings are used today in a large variety of applications, e.g. coatings for steel and concrete towers and rotor blades of wind energy devices, protective coatings for steel structures like bridges, ACE and flooring applications and as chain-extenders for polyurea spray coatings.

Regarding to existing VOC regulations, i.e. AgBB in Germany, it is impossible to use solvents or plasticizers for the formulation of coating systems for construction applications, like flooring. In addition these coatings are typically applied by roller or brush at ambient temperatures. With the existing product portfolio of polyaspartic esters it is very difficult to nearly impossible to formulate manually applicable coatings as the viscosity of these products is too high. Resent research lead to the development of a new low viscous polyaspartic ester based on a more flexible amine. This product combines a low viscosity with an appropriate curing profile at ambient temperatures. It is typically used as a co-binder in combination with exiting products like Desmophen NH 1420.

Another obstacle for flooring applications is the lack of flexibility respectively the right combination of flexibility and toughness of existing polyaspartic coatings systems. Therefore a new flexible aliphatic polyisocyante prepolymer was developed.

Within the presentation it will be shown that by combining these newly developed products one is able to formulate polyaspartic ester based coatings combining ease of use for roller or brush application at ambient temperatures and a unique combination of flexibility and toughness. This opens up a completely new range of applications for the polyaspartics technology.

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Sustainable Solutions for Coatings and the Role of Renewable Raw Materials

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Bayer MaterialScience AG

Sustainable development is the key concept of the 21st century – it combines the social, political and technological efforts of our society to meet our needs while conserving the environment at the same time to enable upcoming generations to meet their needs. Sustainability is an important driver for new business opportunities as well as for mitigating risks and reducing costs. For Bayer, this means balancing its impact on the environment with the needs of the society and commercial success. Therefore, it is an integral part of our functional strategies such as R&D, procurement, marketing, plant safety, waste management and production.

Polyurethane based adhesives and coatings are key enablers for a more sustainable world. Offering a high durability, they improve the life time of daily-used articles, thus reducing resources needed to produce new articles. Besides this it is state of the art that with polyurethanes reduction of volatile components as well as monomer content can be achieved both to improve occupational health and to protect the environment.

Continuous efforts are being done on reducing the environmental impact of technologies especially by increasing the resource efficiency and promoting the social acceptance of the offered solutions. Therefore an analysis of the technical solution along the whole value chain is necessary in order to select the optimum technology. The use of renewable raw materials can be one option to further improve the carbon foot print and the overall sustainability of the product.

The introduction and the success of renewable raw materials are driven by several factors. Besides the general trend for "green" products and their potentially reduced carbon foot print, such new materials are as well driven by breakthroughs in biotechnology which can offer efficient processes to these raw materials. On top, many of these molecules were not available so far from petro sources which brings opportunities for new product formulations.

New and "drop-in" biobased chemicals are being commercialized at an accelerating pace. Accordingly, the total global production of biobased polymers has increased significantly and is expected to hit the million ton market in near future. However, this industry is still in its early stage of adaption, unavoidable smaller and therefore more costly productions in most cases delays its wide applications. But, continuous technical innovation and increased production capacity will likely enhance the availability and decrease the price of biobased chemicals and of the derived polymers.

The polyurethane chemistry is a polyaddition chemistry based on functional building blocks. This allows relatively easily the incorporation of OH-functional components. It is therefore not surprising that natural oil polyols and derivatives are used since decades due to cost and performance reasons. In addition, Bayer MaterialScience has developments in the area which were traditionally the domain of petrobased raw materials.

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Lectures

Progress in production, application and processes

Extensional Rheology as Related to Paint Atomisation

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Formulators understand that improved application can be achieved by modifying the shear rheology of paint to be somewhat pseudoplastic and thixotropic. Axalta Coating Systems has been interested to find methods to measure extensional rheology that we believe more directly relates to paint atomization. When these methods are fully developed, we believe formulators can more precisely tune paint rheology for optimal application.

Studies using the Capillary Breakup Extensional Rheometer (CaBER) have been used to demonstrate capillary thinning and filament formation. This is consistent with observed droplet formation during paint spray (e.g. high speed photos of rotary atomisers). We recognize some limits to this approach as a result of relatively low relaxation times observed in commercial paints [1].

More recent work at MIT [2] provides a promising improvement on measuring techniques. Stroboscopic recordings of a jetting paint stream can be mathematically modelled to reveal domains of visco-capillary and elasto-capillary behaviour as a free stream jet is breaking up. Fitting these models to time dependent jet dimensions provides fundamental paint rheology values. Characteristic relaxation time(s) of OEM paints have been determined to be less than 0.2 milliseconds.

We explain test methodology used to characterize the paint rheology and share data collected from both model fluids and commercial coatings. Current work is to use these material properties to predict suitability for spray. We use strobed shadowgraphy methods to collect sprayed droplet particle size distributions. If the rheology has been correctly described, then it should directly relate to the quality of spray.

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Process Optimization and -Simulation in the Coatings Industry

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The standard manufacturing processes for pigment dispersions and paints have been established a long time ago (e.g. high speed dissolvers, sand and bead mills, mixers, etc.) and were more recently complemented by rotor-stator dispersers. They are well understood. Yet the optimization of the work flow and process parameters to improve capacity, quality consistency and planning/scheduling suffers from the inherent complexity and variability of the process and the product mix. This makes it difficult to estimate the effects of changes in manpower allocation, shift patterns and potential investments in equipment.

This talk presents a successful approach to solve these problems through analysis and modeling of the current and alternative processes, followed by a computer based simulation of the options. The simulation reveals the advantages / disadvantages of the different measures (expressed in throughput, capacity utilization, cycle time, up-/down time, etc.) in a quantitative and statistically relevant way. It is based on simulating process parameters that are ideally identified with the help of those who are imbedded in the process – the employees. The first step – the development of a visual process model – typically leads the participants (the employees!) to already recognize first improvement options. Their involvement also increases the chance to implement accepted, sustainable enhancements – very often first small changes that can be quickly implemented yet make a big difference.

As a result, decisions pro or contra potential alternatives can be taken with considerably lower risk and without expensive and troublesome trial and error experiments – e.g. a failed investment.

Key words: pigment dispersions, paint production process, process analysis, process optimization, process simulation, quality, productivity, Kaizen, 6Sigma

Selective and Overspray Free Painting Technology

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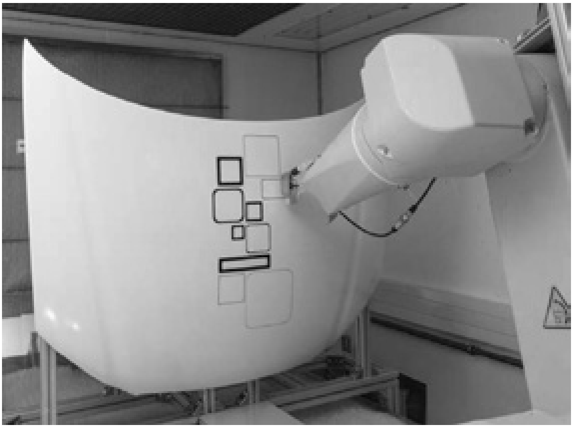
In the cooperative research project funded by the German Federal Ministry of Education and Research BMBF Green Carbody Technologies – InnoCaT "Energy efficient painting" (duration March 2010 to December 2012) new methods for the painting process in the automotive industry has been investigated in close teamwork with automotive and machine building industry. The overall project aimed to reduce the energy demand in the carbody production in which 60 companies joined in 30 projects using 100 million euros innovations. Three of them concentrated on painting, namely "overspray free coating", "energy efficient dryers" and "modular product and facility concepts" to reduce the most demanding energy consumers in painting.



The overspray free painting works with the well-defined generation of paint drops by a short opening of a micro dosing valve. The droplet generation is investigated by high speed cameras and laser Doppler anemometry. The film building process is simulated by numerical methods and demonstrated by painting patterns on a hood. The possible energy savings are calculated by regarding the primary energy consumption. An overview of applications in automotive painting and other industrial sectors will be shown and the limitations and challenges for further developments will be shown.

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Air entrapment in droplets impacting the surface

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Droplet impingement and spreading on a solid surface are phenomena that happen frequently in many industrial applications, such as coating processes using liquid sprays. The paint film quality of such coating processes can be affected by the entrapment of air bubbles in the liquid film which may not release completely later in the drying process, resulting in pinholes in the dry paint film. In general, there are two presumptions on where air bubbles come from. One is the air entrapment resulting from the impact of the liquid drops, which has been observed by many researchers using different liquid materials and impact velocities. The other is the air inclusion in the droplets after the atomisation processes, probably due to the release of dissolved air in the liquid, which is however quite difficult to be experimentally observed.

Although the air entrapment phenomenon under drop impact onto a solid surface is well known experimentally, the knowledge on the detailed process and on the mechanisms underlying air bubble entrainment as well as air bubble release from the liquid film is still limited, especially for high-viscosity and non-Newtonian liquids. There are not so many numerical studies that focus on the air entrapment under drop impact. In this work, we present numerical studies of viscous drops (0.04 – 1 Pa·s) impacting onto a dry smooth solid surface, aiming to observe the air entrainment and release at relatively low Reynolds numbers (Re < 500).

Two initial states of viscous droplets, namely with and without previous air inclusion were considered in the study. It was found that previous included bubbles release from the liquid film easily during the droplet spreading, whereas bubbles on the target surface, resulting from the air entrapment in the droplet under impact on a solid surface, release from the liquid film quite difficult and slowly. An analysis of the sum of air volume in the liquid phase as a function of the dimensionless numbers has been performed for the static situation of the liquid phase. The influence of the contact angle on the simulation results has been discussed. Video animations of the drop impact processes with the focus on air entrapment and release have been made. The simulation results are helpful for understanding the detailed processes of air bubble entrapment and release, and deliver useful information for the development of new paint materials and the process optimisation in spray painting applications.

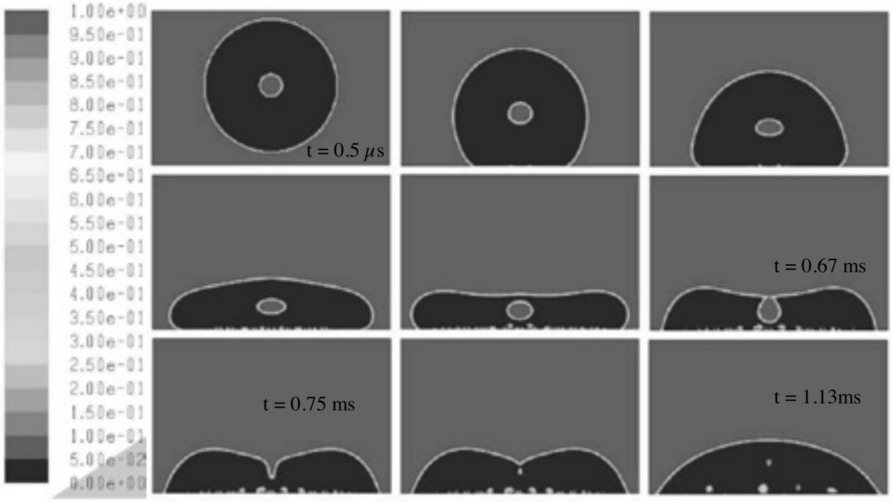

Figure 1. Contours of volume fraction (1: air, 0: liquid paint), impact of a paint drop (D = 300 μm, impact velocity = 1 m/s, μ = 40 mPa·s, σ = 0.025 N/m, corresponding to Re = 8.25, We = 13.2)

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Improving efficiency and quality by High Throughput Technologies in development of coatings

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Nowadays High Throughput Experimentation (HTE) is used more and more for the development of new coating materials. Nearly ten years after development of a cleaning free spray application the automated preparation and application of coating formulations and applications enables the scientist to reach a higher efficiency and better reproducibility in the laboratories. In other words: preparing a large number of coating materials and applying these in a close-to-reality spray application is no longer a challenge.

In the presentation we will show the wide variety of formulation, application and characterisation modules which are available today. In combination with Design of Experiment (DoE) new formulations can be produced, applied, and characterized in an automatic manner. The influence of two different additives, two solvents and two binders on coating properties such as DOI were investigated. A matrix of over 200 samples was tested within a few days. In a second set of experiments the effect of varying the rheology module and its concentration in an existing formulation was investigated. Another key issue in the development cycle is automated analysis of the coatings. While standard measurement tools for properties such as film thickness, colour, gloss or haze are readily available, we will show solutions for automated analysis of chemical resistance, rub-out-testing, scratch resistance and cross hatch test.

The results of our investigations show, for example, that systematic optimisation of a coating can be carried out much faster and easier by utilizing DoE and lab automation. Interaction between the components of a formulation is not always linear. In the present case such non-linear relationship between the effects of the two additives lead improved coating properties. Automating the lab work flow and thus preparing a large number of formulations and coated substrates can help to find such non-linear behaviours and enable the scientist to quickly optimize coating systems by applying this knowledge..

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Lectures

Measuring and testing/ New optical properties in coatings

Towards a durable, water-based coating for wood-based composites

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After a long initial phase at the beginning of the 90s of the last century the breakthrough succeeds for wood-polymer composites (WPC) on the market. 2012 260,000 tons of WPC were produced in Europe [1].

Most of the composites are confected of 30 % polyolefin or PVC and 70 % wood flour. The European WPC total annual production of 260,000 tons in 2012 went to 67 % in the production of deckings and to 23 % in car interiors. The remaining part was used for consumer durables, furniture, facade cladding, fences and engineering applications [1].

The combination of thermoplastic polymers with lignocellulose particles opens up new processing capabilities compared to pure wood materials. The thermoplastic component allows for a three-dimensional processing workpieces by means of extrusion and injection molding.

The use of such materials in the façade opens architects new interesting possibilities. Such use on a larger scale may be feasible only, if it manages to coat the WPC elements in order to protect them from UV radiation and water, and on the other site to increase its decorative possibilities.

However, a coating of WPC parts is difficult due to the low surface energy and poor wettability of the WPC surfaces. The aim of this study was, to functionalize the WPC surfaces and consequently to increase the surface energy and the wettability.

For functionalization of polymers, there are known various technologies, which may also be usable for WPC surfaces. In this paper, the activation was selected with three different treatments. These procedures are treatments by a flame, an atmospheric plasma and a mechanical treatment of the surfaces. Because WPCs filled polyolefins are, it was to determine as the various formulations and processing conditions affect the resulting properties of activation.

For the evaluation of the quality of the functionalization the following investigations were performed:

- Dynamic contact angle measurements of sessile water drops with the “OCA 35 XL” by Data Physics, G
- Characterization of the surface roughness with the confocal microscope “µsurf” by the NanoFocus AG, G and the stereo photogrammetric instrument “TRACEiT” by INNOWEP Measuring & Testing, G. Both devices differ markedly in their resolution and their measurement range.
- Determination of the chemical composition at the surface by X-ray photoelectron spectroscopy (XPS), Photoelectron spectrometer AXIS ULTRA by Kratos Analytical, UK
- Coating experiments

[1] Press release, nova-Institut GmbH, Hürth, 26.11.2013

Early recognition of weathering defects: evaluation of two newly elaborated methods for detecting coating degradation

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Outdoor weathering and laboratory tests are indispensable elements during the process of developing protective coatings. These elements are, however, time-consuming, which increases the price of such coatings significantly. Thus, considerable efforts are undertaken which aim on the development of short-time tests. In many cases, however, such short-time tests do not correlate with practice convincingly.

Another approach to solve this problem could be to identify detection methods, which are sensitive enough to record processes, which run during the early stages of coating degradation and which result in or contribute to the formation of a specific coating damage.

Here, two newly elaborated methods for detecting coating degradation are presented. The first one utilizes ESR (Electron Spin Resonance) spectroscopy, by which radicals, which are the earliest possible chemical messengers of an initiating photodegradation process, can be detected quantitatively.

The second method utilizes EIS (Electrochemical Impedance Spectroscopy) in order to detect changes regarding the water uptake reversibility of the coatings exposed to weathering. Since the latter causes the formation of additional pores and increases the hydrophilicity of the matrix already in the early stages of the weathering process, water uptake reversibility may also be utilized as an early and quantifiable messenger of the coating degradation.

Within this work three complete coating systems, which consist of a steel substrate, an electrophoretically deposited primer (EDP), a spray-coated primer, a basecoat and a clearcoat as well as the respective three systems consisting of the clearcoat on a metal substrate, were exposed to outdoor weathering and standardized laboratory tests (SAE J 2527). The samples were characterized after defined periods of weathering and the results were interpreted with respect of the value of these methods in the given context.

Film formation and subsequent environmental degradation of crosslinking polymers: exploration using computer simulations.

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Crosslinked coatings are frequently expected to perform as barriers and protect materials from attack by the environment, e.g. metal substrates from corrosion by ionic or other species in a moist environment. In order for such species to pass through the barrier, not only must they find open passageways, but they must also encounter a compatible environment. Reductionist approaches can provide a detailed understanding of the chemistry, formation and degradation of a particular polymer coating, but do not furnish useful predictions regarding the physical integrity of that coating. Further, such knowledge is seldom useful for understanding any other type of polymer. It became very clear from previous efforts to link macroscopic performance with microscopic damage accumulation [1] that it was necessary to appreciate how crosslink density and other structural qualities become distributed during film formation, and how they break down during weathering degradation.

Coarse-grained molecular dynamics were used in this work to study polymer network formation by reactive species. After network formation, the simulations then effected degradation by removing a small fraction of the bonds from the simulated networks. Network integrity, pore space distribution and its evolution during degradation depend on the functionality of the initial reactive species, the glass transition of the polymer network and the external constraints. These studies show how crosslinked polymer networks might permit the passage of corrosive species after suffering environmental degradation, and sometimes, even prior to degradation.

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3.17

A multi-method approach for the prediction of the weather-related ageing of wood coatings

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In the current work weather-related alterations of selected physicochemical and functional properties of PBA-PMMA and PBA-PS based natural and artificial weathered wood stains were investigated and related to structural changes of the corresponding copolymers. This was accomplished by thermal (DSC) and micromechanical (microhardness) analysis connected with FTIR and Raman spectroscopy and the application of unconventional methods such as UV-GC/MS and chemiluminescence (CL) analysis. The combination and evaluation of these methods is connected with the clarification of degradation mechanisms and provides reliable information about the weather fastness of the materials. The data obtained are very useful for the study of ageing processes and are considered to be essential for a rapid forecast of the durability of wood coatings.

It is shown that weather-related structural changes of binding agents and respective copolymers can be rapidly identified using FTIR spectroscopy: Structural changes are related to hydroxylation and peroxide formation (broadening of υ(O-H) in the region 3700-3200 cm^{-1}; Fig. 1a) polymer chain scission (decreasing intensities of υ(C-H) and to υ(CH_2) in the region 3000-2800 cm^{-1}; Fig 1a) and the formation of aliphatic and aromatic carbonyls (broadening of υ(C=O) in the region 1800-1600 cm^{-1}; Fig. 1b, c) which could be responsible for discolouration [1,2].

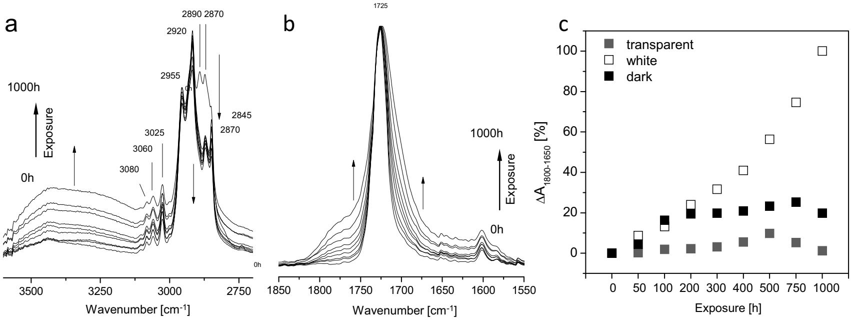

Fig. 1: ATR FTIR spectra of a white pigmented PBA-PS based coating in the spectral regions between a) 3500-2750 cm^{-1} and b) 1850-1550 cm^{-1}; c) respective percental changes of the peak areas $A_{1800-1650}$ of the respective coating and pigmented counterparts

GC/MS analysis equipped with an online micro-UV irradiation module allows a rapid detection of volatile degradation products (for PS: acetone, styrene, phenol, acetophenone, benzaldehyde, Fig 2a; for PMMA/ PBA: MMA and ethylene diacetate, not shown) formed in the course of the photolytic deterioration of respective binding agents [3].

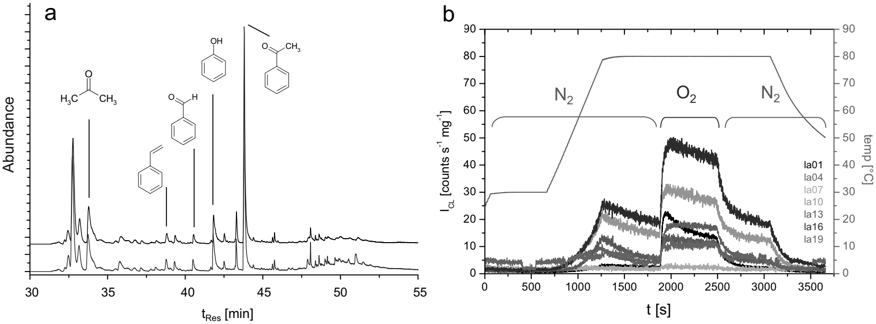

Fig. 2: a) TIC of volatile photolytic degradation products from an artificial weathered and online micro-UV irradiated PBA-PS-based coating; b) chemiluminescence of transparent PBA-PS- (blue and orange line) and PBA-PMMA-based coatings

Not surprisingly CL experiments revealed a markedly higher oxidation sensitivity of PS-containing copolymers compared to PBA/PMMA variants and should provide an early indication of weather-related and photooxidatively induced structural alterations and degradations of polymers [4].

Subsequent alterations of physicomechanical and functional properties of coatings are increasing T_g and microhardness values which are indicative for an embrittlement caused by a polymer network densification, chain scission and leaching of low molecular degradation products and plasticizers [5].

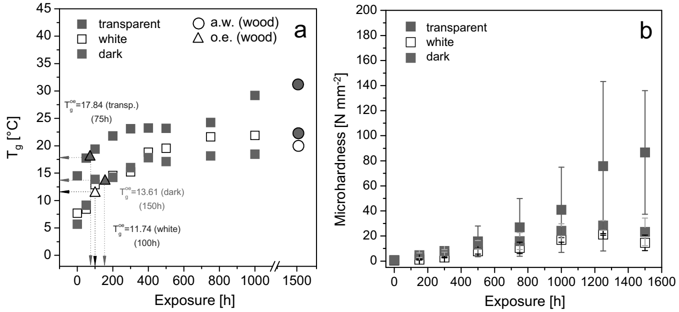

Fig.1: a) Glass transition temperature T_g and b) microhardness of artificial weathered transparent and pigmented PBA-PMMA based coatings

Acknowledgements
The IGF project 16738BR of the Deutsche Forschungsgesellschaft für Oberflächenbehandlung e.V. is supported via the AiF by the Federal Ministry of Economic Affairs and Energy within the framework of Industrial Collective Research, based on a decision of the German Parliament.

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Measuring and optimizing the efficiency of titanium dioxide in paint

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One of the main functions of architectural paint is to hide a surface and improve its appearance. Hiding can be obtained by either scattering visible light or absorbing it. For white paints, absorption is not wanted, therefore hiding in thin paint films can only be obtained by light scattering. Because of its high refractive index, titanium dioxide is the most efficient pigment for scattering visible light and the lack of visible light absorption makes it the best white pigment available.

Since light scattering is the key parameter to obtain optimal hiding in white paint or whitening strength in tinted paints, measuring the efficiency of TiO2 light scattering is the first step when one wants to optimize the use of it. In lightly tinted paints, optimized light scattering can increase the whitening strength of the used TiO2 and result in reduced TiO2 consumption for the same tint. Improved hiding can lead to thinner films, and more cost efficient paints. Optimized use of TiO2 can also result in reduced raw material consumption, while maintaining the performance and therefore lead to more sustainable paint. This paper describes how the TiO2 efficiency can be assessed and how that knowledge can be used to prioritize hiding optimization programs.

Once the optimization potential is determined, light scattering can be optimized by increasing the TiO2 efficiency. Many factors influence TiO2 efficiency, primarily crowding as TiO2 concentration increases and non -ideal spacing which is a result of large particle size extenders, resins and to some degree chemical flocculation. The nature of the pigment itself can play an important role. Depending on the paint and the properties needed, special surface treatments of TiO2 pigments can enhance the spacing.

3.19

Simulation of Temperatures on Surfaces Exposed to Solar Radiation

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Objects which are exposed to and absorb radiation from the sun heat up. The actual surface temperature depends on the material, the shape of the object and the weather factors (sun, air temperature, wind, humidity) [1,2].

The properties of use of most materials are also determined by the actual temperatures in the application [3,4]. These materials may be window profiles [5] or other polymer base materials for example. The micro climate on and in building walls is also influenced essentially by the absorbed solar radiation depending on the material properties [6]. The same applies for temperatures inside buildings and automobiles.

These examples show clearly that the knowledge of the temperatures on surfaces exposed to solar radiation is important; because, if it is known what temperature values can be realistically expected, measures for optimizing the micro climate can be taken, for example to reduce the useful temperature by improved spectral reflection properties or by adapted design measures as well as improved acclimatization.

A simple model for calculating surface temperatures is presented in this study. The input data are the actual weather data and the specific material properties. The possibilities and limitations of the model are discussed.

Table 1: Measured (meas) and calculated (calc) surface temperatures for a set of colored specimens (surface temperature sensors) and weather parameters at different times of the day in Arizona on a cloudless day on September 4, 2008 (10 minute averages).

Unit	Date	September 4, 2008				
h	Time of the day	9:00 AM	11:00 AM	1:00 PM	3:00 PM	4:00 PM
W/m²	E_{TOTAL}	593	939	990	743	523
°C	$T_{AMBIENT}$	32.3	36.2	38.5	39.8	39.5
%	U	16.5	17.4	11.6	8.6	9.1
m/s	Wind	2.7	2.4	1.7	3.0	2.1
°C	white (meas)	37.4	43.5	46.1	45.0	44.0
	white (calc)	36.2	43.0	46.4	44.4	43.2
	yellow (meas)	40.9	49.8	52.5	49.5	47.8
	yellow (calc)	39.2	47.9	52.0	48.0	46.0
	orange (meas)	42.0	50.4	54.4	50.5	48.0
	orange (calc)	40.4	49.4	53.8	49.1	46.9
	red (meas)	44.2	51.9	57.8	53.5	49.7
	red (calc)	41.0	50.8	55.4	50.1	47.7
	blue (meas)					
	blue (calc)	42.0	52.4	57.2	51.3	48.6
	green (meas)	44.7	55.4	58.2	53.0	51.1
	green (calc)	42.3	52.9	57.8	51.7	58.9
	black (meas)	45.9	55.9	60.2	55.3	52.1
	black (calc)	43.7	55.3	60.6	53.5	50.3

An additional backup and often the only possibility for a realistic estimation of the surface temperature to be expected under natural conditions is a simulation in a climate chamber. A prerequisite for this is that it simulates the natural weather conditions as realistically as possible. A climate chamber with a laboratory light

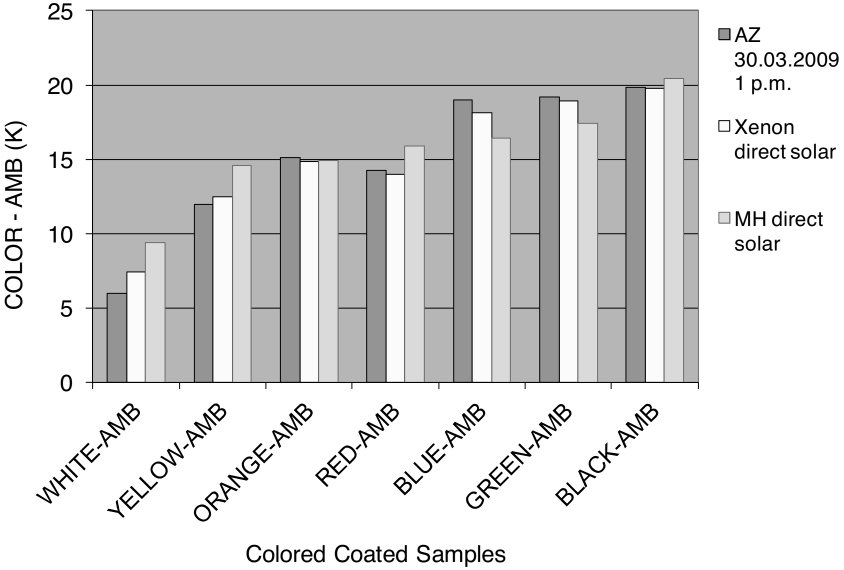

Figure 2: $T_{SURFACE}$ - $T_{AMBIENT}$ = COLOR – AMB of color painted sheets (surface temperature sensors) in Arizona on March 30, 2009 at 1 PM in a xenon and an MH laboratory weathering device. The total irradiance E_{TOTAL} is 1070 W/m². The wind velocities are between 3 m/s and 6 m/s for Arizona and for xenon approx. 3 m/s, for MH approx. 0.2 to 0.4 m/s For MH the total irradiance had to be set to 850 W/m² for the measurement to achieve the specified temperatures because it was not possible to increase the air speed in the special device.

source is considered by means of which temperatures can be simulated and measured on surfaces exposed to the sun's radiation. Surface temperature sensors with different solar absorption are used to validate such a climate chamber.

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Water in coatings

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Coatings are applied for protective and esthetic reasons. They have to act as barriers for molecules that should not reach the underlying substrate. In general water is one of the substances that should not accumulate on or in the substrate. For example, wood becomes prone to wood rot and metals start to corrode due to water. Therefore knowledge of the interaction between a coating and water is needed.

To understand the coating-water interaction first a technique is needed to detect water migration inside a polymeric matrix without interfering with the process. We have shown that the NMR imaging based on the so-called GARField concept can be used to trace both water and its effect on the polymeric matrix. Experiments were performed with multilayer coatings inspired by automotive applications and nylon-6 films. Depth profiles of water and plasticized polymer could be measured real-time with micrometer scale resolution [1-3]. On the basis of these depth profiles a kinetic model for water sorption in multilayer coatings was developed, which was based on the sorption isotherm of the base coat and permeability of the top coat. The model predicted a strong asymmetry in uptake and drying (slow uptake and fast drying), which was indeed found in the experiments [4].

In general water is attracted by hydrophilic components in a coating. While studying multilayer coatings that had at least one waterborne layer, it was found that waterborne layers attract water for two reasons. First, NMR relaxation studies showed that the dispersants of the pigment mixed with water during uptake, indicating that these molecules attract water [5]. Further it was found that neutralization agents of latices matter a lot. In this case the driver for sorption is entropy, because the disorder is increased by dissolving the neutralization agents with water.

With the previously mentioned model for water uptake in multilayer coatings, the response on humidity fluctuations can be predicted. Calculations made clear that there is huge difference in response between cycles of a few hours or cycles of a day or more [6]. The coating cannot respond on fast fluctuations in humidity and the water content in the coating remains on an average value. Slow fluctuations lead to more uptake and shrinkage. Therefore, it is questionable if the role of water in artificial weathering test is representative for its role in practice.

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Seeing clearly through the mist

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The content of free formaldehyde as a preservative in water-based dispersion paints is commonly determined via the acetyl acetone method, recommended by the VdL-RL 03 directive. This method is well-known and established since 1953 by T. Nash [1]. It is based on a chemical reaction of formaldehyde with acetyl acetone in the presence of ammonia to form a heterocyclic species, dihydro diacetyl lutidine (DDL), of yellow colour. Based on this colour, the amount of formaldehyde can be quantified by UV/VIS-spectroscopic measurements at 412 nm.

However, for a single wavelength measurement this method relies on clear solutions. Difficulties arise when samples such as dispersion paints turn out to be turbid even after centrifugation, which in practice is more a rule than an exception. In such cases other techniques are recommended, however, for reasons of costs and convenience it would be better if with just one relatively simple spectroscopic method one could study samples regardless of the level of turbidity.

The current presentation shows that even for turbid solutions, UV/VIS-spectroscopy can still be used to get accurate results on the formaldehyde content, when employing an integrating sphere of sufficient size [2]. Data obtained from turbid samples, which were placed in the centre of an integrating sphere, are compared to those data obtained on samples placed in the conventional sample compartment of the spectrophotometer used.

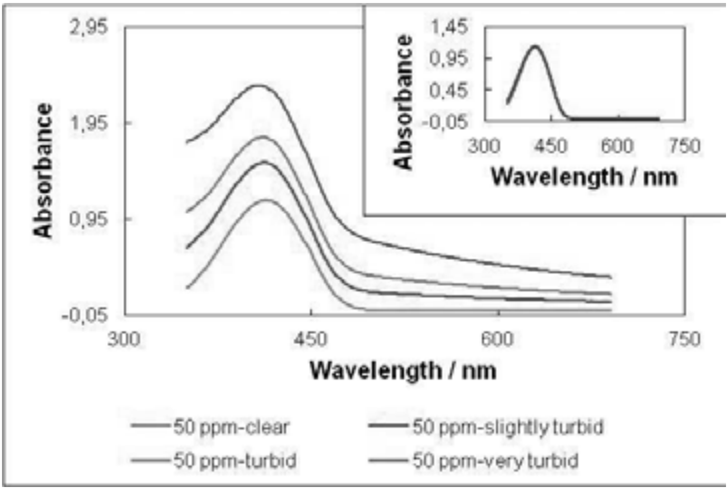

Figure 1: UV/VIS-spectrum of a 50 ppm clear formaldehyde sample compared to the spectra of three samples of the same formaldehyde content, but at different turbidity levels, recorded with a cuvette placed in the conventional sample compartment. The inset shows the spectra of the same samples recorded with the cuvette positioned in the centre of an integrating sphere.

Figure 1 demonstrates that all spectra merge into one when the cuvette sits inside of the integrating sphere.

Table 1: Recovered formaldehyde (FA) contents for more or less turbid samples either placed in the sample compartment or inside of the integrating sphere. The nominal formaldehyde content was 50 ppm.

position / level of turbidity	sample compartment		integrating sphere	
	FA-content / ppm	error / %	FA-content / ppm	error / %
clear	51,3	2,7	53,1	6,2
slightly turbid	62	23	51,3	2,7
turbid	72	44	51,4	2,9
very turbid	93	59	52,1	4,1

Table 1 shows that the recovered formaldehyde contents are strongly affected by the level of turbidity when the sample is placed in the conventional sample compartment of the spectrophotometer. When placing the same samples inside of the integrating sphere, correct formaldehyde contents are obtained within reasonable errors.

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The effect of coating thickness on pendulum hardness

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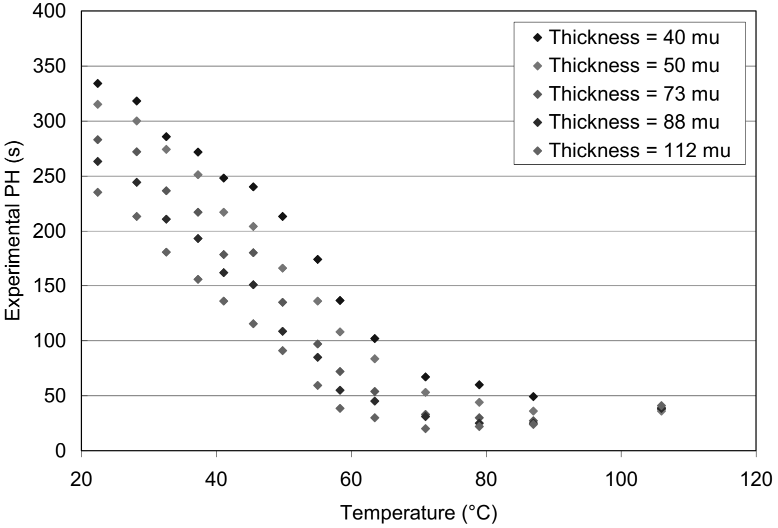
ABSTRACT

Pendulum hardness is one of the most popular tests within the paint industry to determine the (development of) mechanical properties of coatings. Often coating systems are approved or rejected based on their pendulum hardness. It is generally understood that pendulum hardness can depend on the thickness of the coating although this effect is seldom taken into account in daily practice. We have tested the Persoz hardness as a function of layer thickness (thickness range: 40 to 110 micron) for a fully dried and cured, homogeneous 2K coating. The hardness was determined at various temperatures in order to determine the effect of coating thickness over a broad range of Persoz hardness, see Figure below.

We have derived a semi-empirical mechanical model which describes the effect of coating thickness and mechanical coating properties on Persoz hardness quantitatively. In this presentation it will be shown that the correlation between experimental hardness data and hardness values predicted using the measured layer thickness and DMTA-properties of the coating is very good.



Limit Values for VOC Emissions from Decorative Products around the Globe

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Caroline LAFFARGUE[1]

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Volatile Organic Compound (VOC) emissions from construction products and decorative products can contribute to indoor air pollution for some time period after the completion of building construction. Several low VOC rating systems contain restrictions on VOC emissions into indoor air but the limit values differ, and some of the testing and modeling parameters are not harmonized.

The requirements of the most relevant low VOC rating systems were identified and compared in terms of limit values, test methods, and implementation procedures.

VOC emissions are limited by legislation in several European countries. Some of these include coatings and decorative products. In addition, special regulations are in place for formaldehyde emissions in several more countries, but mostly for wood-based products. And in addition to that, the VOC content of paints and coatings is regulated in a number of countries. A large number of voluntary labels specify low VOC emissions criteria (Blue Angel, EMICODE, M1, Indoor Air Comfort, FloorScore, Indoor Advantage, …). The same applies to programs for sustainable buildings (LEED, BREEAM, CHPS, DGNB, GreenStar, …), and related standards (e.g. EN 15251, AHSRAE 189.1, IgCC 2012, …).

All these programs contain restrictions on VOC emissions into indoor air but the limit values differ, as do some of the testing and modeling parameters. VOC content does not correlate with VOC emissions into indoor air after application of an interior coating. The program for sustainable buildings, LEED, now requires VOC emissions testing on top of VOC content testing.

The variety of VOC limits creates the need for many different tests as long as no harmonization exists between the regulations, and between the other programs. This is a significant cost burden for companies if they distribute construction products and decorative products in more than one country.

An analysis of the most often used low VOC specifications shows both obstacles and opportunities for harmonization. The new European testing methods EN 16402 and CEN/TS 16516 help bringing together testing requirements within Europe. The new version of LEED allows showing compliance with its specification of low emitting interior materials not only with US-based testing methods, but now also with European test data.

This overview can help specifiers and regulators to establish meaningful low VOC requirements without re-inventing the wheel. And it can help manufacturers to save significant costs by combining tests for several purposes into one single test setup.

Posters

Selectively functionalized mesoporous silica for pH-controlled delivery of aromatic amino acids

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Due to the high surface area ($>$1200 $m^2 \cdot g^{-1}$), large pore volume (~1 $cm^3 \cdot g^{-1}$), well-defined and tunable pore size (1.5–10 nm), adjustable functionality and biocompatibility mesoporous silicas of MCM-41 type are widely used for biomedical applications. The most significant of them is controlled release of biologically active guest molecules. The retention of active substance in the pore volume of carrier and its delivery on demand can be achieved by chemical design of the pore walls and exterior surface of carrier. Interior surface of pore channels can be tailored with sufficient groups to selectively store active substances and deliver ones on demand. To gain control under the release processes construction of external stimuli responsible nanovalves on the outer surface of carrier particles can be realized.

In the present work, decoration of MCM-41 silica surface around entrances into the pores with ionizable N-[N'-(N'-phenyl)-2-aminophenyl]-3-aminopropyl groups was carried out. In the first step, MCM-41 was prepared by sol-gel condensation of tetraethylorthosilicate in water-ethanol-ammonia medium. Then, introduction of highly reactive 3-chloropropyl groups onto the outer surface of the template-filled MCM-41 silica was performed in vapor phase by use of (3-chloropropyl)triethoxysilane as modifier. Thereafter postsynthetic selective modification of 3-chloropropyl groups of the external silica surface with 2-aminodiphenylamine in acetonitrile was fulfilled. Chemical composition of silica materials was estimated by IR spectral and chemical analysis of surface reaction’s products. Parameters of porous structure of MCM-41 silicas were determined from the data of X-ray and low-temperature nitrogen ad-desorption measurements.

The ability of the mesoporous silica with N-[N'-(N'-phenyl)-2-aminophenyl]-3-aminopropyl groups chemically fixed near the entrances in its pores to release the encapsulated biologically active compounds was studied for para-aminobenzoic acid. Encapsulation of aromatic amino acid was carried out from ethanol solution, and its exclusion from the pores was realized in phosphate buffer (pH 6.86) or hydrochloric acid (pH 1.00). The content of encapsulated aromatic amino acid by UV spectroscopy analysis is equal to 0.83 $mmol \cdot g^{-1}$.

It was found that N-[N'-(N'-phenyl)-2-aminophenyl]-3-aminopropyl groups block pore entrances at neutral pH preventing para-aminobenzoic acid release from the pore volume of MCM-41. At pH 1.00 repulsion of protonated (positively charged) surface amino groups provides unhindered exclusion of loaded aromatic amino acid from mesoporous channels of selectively functionalized silica.

Title: TEXSHIELD – Environmental friendly and Durable Oil and Water Repellence Finish on Technical Textiles

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Abstract

In the current market, the well-known brands of technical textiles, including protective textile are coated- finished with perfluorocarbon chemistry (PCFs) to possess highly durable oil and water repellent (OWR) properties. PFOS and PFOA are the main chemicals belonging to the family of perflourochemicals also known as C8 chemistry. However, healthy and environmental issues are causes for the potential banning of these products. Moreover, recent studies have found PFC-C8 present in the blood, tissues and foetal-cords of human and its bio-persistence and bioaccumulation in the environment has caused significant concerns. Notably, due to these concerns, 3M withdrew Scotchguard from the market in 2000. C8 Fluorocarbons are currently under high regulatory pressure (2006/122/EC) and it’s outlawed in favour of C6 or C4 chemistry, which performs lower to meet the industries durability and repellence standards.

There is a strong demand for replacing the C8 chemistry with an equally performing chemistry. The European TEX-SHIELD-project aims to develop a novel, multifunctional molecular structure with silica backbone that is chemically bondable to the fibre/filament to achieve a highly durable textile finish that is resistant against the oil/grease/powder stains by biological route. The reasonable silica content in it will replace the C8 chemistry while providing equal performance. In addition the project evaluates also suitable deposition techniques. TEX-SHIELD will provide the textile industry with a cost effective and environmentally safe OWR-finish on textiles, revolutionising the current market place, whilst resolving the concerns of the current PFC-C8 based stain-resistant coatings. This will profoundly reduce water consumption during washing for the consumers.

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New generation of synthesis nanocrystalline biomaterials for coating on Ti-6Al-4V Implant with EPD technique

cancelled

Reduced fluorine content oil and water repellent treatments for technical textiles

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Textiles in various applications such as PPE clothing, sportswear and furniture etc. require oil and water repellent (OWR) treatments. In the current market, the well-known brands of technical textiles perfluorocarbon (PFC) chemistry is used to provide highly durable OWR finishes. The raw materials that have historically been used to make PFCs had eight carbon atoms and so the products they made were known as PFC-C8.

Studies have found PFC-C8 present in the blood, tissues and foetal-cords of humans and its bio-persistence and bio-accumulation in the environment has caused significant concerns. Notably, due to these concerns, the major manufacturers of PFCs withdrew their C8 products from the market place. Fluorocarbons based on C8 chemistry are under high regulatory pressure (2006/122/EC) and are outlawed in favour of other PFC chemistries. However, raw materials with fewer carbon atoms in the polymer chain (C6 or C4 for example) have not yet been demonstrated to provide the same level of oil and water repellence that the C8 based chemistry was able to achieve.

Tex-Shield is an FP7 funded project that aims to develop a novel, multifunctional molecular structure with silica backbone that is chemically bondable to textile fibre/filaments to achieve a highly durable textile finish that is resistant against the oil/grease/powder stains by biological route. The objective of providing a cost effective alternative treatment to C8-PFCs by reducing the total fluorine content in the treatment for the textile industry is being approached by sol-gel fabrication of nanoscale silica to achieve the target roughness and by following a novel route to functionalisation of silica to give the required surface chemistry.

A review of the state-of-the-art is provided together with provisional results that demonstrate the ability to provide water repellence via a fluorine free treatment.

Key words: Oil and water repellent, silica functionalisation, low surface energy coating.

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Practical application of easy-to-clean coatings

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Easy-to-clean coatings are very popular nowadays to be applied on a number of substrates in various applications. The “easy-to-clean” functionality means that a surface can be cleaned more easily, but a cleaning step is still required. Depending on the “dirt” (graffiti, fingerprints, acids, environmental dirt, etc.) the coating has to satisfy different conditions, like being a complete sealant, or being water and/or oil repulsive. In addition the durability of the easy-to-clean functionality is an important extra requirement: to what extent permanence of the easy-to-clean effect is needed, depends on the application. Moreover, for some applications, extra conditions apply, e.g. food or medical approval of the coating. For all these conditions, coating solutions have to be found. A multitude of commercial easy-to-clean coatings and coating additives are already on the market and applicable to different situations. Of them, the wet-chemical coatings are very versatile to adapt to the specific needs of the customer. Wet chemical coatings comprise solutions with resins, reactive diluents, sol-gel networks, nanoparticles etc. as hybrid systems. In the Sirris Smart Coating Application Lab, a number of ready-to-use commercial and self-engineered coating formulations have already been tested and adapted to be suitable for different customer applications requiring easy-to-clean properties. In this work, three practical cases will be presented: a superhydrophobic coating as anti-mud layer on a racing bike, an easy-to-clean and acid resistant coating on natural stone and an easy-to-clean coating on a building sun-screen. The easy-to-clean properties will be shown (contact angle, dirt tests), next to their durability (abrasion resistance, chemical resistance). Focus is on polysiloxane, polysilazane and superhydrophobic coatings.

How key variables affect hot tack of emulsion polymers

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Hot tack is the melt strength of a heat seal immediately after sealing, while the polymer is still molten. This value is especially critical on high speed packaging lines. A range of waterborne styrene-acrylic core/shell dispersions was evaluated.

Surprisingly, the parameters controlling hot tack and final bond strength are not the same.

The use of waterborne dispersion technology for adhesives has some distinct advantages over other (homogeneous) technologies. While this is well recognised in the pressure sensitive adhesive (PSA) area [1], in heatsealing applications solventbased technology is still common. The promise for dispersion polymers as binders for heatseal lacquers lies in the heterogeneous nature of these systems. The formation of individual segregated particles during the polymerisation process allows for control of particle morphology during synthesis [2]. Upon application, this morphology can be maintained during the film formation stage, but then allows a phase inversion to take place after heat treatment [3]. Thus, the system has the potential for being non-sticky, non-tacky and non-blocking at ambient conditions, while having (irreversible) adhesive properties at elevated temperatures. Another obvious advantage of waterborne systems over solventborne ones is that the absence ofretained solvent in the packaging material minimises potential sensory impacts of the packaging on the food. In this paper, the results of a systematic investigation of the hot tack behaviour of styrene-acrylic dispersions are presented. The influence of key variables in synthesis, polymer properties and heat seal operation on hot tack are discussed.

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Patterned Hydrophilic/Hydrophobic Recycled Paper Modified by Tuned Graphene Oxide Reduction

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Chemical modification of recycled paper with reduced graphene oxide (rGO) is studied to enhance its conductivity and manipulate its surface properties. The process acts selectively by vapour reduction of GO at different oxidation states to create hydrophilic/hydrophobic surfaces. Morphology of the paper was studied by scanning electron microscopy (SEM). Electrical conductivity was examined by two point probe test and hydrophobicity was studied by contact angle measurements.

Keywords: conductive, hydrophobic, patterned, graphene oxide, paper pulp

Introduction

Functional eco-friendly nano hybrids with lightweight and flexible properties have attracted a great deal of attention, in applications such as solvent selective membranes and electroactive materials. Modification of biocompatible materials with conductive nano particles make them suitable for applications like anti-static packaging, energy storage devices and wearable strain sensors. Tuning the conductivity pattern is required in electrochemical sensors and radio frequency identification tags.

Surface free energy can result in selective permeability for separation of liquid mixtures, filtration, and absorption of electrolytes [1]. Cellulose as one of important natural polymers have been used in paper industry and modified to have better electrical, and mechanical properties. In this work, we use reduced graphene oxide as a 2D flexible, atom thick material to modify recycled paper. Rationally designed graphene oxide reduction led to patterned conductive pathways with specific surface free energy for each part that was evaluated by contact angle measurements.

Experimntal

Materials

Graphite flake, Potassium permanganate, Sodium nitrate, Sulfuric acid 98%, Hydrazine 80% and hydrogen peroxide 30% were purchased from Merck chemicals and used as received. Recycled paper pulp was provided from repeatedly used 80 g paper.

Graphene Oxide synthesis

GO was synthesized from natural graphite flake employing typically modified Hummer's method [2]. 1 g of natural graphite Flake and 1 g of $NaNO_3$ were mixed in 180 ml of H_2SO_4 for 2 hrs. Subsequently, 6 g of $KMnO_4$ was carefully added where the reactor was kept in ice bath, to avoid unintended temperature raising. Then the mixture was allowed to react at room temperature for 10 hrs., to result in a thick paste. Water was added and the reaction was terminated by addition of 15 ml of aqueous solution of H_2O_2(30 wt%), resulting in a brownish yellow mixture. Then the mixture was centrifuged and washed three times with water. The sediment was sonicated for 1hr to produce GO dispersion.

Fabrication of graphene oxide modified paper

Paper pulp was dried at 70 ^{0}C in vacuum oven, then 1.28 g of dried pulp was dispersed in 400 ml water under vigorous stirring for 24 hrs. Subsequently, graphene oxide suspension (1 mg/ml) was added to obtain GO-paper (GO-P) composite with different weight percentage (w/w) (0.5, 1, 2, 4 and 8 %). As-prepared mixtures were kept under stirring overnight and left to dry at 70 ^{0}C to obtain GO modified paper. Reduction of GO in GO-P was performed in two ways. First, the whole GO-P film with various GO content get was dried in contact with Hydrazine vapor at 80 ^{0}C for 2 hrs in closed reactor to produce reduced graphene oxide paper composite (rGO-P). In order to show selective reduction one negatively pattern masked GO-P sample (2%) was exposed to Hydrazine vapor at 80 ^{0}C in a closed reactor for 2 hrs.

Results and Discussion

Morphological study

Dispersion of Graphene oxide sheets in final composites studied with SEM. Figure 1 depicts morphology of GO-P and represents adsorbed Graphene oxide sheets on cellulose fibres in samples containing 2% GO.

Electrical conductivity

Samples with different GO content was tested by two probe configuration to examine their electrical conductivity. Results are presented in figure 2 showing; decreasing electrical resistance by increasing reduced graphene oxide content.

Contact angle measurement

GO-P and rGO-P have different surface free energies due to the different chemical structure of GO and rGO. Oxygen containing groups in GO are responsible for hydrophilicity. Hydrophobicity is due to conjugated carbons. GO content and state of reduction control the amphiphilic properties of rGO-P. Contact angle measurement results are listed in table 1 and increased hydrophobicity proportional to the GO content is presented. Figure 4 shows partially reduced GO-P (2%) showing a dual area hydrophilic/hydrophobic recycled paper.

Conclusions

Effect of graphene oxide content and degree of reduction as two main factors on electrical conductivity and amphiphilicity of Graphene oxide modified recycled paper, were studied. This novel and facile mixing and reduction method produces flexible patterned conductive paper.

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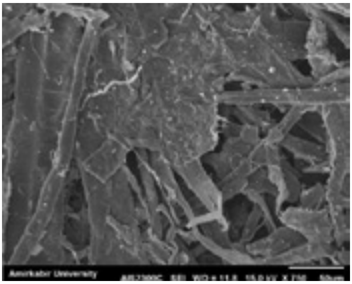

Fig 1. SEM image of GO sheets modified paper.

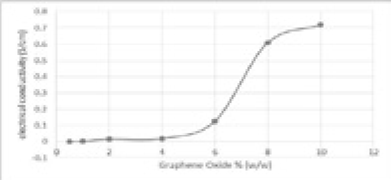

Fig 2. Electrical conductivity of RGO-P with respect to GO content.

Table 1. contact angle measurements of water micro droplets on paper surface.

GO content %	Contact Angle
0.5	Wet
1	Wet
2	79
4	83
6	88

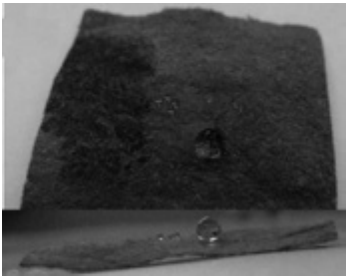

Fig 3. Hydrophobicity Patterned reduction of GO-P.

Alternative Strategies for Permanent Easy-to-clean Effects in Exterior Coatings

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Coatings for exterior surfaces are exposed to a variety of destructive mechanisms – UV, moisture, temperature extremes, biodegradation, etc.. While dirt pick up may not be the most destructive mechanism it can provide sites for mold and mildew growth and look unsightly. Existing easy-to–clean additives are based on fluorosilanes and polysiloxanes which migrate to the surface of the coating but have limited binder compatibility and will lose effectiveness over time. One alternative strategy to generate permanent easy-to-clean effects is based on nonionic monomeric and polymeric fluorinated surfactants that can be used in a wide range of coatings applications. Such additives have additional acrylic- and hydroxyl- functionalities which can cross-link into the binders of a variety of waterborne and solventborne coatings systems for permanent dirt repellency and easy water clean-up. We have recently expanded the concept by developing alternative chemistry based on functionalized polysiloxanes to replace fluorine – early data indicates a strong permanency effect coupled with the easy-to-clean effect.

Producing a piano-black design with plastics – Comparison of coating and alternative technologies

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picture: bezel for a navigation-system [Kunststoff-Institut Lüdenscheid]

Plastic-based high glossy and black surfaces are in the vogue of users: Coffee machines, TV-housings or automotive interior parts with “piano-black” optic are frequently asked in the market. But producer of theses molded parts know, how complex and complicated the zero-defect production of these surface treatments is. Piano black excuses no fault or blemish – even very small deviations on the surface increase the waste dramatically.

Because of this a lot of different technologies were used, to produce such surfaces and it is important to know the advantages and disadvantages of everyone of this.

Herstellverfahren für piano-black Designs

IMD (Inmold decoration)

FIM (Film insert molding)

Lackieren

Ink Jet

LIW (Lackieren im Werkzeug)

Picture 2: possible production methodes

Novel Non-Tin Catalysts for Polyurethane and Organosilane Applications

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A series of tin free catalysts for polyurethane and organosilane applications have been developed to address increasing European regulatory restrictions. These new catalysts contain no mercury, lead or other environmentally hazardous components. The catalysts are based on unique bismuth, zinc and other innocuous metal compounds that also address common short falls of more typical bismuth and zinc catalysts.

Body and Gloss - Precipitated Calcium Carbonate supports sustainable coating performance

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Ultrafine preciptated calcium carbonates are typically used in adhesives and sealants to manage rheology and improve mechanical performance. This paper will give two examples how PCC can add value to coatings.

Zero-Color paste for volume and weight control in tinting systems for DIY emulsion paints:

It is well known that inorganic particles below 100 nm show translucent behavior in paint systems. Ultrafine PCC with homogenous particle size of 80 nm was tested in colorant pastes where it renders body to the paste while not influencing the color point. The new product is an ultrafine, coated PCC which is well dispersible and can be used in colorant pastes themselves or as a neutral color paste which can be added to tinting systems as needed.

This study will show the performance of a paste having a high solid content but low viscosity, good flowability and storage stability. (Ultrafine PCC will be compared to fumed silica and transparent iron oxide.)

PCC in glossy coatings – route to sustainability:

In this part of the paper we will look at the performance of PCC in regard of optical properties like gloss and haze in coating systems. With the addition of 5-10% of ultrafine, coated PCC to an unfilled coating system gloss can be maintained.

This mineral filler can be used in water or solvent free coatings without any impact on the optical properties, like gloss, curing behavior or on the mechanical performance. Actual cost savings can be achieved when HAKUENKA® CCR-S is used to boost the performance of TiO_2.

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New driers for high solids alkyds paint

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Coatings containing drying oils and their fatty acid derivatives, as alkyds, dry by oxidative cross-linking. Driers are added to air-drying coating systems to accelerate or promote, after application, the transformation from the liquid film into the solid stage within appropriate time.

Different metal driers have different drying properties as some metals have much more catalytic effect than others. Driers are commonly divided into two main classes according to their catalytic activity. The primary driers have some catalytic effect, whereas the secondary driers have no catalytic effect at all. Cobalt carboxylates are the most widely used driers in solvent-based alkyd paints. They are used for their high efficiency but the toxicity of cobalt is their disadvantage. In the context of new legislative provisions, alternative Co-free driers are searched.

Conventional solvent borne alkyds don't correspond with recommendations of European institutions with regard to the content of volatile compounds due to high content of organic solvents. This problem can be solved by the use of high solids alkyds. However, many of these binders have insufficient properties such as long drying, bad surface and also very low hardness. In recent years, new types of driers for high solids coatings have been developed.

This paper describes the use of highly active iron or manganese as suitable driers for these binders. Their effect on drying time, pendulum hardness and mechanical properties of varnish prepared based on high solids alkyd modified by fatty acid tall oil was tested. The results are compared with the standard system containing Co drier and methyl ethyl ketoxime as antioxidant. Several concentrations of primary Fe and Mn driers, the effect of the addition of secondary driers based on Ca, Zr, Sr and Al, were evaluated. It can be concluded that an achievement of good properties of high solids alkyd coatings requires the use of appropriate mixtures of additives.

The author would like to thank the Ministry of Industry and Trade of the Czech Republic for the financial support of this work (project MPO FT – TI3/175).

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Develop your “Green” Water Based DTM Coatings with Nubirox 300

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The key function of an anticorrosive coating is protecting a metal substrate from corrosion by slowing doing its electrochemical oxidation process. Generally, these Coatings are part of a multi-layer system, so they work as a primer on which two or three layers of other coatings are normally applied.

The search for more economical and easy-to-apply coating systems has promoted the use of single-layer paints even for metal substrates, so both protection against corrosion and aesthetics are requirements for this one-coat paint. This is the concept behind Direct To Metal (DTM) coatings, which must meet the optimal balance between anticorrosive properties, color and gloss.

Offering “more sustainable” solutions has been one of the targets of paints manufacturers for years, especially for those coatings aimed at end consumers and professional painters whose work is not carried out under specific conditions to prevent the contact with components that are potentially harmful for them and the environment. This is the case of DIY, decorative and some light industrial applications, which are mainly the areas where DTM coatings are applied.

The formulation of DTM coatings is quite challenging then, as the optimal balance between anticorrosive protection, aesthetic function and “green” profile must be met.

Nubirox 300 Series are Nubiola’s recommendation for water based DTM coatings because they contribute to the fulfillment of these three requirements.

“Green” profile

Nubirox 301 is a calcium strontium phosphosilicate. Nubirox 302 is based on the same chemistry but has an additional surface treatment. Both products are zinc and labeling-free, being suitable for water and solvent based systems.

Aesthetic function

Due to its particle size distribution, conventional zinc phosphate anticorrosive pigments have a negative impact on gloss. Nubirox 300 Series show a smaller average particle size (around 1 micron) than conventional zinc phosphate, being the biggest aggregates and agglomerates below 10 microns. Therefore they contribute to a lesser extent to the roughness of the coating film surface, so it is smoother and thus glossier.

Anticorrosive properties

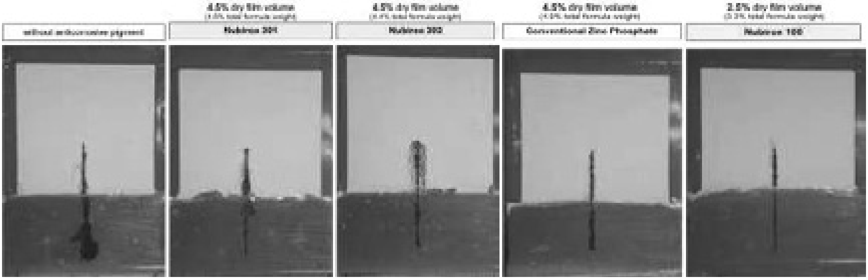
Typical water based DTM coatings are based on acrylic, styrene acrylic and urethane binders. In this study the performance of Nubirox 300 Series against a blank formulation (no anticorrosive pigment), conventional zinc phosphate and/or Nubirox 106 is compared. Nubirox 106 is Nubiola’s highest cost efficient anticorrosive pigment and it is based on a unique small particle size and high specific surface area zinc phosphate which is chemically modified with zinc molybdate and an organic surface treatment. It is also a labeling-free anticorrosive pigment but not zinc-free. As an example, the results in a water based acrylic system are presented below:

Formulation parameters

Solids in volume (%)	44.0
CPV/CPVC	0.5
Dry Film Thickness (DFT, microns)	90 approx.

Substrate	Standardized cold rolled steel S-46 (Q-Panel)

Salt Spray Test Results (ASTM B-117, 310 hours)



Gloss Evaluation

	Blank	**Nubirox 301**	**Nubirox 302**	**Conventional Zinc Phosphate**	**Nubirox 106**
Gloss 85º (Gloss Units, GU)	69	69	71	57	59
Gloss reduction vs blank (%)	-	0	+2	-18	-15

Effect of conductive polymers and amorphous chalcogenides on mechanical and corrosion properties of organic coatings with high metallic zinc particle contents

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This work is aimed at reducing the zinc metal content of organic coatings while preserving their high anticorrosion efficiency. A high anticorrosion efficiency combined with a reduced zinc metal content can be achieved by using conductive polymers or amorphous chalcogenides in the organic coating formula. The present work used specifically polyaniline phosphate (PANI-H_3PO_4) and, from among amorphous chalcogenides, the $Ge_{20}Se_{80}$, $Ge_{30}Se_{70}$ and $Ge_{40}Se_{60}$ systems. The pigments were specified based on their physico-chemical properties. An epoxy-ester resin was selected as the binder for the protective organic coatings. The protective organic coatings were formulated by combining zinc metal with the pigments. Mechanical resistance of the paint films was evaluated based on mechanical tests. Anticorrosion efficiency of the paint films was assessed based on accelerated corrosion tests.

Synthesis and examination of properties of tungstate and molybdate based anticorrosion pigments in paints

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Anticorrosion efficiency of paints with pigments containing tungstate and molybdate in an organic carrier was examined. The tungstate and molybdate based pigments were synthesized in the laboratory. The properties of the pigments were assessed based on a comparison with a commercial tungstate/molybdate based pigment which served as the standard in this study. Model epoxy resin based coating materials were prepared to study their anticorrosion efficiency. The anticorrosion efficiency of the pigments was evaluated through corrosion tests indicating resistance of the paints to the mist of a 5% neutral sodium chloride solution, to an atmosphere with sulphur dioxide (SO_2), and to condensing moisture combined with a mist of 5% sodium chloride plus copper chloride. The results indicate that the pigments provide good corrosion protection.

High-Temperature Corrosion of Aluminized and Chromized Fe-25.8%Cr-19.5%Ni Alloys in $N_2/H_2S/H_2O$-mixed

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Alloys of Fe-25.8%Cr-19.5%Ni (SUS310 stainless steel) were either chromized or aluminized via pack cementation, andcorroded at 800 ^{o}C for 100 h in 1 atm of (0.9448 atm of N_2+0.031 atm of H_2O+0.0242 atm of H_2S)-mixed gases. The chromized layer consisted primarily of $Cr_{1.36}Fe_{0.52}$ and some $Cr_{23}C_6$. Its corrosion resulted in the formation of Cr_2S_3 and some FeS and $Fe_5Ni_4S_8$. The aluminized coating consisted primarily of FeAl. Itscorrosion resulted in the formation of α-Al_2O_3, Al_2S_3, and Cr_2S_3. Aluminizing was more effective than chromizing in increasing the corrosion resistance of the substrate, due mainly to the formation of α-Al_2O_3.

Acknowledgments This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education(2013R1A1A2064793) (M.J. Kim), This work was supported by the Human Resource Development Program (No. 20114010203020) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy. (D.B. Lee)

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Inhibispheres™ as Alternative to Chromates for Corrosion Protective Coatings in Aerospace

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This collaborative project, partially supported by the French DoD (DGA), fits with Airbus Group Innovations' approaches for the assessment of new Cr-free self-healing materials for corrosion protection of metallic structures.

We study the technical interest of smart containers, called Inhibispheres™ developed by the Australian SME Ceramisphere (http://www.ceramisphere.com), as additives for environmentally friendly paint primers, developed by the French SME Mapaero (http://www.mapaero.com/).

These containers, developed in partnership between Airbus Group Innovations and Ceramisphere, are submicron ceramic spheres, containing *green* corrosion inhibitors. Ceramisphere technology enables the control of both the particle size and their release rate. Inhibispheres™ are designed, produced and supplied by Ceramisphere and incorporated by Mapaero in their paint primers, using their regular paint production process. Airbus Group Innovations and the French Laboratory Cirimat-Ensiacet are in charge of the assessment of the coatings' performances (based on aeronautical requirements). They also investigate release mechanisms and corrosion behaviour through global and local electrochemical techniques.

This poster will present the characterization and performance assessment of environmentally friendly paint primers, applied by spray-coating on pre-treated aluminium samples. The samples will contain different kinds of Inhibispheres™ loaded with *green* inhibitors. We will compare their characteristics (chemical composition and morphology) and performances, particularly in terms of release efficiency and corrosion protection.

Characterization of the fatigue behavior of reactive resin-bound concrete protection systems under load

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a) KÖSTER BAUCHEMIE AG, Aurich (Germany), b) University of Applied Science Emden/Leer

Resin based concrete protection systems which are used for application on e.g. parking deck areas where characterized using physical parameters under dynamical versus static loads. Besides using standard testing methods a new procedure for quantitative dynamic characterization of a full coating setup (substrate, primer, main protective surface layer) was developed. Artificial weathering and chemical attack of the coating systems was investigated in parallel. For a coating system the durability is also related to adhesive integrity of the coating parts during dynamic, static and chemical loading. Therefore part of the research aimed to develop a meaningful quantitative method for tensile adhesive strength characterization. A simple device was constructed which enables use of the literature known shaft-loaded blister test (SLBT) inside a standard tensile testing machine.[1] Using this setup it was shown that with only low effort much more reliable quantitative data in terms of critical energy release rates could be gathered. Comparing these critical energy release rates before and after loading events (e.g. contact with chemicals) differences in adhesive tensile strength properties could be seen with the SLBT not observable with the established cross-cut adhesion test.

References:

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P20

Measurement of Sparkle & Graininess

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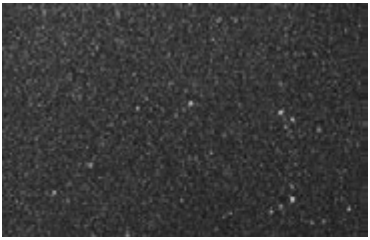
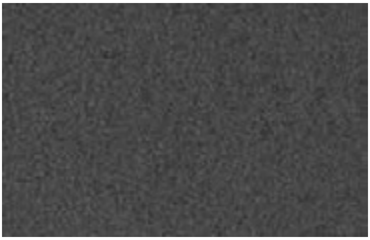
Today effect finishes play a dominant role in many applications as they make an object distinctively appealing. In contrast to conventional solid colors, effect finishes change their appearance with viewing angle and lighting conditions.

Interference finishes show not only a lightness change with different viewing angle, but also a change in chroma and hue. The latest developments are special effect pigments, which create sparkling effects when lighting conditions change from sunlight to cloudy sky.

In addition to color changes our total perception is also influenced by the effect of the metallic flakes or other sparkling pigments. This effect changes with the lighting conditions, for example direct sunlight versus cloudy sky.



Direct sunlight: Sparkle effect



Cloudy sky: Graininess

Sparkle

A sparkling or glitter impression can be observed under direct sunlight. This effect is often described with different words such as sparkle, micro brilliance or glint and is generated by the reflectivity of the individual effect pigment. Therefore, it is influenced by:

- flake type and size
- concentration level of the effect pigment
- orientation of the effect pigment
- application method

The sparkle impression changes depending on the illumination angle.

Graininess

Apart from the sparkle effect under direct sunlight, another effect can be observed under cloudy conditions, which is described as coarseness or salt and pepper appearance. This visual graininess can be influenced by the flake diameter or the orientation of the flakes resulting in a non-uniform and irregular pattern. The observation angle is of low relevance when evaluating graininess.

---

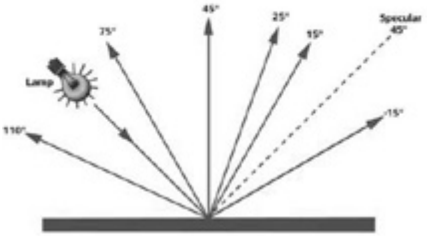
[1]

To characterize objectively the impression of effect finishes under different viewing angles and illumination conditions, new testing technologies, like the BYK-mac i were developed.

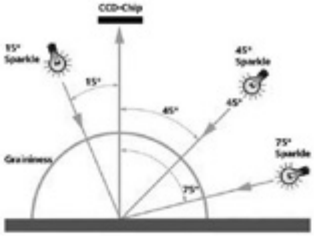
- Multi-angle color measurement (6-angles) clearly defines the light-dark as well as color flop behaviour of effect finishes
- Sparkling and Graininess control with a high resolution CCD camera simulates effect changes under direct and diffuse lighting conditions

The sparkle impression changes with the angle of illumination. Therefore, the BYK-mac i spectrophotometer illuminates the sample under three different angles 15°/45°/75° with very bright LEDs and takes a picture with the CCD camera located at the perpendicular. The pictures are analyzed by image analyzing algorithms using the histogram of lightness levels as the basis for calculating sparkle parameters.

Graininess is evaluated by taking a picture with the CCD camera under diffused lighting conditions, created by a white coated hemisphere. The picture is analyzed using the histogram of lightness levels whereby the uniformity of light and dark areas is summarized in one graininess value.



BYK-mac i color measurement



BYK-mac i effect measurement

Rotational and oscillatory methods for determining the rheological behaviour of coatings, paints and inks

Dr.-Ing. Oliver Arnolds, Dipl.-Ing. Oliver Sack

Anton Paar Germany GmbH, Ostfildern (Germany)

Understanding rheological properties of coatings, paints and inks is of great importance for manufacturing, processing, industrial application by practical users and curing / hardening.
Simple rotational experiments like controlled shear stress (CS) tests and controlled shear rate (CR) tests give only information about viscosity values, the “apparent” yield point and thixotropic effects. Since it is known for many years that these values are not sufficient to describe the complex visco-elastic properties of paints, the use of more sensitive rheometers is recommended for a better rheological characterization.

Modern air bearing rheometers provide the possibility to perform rotational tests as well as oscillatory tests. Measurements which are carried out under oscillatory shear conditions provide the advantages for characterizing liquid coatings and paints as well as in the form of cured films. In addition the curing or hardening process can be investigated and the glass transition temperature T_g can be determined. The most common used oscillatory experiments are the amplitude sweep (AS), frequency sweep (FS) and the structural recovery test (thixotropy). While the AS is used to determine the yield point, flow point and the structural strength, the FS provides information about the sedimentation stability of a dispersion. Thixothropy tests are used to describe after the application the resulting time dependent structural recovery.
Curing and hardening processes can not only be performed time-controlled and temperature-controlled but also under UV exposure. For this reason an air-bearing rheometer is essential to avoid any external influences to the 3-dimensional structures which are generated during the curing process.
Compared to a conventional viscometer, a modern rheometer system can be used for the complete rheological characterization of coatings, paints and inks. The generated data provide a deeper view inside the structure of these kinds of materials, making it possible to understand and to improve as well their production as well as their application.

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New measurement systems to drive process innovation

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Success or failure in the paint industry is dependent on innovation and productivity improvement. Developments were focused on new materials to reduce volatile organic compound and to improve the ecological footprint of companies. Unfortunately, we didn't do the same in developing advanced processes to produce paints. Traditional testing methods were adapted to new products, but the processes continued to follow old principles: Retrospective tests of quality.

We will describe how advanced testing technologies can be used to control raw materials, intermediates and finish products. Changing the production principle from retrospective to provident tests allows conversion to process designs following Lean Six Sigma principles with a strong effect on production cost and service level.

Examples for new measurement systems are the Q-Chain® Liquid Color Measurement of DEWIS GmbH and the Acorn NMR Particle Measurement device of XiGo Nanotools. We will demonstrate how these technologies drive innovation.

Q-Chain® Liquid Color Measurement measures color of coating materials in liquid phase. The 3-angle high performance spectrophotometer allows characterization of solid and effect colors directly in manufacturing process.

XiGo Nanotools particle technology measures the particle liquid interface of suspensions without dilution, providing a sensitive tool not just for research and development studies but also to control quality in manufacturing.

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Improving the properties of biobased PLA matrices by addition of surface treated nano- and microscale particles

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Fraunhofer Institute for Manufacturing Engineering and Automation, Stuttgart

Due to the climate change debate and the awareness of the finite nature of fossil fuels, organic polymer materials based on fossil fuels are intended to be increasingly substituted by polymers based on renewable resources.

Presently, polylactide acid (PLA) represents a biobased polymer material with highly promising economic perspectives [1]. The properties of pure PLA matrices, however, do often not meet the technical demands of the industrial application. Thus, systematic studies were undertaken in order to improve relevant properties of PLA matrices by the addition of commercially available supplies as well as of nano- and microscale particles, which were furnished with special surface treatments [2].

Such measures were performed in order to especially improve the photodegradation resistance, the water vapour barrier properties and the scratch resistance of bulk PLA matrices. Since at least the photodegradation and scratch resistance are properties, which are highly influenced by the composition and structure of the matrix close to the surface, a particle surface treatment, which results in stratification of the added particles towards the PLA surface, could contribute to an especially effective improvement of these relevant properties.

As microscale particles, which were used as barrier pigments, special types of talcum, mica as well as Minatec® were selected, surface treated and characterized regarding their effect in a PLA matrix. Moreover, e.g. nanoparticular CeO_2 was added in order to improve properties like scratch and photodegradation resistance.

Generally spoken, the addition of Minatec® components resulted in significant improvements of properties relevant for industrial application. Further improvements can be achieved by adding nanoparticular components as well as by optimizing the surface treatment of these additives.

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[1] Endres, H.-J., Siebert-Raths, A. (2009). Technische Biopolymere, Hanser, München, 162, 348-349.

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Evaluation of bio-based additives in architectural paints

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Currently the use of bio-based products (i.e. non-food products derived from biomass) in numerous industrial domains arouses an increasing interest. Regarding the use of these raw materials in the field of paints, this industry is facing two main challenges. Firstly, for this application only a limited range of bio-based products is satisfactory in terms of quality, cost and availability. Secondly, in general a lack of information on these products exists.

This study considers the incorporation of already existing bio-based products in the formulations of architectural paints. More specifically, it focuses on the use of sugar esters as dispersing agents. Compared to conventional petrochemical components these sugar-based additives present several advantages such as being non-toxic, biodegradable, odorless and non-irritating. In this paper their influence on the properties of coatings is evaluated and their performances are compared with those of reference petrochemical additives.

Electrodeposition of nano-aluminium coatings from aromatic cation based ionic liquids

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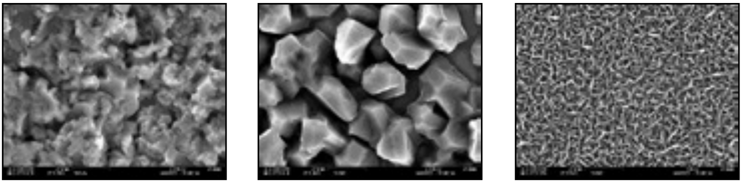
Abstract. The present paper discuss the electrodeposition of nanometals like aluminium from different imidazolium based chloroaluminate ionic liquids: $AlCl_3$/l-ethyl-3-methyl-imidazolium chloride ($AlCl_3$/[EMIm]Cl), $AlCl_3$/l-benzyl-3-methyl-imidazolium chloride ($AlCl_3$/ [BzMIm]Cl) and $AlCl_3$/l,3-dibenzyl-imidazolium chloride ($AlCl_3$/[DBzIm]Cl) ionic liquids, respectively. This research aims to achieve this goal by investigating the aluminium coatings on gold substrate and study the effect of changing the ionic liquids, like. e.g. changing the organic cation on the properties of the resulting Al-coatings. It was found that the particle size of the Al-deposites was significantly reduced from the micrometer regime down to the nanometer regime when only changing the substituents of the imidazolium cations from EMIm to DBzIm, respectively (Fig.1). This means; the more the aromatic rings in the cation, the finer the particle size is. Whereas, the thickness and the adhesion of the Al-deposits were decreased with the presence of the aromatic rings [1,2].



a) $AlCl_3$/EMImCl, b) $AlCl_3$/BzMImCl, c) $AlCl_3$/DBzImCl

Fig. 1: SEM micrographs of Al films on Au substrates in the three ionic liquids.

References:

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Nano modified coatings with high durability, for the protection of various supports from the outside and aggressive environments.

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In this paper we present the anticorrosion performance of some modified nanocoatings used for a long life time protection of metal. The coatings have anticorrosion properties due to the presence of nanosilicon carbide in their composition. The multifunctional composite has the ability to form a nanomodified polymer matrix which generates in the mono component polyurethane binder, nano-structured configuration. This gives the composite material properties, feature and superior performance impossible to achieve at a micro scale.

The structure and morphology of smart coatings were determined by infrared spectroscopy (FT-IR), and Scanning Tunneling Microscopy STM. The corrosion resistance of the modified coatings was measured by corrosion testing apparatus for salt spray. The introduction of 2%-3% nanosilicon carbide produces an optimum improvement in the corrosion resistance.

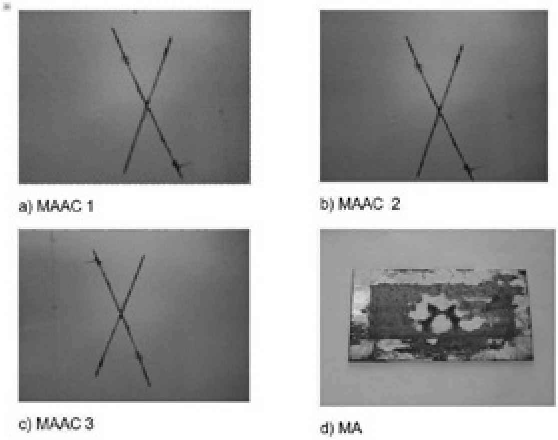
a) MAAC 1
b) MAAC 2
c) MAAC 3
d) MA

Figure 1 - Evaluation of surface degradation of the films after salt spray exposure a) MAAC 1 after 720 hours of exposure to salt spray test; b) MAAC 2 after 720 hours of exposure to salt spray tes; c) MAAC 3 after 720 hours of exposure to salt spray tes; d) MA(without nanoparticles) after 240 hours of exposure to salt spray tes**t.**

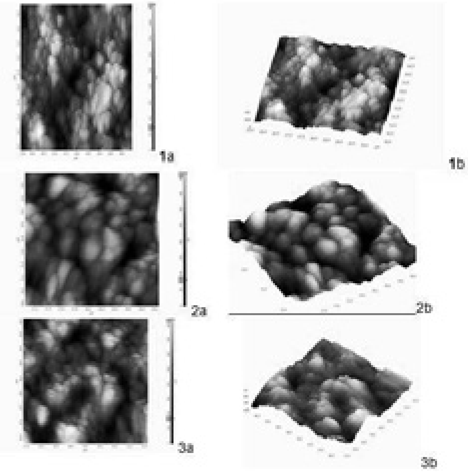

Figure 2- Surface topography of anticorrosive coatings – **1a**- images (2D) for MAAC 1; 1b - images (3D) for MAAC 1 – **2a**- images (2D) for MAAC 2; 2b - images (3D) for MAAC 2- **3a**- images (2D) for MAAC 3; **3b** - images (3D) for MAAC 3.

Advanced nanostructured coatings is used for long-term protection of constructional steel and aluminum, these mean**, building industry** (industrial halls, petrol and chemical equipment, on the shore or working on the sea, metallic bridges, etc), **railway buildings (r**ailway bridges, railway carriages including those transporting aggressive substances), **modern transport** (cars, aviation, fluvial and marine naval construction) **and nuclear power plant**.

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NIR-Reflective Pigment Formulations

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A range of different RAL-shades, based on NIR-reflective pigments, was formulated as a 2K PUR system. These coatings were spray-applied onto white and black substrates. The total solar reflectance (TSR) values of the coatings formulated were obtained and the heat build-up upon irradiation was investigated and compared to commercial reference systems without specific NIR-reflective properties. Despite 40-50 µm thick coating layers, appearing as visually opaque, an impact of the individual substrate became obvious in the NIR-regime of the corresponding reflectance spectra. To describe this effect, a simple model is presented that accounts for the wavelength dependence of the penetration depth of the incoming radiation [1].

$$(K / S)_{RAL\text{-}BS} = a \cdot [w_1 \cdot (K / S)_{RAL\text{-}WS} + w_2 \cdot b \cdot \lambda^c \cdot (K / S)_{BS}]$$

$(K / S)_{RAL\text{-}BS}$:	reflectance spectrum of RAL-shade on black substrate
$(K / S)_{RAL\text{-}WS}$:	reflectance spectrum of RAL-shade on white substrate
$(K / S)_{BS}$:	reflectance spectrum of the black substrate
a:	scaling factor
b:	scaling factor
w_1:	spectral fraction of component 1 (RAL-WS)
$w_2 = 1 - w_1$:	spectral fraction of component 2 (BS)
c:	exponent
λ:	wavelength

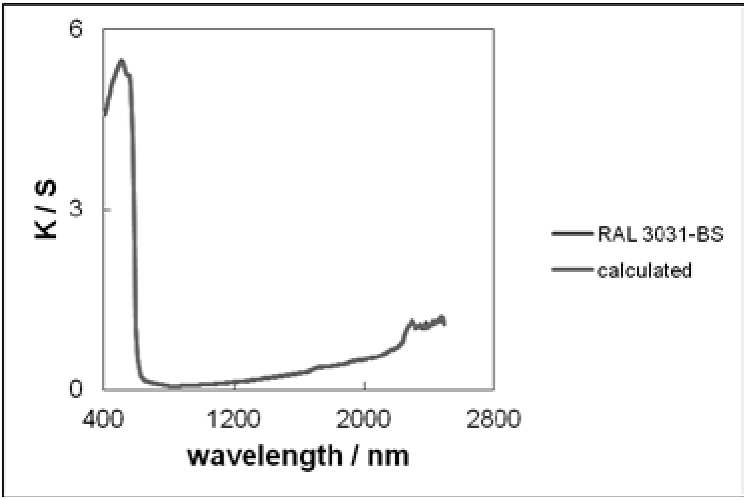

Figure 1: Reflectance spectrum of RAL 3031-BS measured over a black substrate in Kubelka-Munk units compared to the calculated one.

Table 1 shows that the TSR values of the internally formulated RAL-shades are higher than those of the reference systems. However, the final surface temperatures (ΔT_{END}) obtained were expected to reveal greater differences between the internally formulated RAL-shades and those of the reference systems than observed. This finding was related to differences in the heat conductive properties as well as to the individual thermal emission coefficients (ε) of the formulations.

Table 1: Final surface temperatures (ΔT_{END}) upon irradiation and TSR values calculated according to ASTM G-173-03.

Colour-shade	Substrate	TSR / %	ΔT_{End} / °C
RAL 3031	black	44,54	44,4
	white	48,93	41,7
RAL 3031-REF	black	28,46	48,7
	white	31,68	43,4
RAL 4009	black	47,70	45,8
	white	52,72	45,6
RAL 4009-REF	black	29,47	49,4
	white	29,66	50,9
RAL 5012	black	35,29	46,0
	white	42,38	46,4
RAL 5012-REF	black	31,24	46,4
	white	32,57	44,0
RAL 8004	black	38,80	41,7
	white	40,80	41,4
RAL 8004-REF	black	22,85	51,5
	white	26,99	45,0

References:

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P28

New catalysts for ROP of ε-caprolactone

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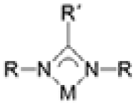
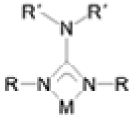
Poly-ε-caprolactone and polylactide are examples of polyesters suitable for biomedical applications, such as controlled release of drugs or surgical suture materials, due to their biocompatibility and degradability. These polymers can be synthesized through either polycondensation of functional acids and alcohols or ring opening polymerization of cyclic esters using cationic, anionic or covalent initiators.

Our work focused on a new class of a complex based catalysts prepared by the insertion of selected substituted carbodiimides into a metal – carbon (nitrogen) bond of various organometallic compounds, e.g. *n*-butyl lithium. Except of lithium also magnesium, tin, zinc and aluminum organometallic compounds were used. Magnesium is particularly attractive for the availability of many precursors in the form of Grignard reagents. Prepared amidinates (I) and guanidinates (II) were characterized by multinuclear NMR approach and X-ray diffraction techniques.



(I)



(II)

Catalytic efficiency was tested in ring opening polymerization of ε-caprolactone carried out in a batch mode. The conversion was monitored by NMR spectroscopy and products were analyzed by GPC. Catalysts reveal high reactivity and high conversion is reached in a several minutes even at room temperature. Molecular weight Mn of prepared poly-ε-caprolactones varied between 6, 000 and 30, 000, while polydispersity index was between 2 and 28. The quality of product is depending on the structure of catalyst, its concentration, concentration of monomer and also on the type of used solvent. Efficiency of these catalysts was not tested only in homopolymerization of ε-caprolactone but also the copolymers of caprolactone with trimethylene carbonate were successfully prepared.

The authors would like to thank the Technology Agency of the Czech Republic for the financial support of this work (project TA02020466).

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P29

Investigation of influence of atomizing assisting gases on the coating process

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The atomization process plays a central role in the spray coating. In the atomization process coating materials break into droplets. An optimized atomization process should provide the high coating quality on the substrate surface with high transfer efficiencies of coating materials. Within the frame of a German joint project "Glaze-Forming" funded by BMBF, the influence of atomizing assisting gases, namely by switching from air to steam on coating processes, is investigated.

Numerical simulations were performed by means of the commercial CFD solver ANSYS FLUENT. The turbulent flow field was calculated by solving the Reynolds-averaged Navier–Stokes equations. Based on discrete phase Models, the trajectory calculation of the droplets was also carried out.

Experimental studies were performed in the technical laboratory using modern measurement methods, such as laser diffraction for measuring droplet size distributions, Laser Doppler Anemometry for measuring droplet velocity, infrared camera for measuring temperature distributions, as well as ultrafast photography and a high-speed camera for the Visualization of atomization. The experimental results were used not only to validate the numerical results, but also to deliver the necessary boundary conditions for numerical studies.

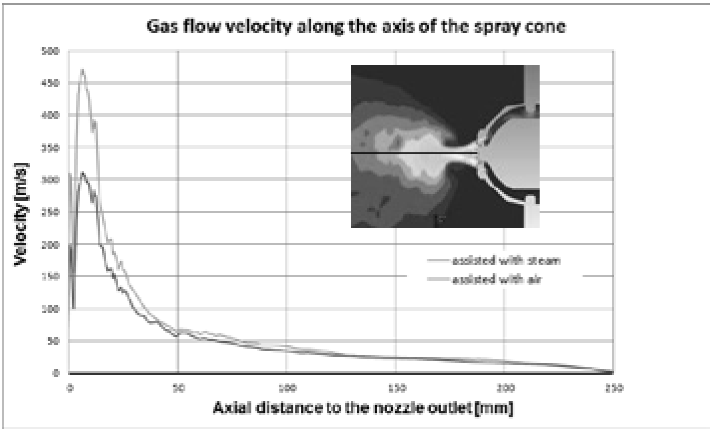

Figure 1 Gas flow velocity along the axis of the spray cone in coating processes assisted with steam and air

Based on the numerical studies it was found that the maximal atomizing gas velocity is 470 m/s using overheated steam, whereas 310 m/s using air. The atomization process is significantly improved by using overheated steam because of the higher velocity, which was validated with the experimental results. On another hand, the steam gas flow relaxes quickly as shown in Figure 1, no differences can be observed between using steam and air as working fluids over a distance of 200 mm. A high transfer efficiency of the spray coating with steam was measured in experiments.

The evaporation and condensation of droplets were considered in the trajectory calculation for a spray with steam as the atomizing assisting fluid, aiming to understand if droplets become dryer or wetter during their flight to the substrate (Figure 2).

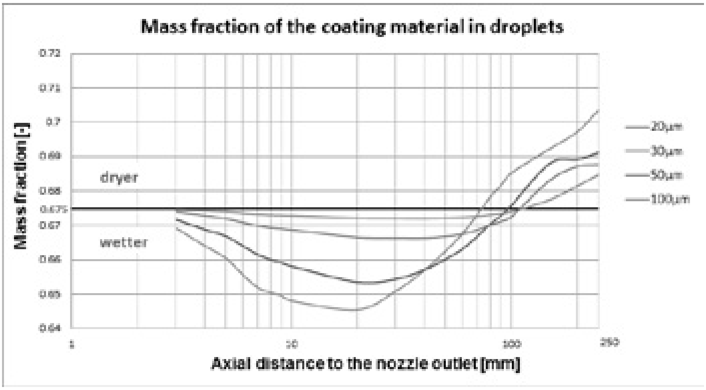

Figure 2 Change in mass fraction of the coating material in droplets during their flight to the substrate

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Synchronization of a DSC with NIR-LEDs: a Simple Way to Photo-DSC

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Photopolymers have received big interest in coating sciences. Quantitative knowledge of reactivity plays one major role to characterize such polymer systems. There are several methods available describing the kinetics of photopolymers operating according to a mechanism in which reaction heat would be released during crosslinking. From this point of view, Differential Scanning Calorimetry (DSC) can be used to determine the reaction heat released upon exposure with light generated either in the UV, visible or near infrared (NIR). Thus, coupling of the DSC with a lamp and synchronization of the begin and the end of exposure opens the possibility to study online photoinduced crosslinking of olefins and epoxies. A commercial solution has been already existing for synchronization between DSC and UV source[1]. Nevertheless, it has not been described a general coupling of the DSC with light sources selected from LEDs or alternative exposure sources operating in the visible or near infrared (NIR). Thus, we describe a hardware and software solution in which nearby every light source can be integrated and synchronized with the DSC.

In this contribution, we describe NIR-photoinitiated polymerization of multifunctional acrylic esters[2], which is followed online by our Photo-DSC setup. We designed a shutter system with flexible use of light sources using the event signal from the DSC (controlled by the software) to start a controlled program running on an Arduino uno Board. This microprocessor controls the shutter in the light path that can be either opened or closed depending on the resistance of the event signal of the DSC hardware (Q 2000 from TA Instruments). The shutter would be closed if the resistance would be close to zero while the shutter opens in case that the resistance would be infinite. Furthermore, the Arduino uno Board can turn on or off the excitation source. It opens therefore a flexible design to build a hardware to study the kinetics of many photopolymerization systems based on exothermal reactions. Figure 1 shows the details of the setup.

Figure 2 shows the heat generated upon exposure. It depicts typical parameters describing the reactivity of a photopolymer. This is the maximum of the polymerization rate (R_p^{max}) and the time to reach R_p^{max}. Integration of the latter results in the conversion as a function of exposure time.

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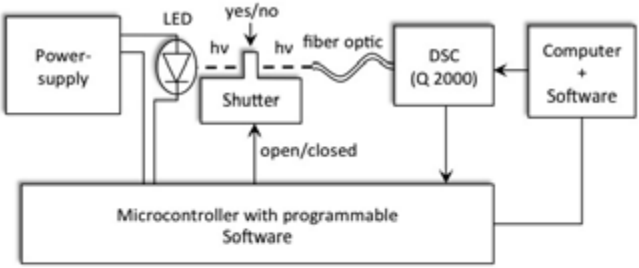

Figure 1: Schematic setup of the Photo-DSC synchronously working with a LED radiation source and a Q2000 available from TA Instruments

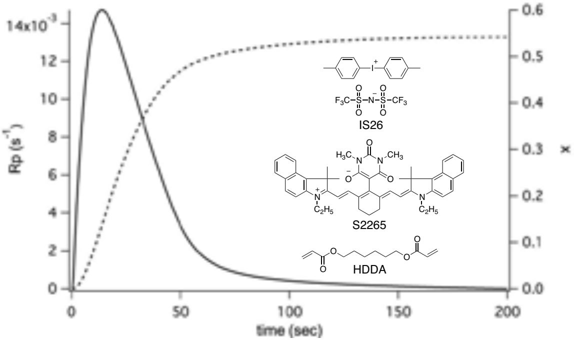

Figure 2: Example results from the Photo-DSC (S2265, IS26 [Bis(methylphenyl)iodonium triflourmethylsulfonylimide], HDDA, LED790-66-60 from Roithner with 790nm)

New methods of specimen preparation of pigment particles for investigations in transmission electron microscopy

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For optimising colour, optical effects or functionality, and creating new properties of pigment particles, the knowledge of the micro- and nanostructure of the latter are essential. Due to its tremendous spatial resolution in the sub-Angström range, both in imaging and analyses, transmission electron microscopy (TEM) is ideally suited for such investigations. In order to utilize the fabulous capabilities of TEM, the preparation of extremely thin sections out of volumes of interest are pivotal. The typical thickness of such specimens is less than 300 nm, sometimes even thicknesses of a few tens of nanometres are mandatory.

Using conventional methods, the preparation of cross-sections from individual pigment particles to electron transparency is a complex and laborious task. In the standard approach, single pigment particles were deposited by means of micro manipulator and fixed on a substrate (H) bar with a thickness of 80 to 100 µm. This assemblage of substrate and pigment particles was to be ion-beam thinned to residual thickness of just a few 100 nm.

In order to improve this preparation technique, a very fast and efficient preparation route was developed by combining laser milling with ion beam techniques. Using the all-new laser processing system microPREP[1] (by 3D-Micromac AG, Chemnitz, Germany), a newly designed pigment-support platform with reduced residual thickness of the area for pigment-particles deposition can be readily prepared, Figs. 1-3. Due to the reduced thickness, the processing time in a focused ion beam work-station is greatly reduced. Furthermore the substrate material is variable and therefore optimum conditions for analytical investigations (EDXS, EELS) in the TEM can be attained. On such specimens of pigment particles the thickness of particles and layers, interfaces, artefacts, grain and crystal structure, morphology, chemical components and other things can be study in the regions up to atomic scale.

Alternatively, wedge polishing of pigments glued to the surface of a sacrificial wafer proved a very valuable way to get statistical information on a larger ensemble of pigments rather than details on individual particles.

Examples of samples prepared both ways will be shown after TEM characterization in our cutting-edge TEM (FEI TITAN³ G2 80-300).

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P32

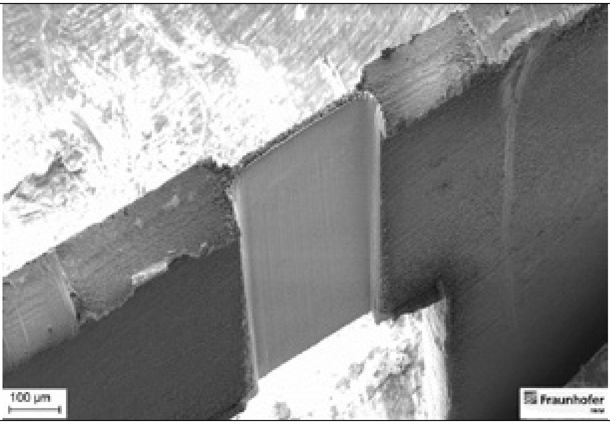

Fig. 1 Newly designed pigment-support platform with reduced residual thickness of the area for pigment-particles deposition (scanning electron micrograph).

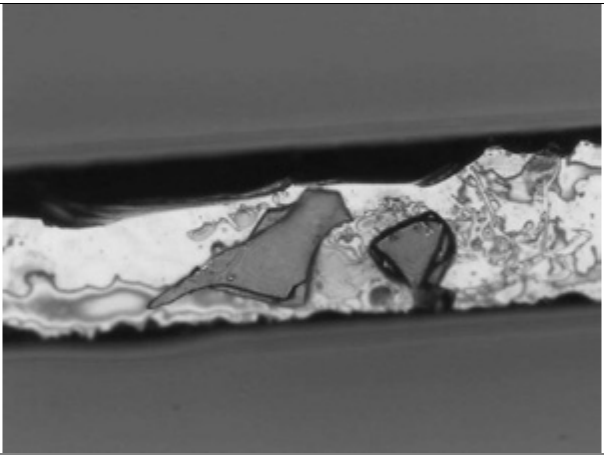

Fig. 2 Pigment particles deposited and fixed on a support platform (light microscopy).

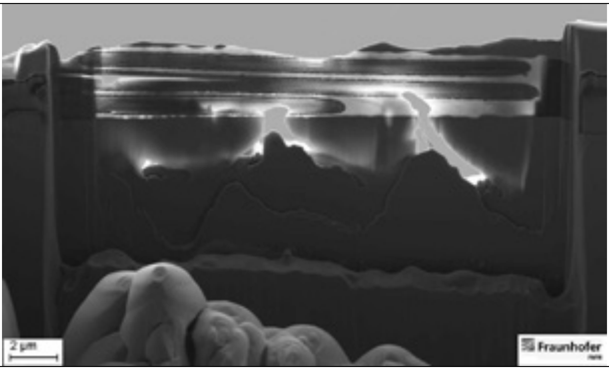

Fig. 3 Ion-beam thinned pigment particles with electron transparency (scanning electron micrograph).

COLOUR BLACK FW 255 - a high jet Carbon Black Pigment for solvent-, water-borne and high solid coating systems

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For decades, Orion Engineered Carbons predecessor has been offering Carbon Black Pigments that meet the stringent performance requirements of premium high jetness coatings.

Several years ago, Orion Engineered Carbons introduced COLOUR BLACK FW 171, a high jetness Carbon Black Pigment, primarily designed for the application dedicated to water-borne coatings. Orion's most recent development based on highly sophisticated particle design – COLOUR BLACK FW 255 – is a universal Carbon Black Pigment suitable for the application to solvent-borne as well as to water-borne coatings.

COLOUR BLACK FW 255 is characterized by a very small mean primary particle size, and both a narrow distribution of primary particle size and aggregate size. This particular particle design, in combination with a good dispersion, results in very high jetness and a deep blue undertone.

COLOUR BLACK FW 255 is an after-treated Carbon Black Pigment. This after-treatment process generates a functional surface with oxygen-containing groups. When incorporated in a coating system, these groups induce better wetting and dispersing properties. An enhanced interaction with polar binders improves the stabilization of the Carbon Black Pigment significantly.

In polyurethane coatings – both solvent-borne and water-borne coating systems – COLOUR BLACK FW 255 shows very high jetness and a very bluish undertone. Therefore it can be used as universal pigment especially but not limited to solvent- and water-borne PU coating systems.

COLOUR BLACK FW 255 is also able to improve the viscosity behavior of a high-jet Carbon Black Pigment in a 2K high solid formulation. After 24 h storage time we measured among the largest shear force (highest shear rate) the lowest viscosity. Upon subsequent reduction of the shear rate, a slight increase in viscosity was observed. Compared to a reference, COLOUR BLACK FW 255 shows higher viscosity in the beginning, but strong reduction during mechanical stress and less increase of viscosity after decreasing the shear force again. This behavior provides the following benefits for the user:

- better storage stability
- less danger of sedimentation
- strong viscosity reduction during stirring
- easy adjustment of viscosity, because of less increase of viscosity after reducing mechanical stress
- higher mill base loading

Thus COLOUR BLACK FW 255 is as well ideal for high jetness, high solid systems.

The alcaline depolimerization as a recovery source of poly (ethylene terephtalate)

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The extensive use of polymer materials in many areas of life is associated with an increase in the amount of waste materials in landfills. In Poland, every year 12 million tons of waste is produced. In most cases, they are stored in landfills. In accordance with EU Directive 2005/20/EC on packaging and packaging waste, before 2014, Poland must reduce the disposal of waste to 35 % and achieve adequate levels of recovery (minimum 60%) and recycling (minimum 55%).

Poly (ethylene terephthalate) (PET) is the raw material of wide use due to its physical and chemical properties. *PET is used for production of bottles, packages for household chemicals*, cosmetics and *packaging films*. *It is also used in the textile industry*. *Such a large application*, especially in *packaging industry, PET owes its* esthetic appearance, *transparency and high mechanical strength*. But the problem is the disposal of PET waste, because it is particularly resistant to prolonged exposure to atmospheric conditions. PET waste does not biodegrade or decompose naturally and stands over in unchanged forms in landfills. It is recognized as the onerous material, creating permanent contaminations of the environment. Due to environmental, economic and legal reasons, it is important to take action to implement a wide recycling of PET.

Currently, one of the most effective PET recycling methods is alkaline hydrolysis, which depends on the acting on material with the appropriate hydroxides, e.g. sodium and potassium hydroxide or aqueous ammonia, usually at the elevated pressure and temperature.

The paper presents a method for the hydrolytic recovery of PET, using potassium hydroxide and aqueous ammonia. The process is carried out to total exuding of terephthalic acid (TA) salts, respectively, potassium or ammonium, followed by precipitation of the terephthalic acid and glycol. Using sulfuric acid, as a neutralizer, there are obtained products in the form of ammonium or potassium sulfates, which are widely used, particularly as a fertilizers. In case of replacement of the sulfuric acid by carbonic acid, ammonium or potassium carbonates are obtained. Ammonium carbonate is used as fire - extinguishing agent and in dyeing, while potassium carbonate is used in the glass industry, ceramic, as well as in detergents production. Efforts, which aim to PET waste disposal are compliant with the requirements of EU law contained in the relevant acts, primarily on environmental protection. Furthermore, the use of secondary raw materials will reduce the usage of natural resources.

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Strategies for Chemical Curing of Coatings by the Use of Sunlight

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Different photoinitiator systems covering the emission profile of the sun were investigated in a radical crosslinking system. Different acrylates selected from polyols, urethanes and epoxyacrylates were used in the studies to obtain a rough image regarding conversion and crosslinking efficiency. The systems were screened by different methods; that is FTIR, photo-DSC, and sol-gel analysis. Experiments were carried out under different solar radiation intensities and compared with experiments obtained using artificial light sources (LEDs, Xe lamp).

Impact of IR-irradiation as powerful curing method to obtain crack free coating for sol-gel derived coating materials

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An important area of sol-gel chemistry is the production of coatings. For the majority of sol-gel systems, a thermal treatment of the deposited solution (sol) is necessary to obtain cured coatings. In addition to the evaporation of the used solvents crosslinking of the material has to be initiated by condensation reactions during the curing process. These processes are typically achieved by thermal treatment in convection ovens. In order to obtain crack free coatings the thermal power as well as the curing time are the most important parameters. Infrared irradiation is an interesting alternative annealing technique, which can be used to decrease the curing time significantly. This impact of using IR-emitters was tested for two model different sol-gel systems: (i) a bridged organic-inorganic hybrid precursor **1** (figure 1) and (ii) methyltriethoxysilane $CH_3Si(OC_2H_5)_3$ (MTEOS) based coatings.

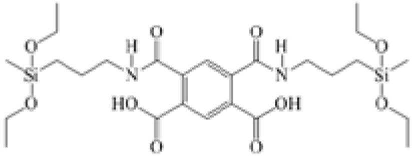

Fig. 1: Bridged alkoxysilylalkyl amide acid used as single-source precursor **1**.

For both systems, the coatings formed from the the sols were cured using classical convection ovens as well as high power IR-emitters. The obtained materials were characterized using elemental analysis (bulk combustion) and CP/MAS ^{29}Si-NMR and FT-IR spectroscopic studies. The imidization process of hybrid precursor **1** was analyzed using ^{13}C-NMR spectroscopy. The obtained coatings were also investigated regarding thickness, adhesion and surface morphology by white light interferometry and scanning electron microscopy (SEM).

The results indicate that IR-irradiation is suitable to dry and cure sol-gel derived coatings. The method produces cross-linked and smooth coatings, which are free of cracks, pinholes or other defects. Much shorter curing times are necessary compared to heating in convection ovens.

P37

Functionalization of Textile Substrates by NIR Initiated Photopolymerization of Multi-Functional Acrylic Esters

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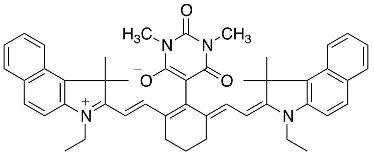
Conventional textile polymer coatings have been often applied as homogeneous solutions or heterogeneous aqueous dispersions using energy intensive thermal drying techniques to solidify the coating. This is either physical drying by removing the coating solvent or chemical curing of the coating components. Nevertheless, both processes require higher temperatures provided by convection dryers and consequently they are cost-intensive and time consuming. On the other hand, radiation induced polymerization of textile coatings represents an ecological and economical alternative[1] using LEDs as energy saving radiation source. LEDs have been available from the UV up to the near infrared (NIR) region. NIR-LED arrays may possess some benefits compared to UV LEDs; that is a larger curing depth profile, the possibility to embed UV absorbers as well as yellow pigments, and initiation of thermal events by deactivation of the excited state that additionally functions as an absorber in the coating formulation[2].

This contribution focuses to develop a chemistry working in coating systems using a new low-energy radiation source; that is a NIR-LED array for the use of technical textiles to provide a basis either to supplement or substitute conventional textile coatings. Thus, the NIR sensitized photoinitiated polymerization using an initiator system comprising a polymethine dye as sensitizer and an iodonium salt as radical initiator represents an interesting alternative to cure typical textile polymer systems with either urethanacrylates or polyol acrylates. This additionally requires to develop a formulation that efficiently cures under the radiation setup chosen. The components of the initiator system, the sensitizer **1** and the radical initiator **2** dissolve well in the coatings taken for solidification of the textile coatings. Particular the iodonium salt **2** comprising the $(CF_3SO_2)_2N^{-}$-anion significantly improves the solubility in the monomers. In some cases, the iodonium slat **2** was 1:1 compatible with the high viscous technical monomers chosen.



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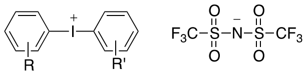

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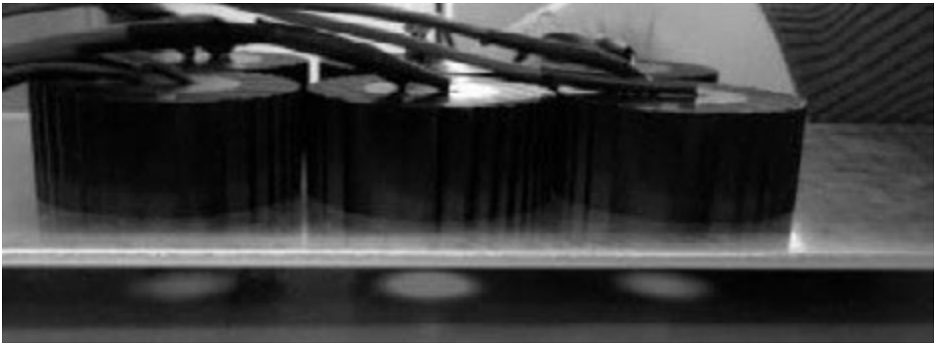
The coating systems developed were first applied on a PE-foil and cured by the NIR-LED array (emission maximum at 790nm). The progress of crosslinking was studied with both FTIR and Photo-DSC. This resulted in a detailed pattern regarding the reactivity. Subsequently, selected formulations were transferred to textile substrates in which finishing effects and their permanence with conventional finishing methods were compared. The focus here was on the physical properties of the composite material such as flexibility, bending stiffness, abrasion resistance, and tear resistance.

In the next step, the results were transferred to a semi-continuous coating machine. Here, in particular, the integration of NIR-LEDs into the coating machine and the application technique (knife, slot die, screen printing) as well as the simultaneous crosslinking will be considered.



NIR-curing setup combining 6 NIR-LED arrays on a specific carrier plate for exposure of a polyester substrate coated with multifunctional acrylic ester

Acknowledgement
This project was funded by German Federal Ministry of Economics and Technology (BMWi) via „Zentrales Innovationsprogramm Mittelstand“ (ZIM), under grant number KF 2914003BN2. We furthermore would like to thank FEW Chemicals GmbH (www.few.de) for providing the polymethine dye 1.

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Design-Strategies for highly-sensitive photopolymers

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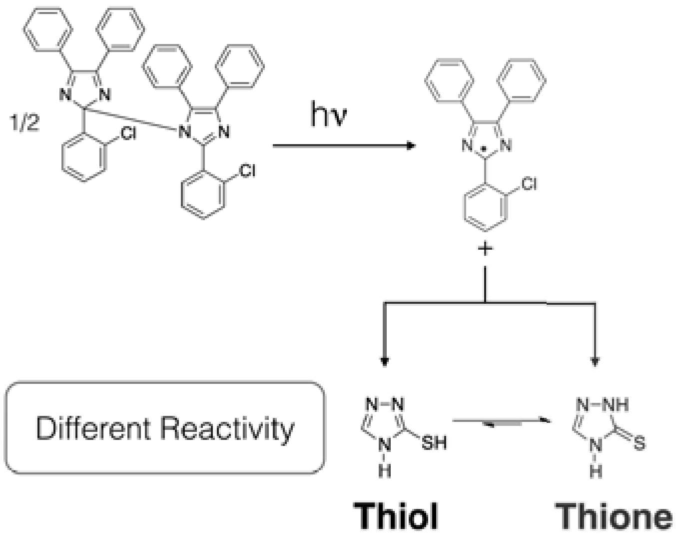
Photopolymer technology has gained increased interest over the past decades. It has developed to a fast, ecologically sustainable, and cost saving method to solidify coatings resulting in good mechanical and solvent resistance. Possible applications include coatings, dental composites, adhesives, stereolithography, and information recording materials [1-3]. Photoinduced radical polymerization and crosslinking has evolved into a fast reliable procedure to solidify coatings, despite the remaining problem of oxygen inhibition. This may lead to an incomplete conversion and subsequently to tacky surfaces, especially when using low intensity light sources: this is the case with an LED. On the other hand, LEDs consume significantly lower energy compared to traditional light sources used in curing. Thus, LEDs can be seen as future light sources in photopolymer technology.

High reactive photoinitiator systems (PIS) contribute to reduce oxygen inhibition. They exhibit a high reactivity even at low light intensity resulting in a solid film without any tackiness in the presence of oxygen. In combination with mercapto compounds, Hexaarylbiimidazole derivatives (HABIs) represent one example. Although such PIS were researched over several decades, there is still a lack regarding the mechanism depicting the formation of high reactive initiating species [4], Scheme 1. Particularly, the interaction between the lophyl radicals generated after exposure and the mercapto compounds was examined in more detail. Different combinations of several HABI derivatives and heterocyclic mercapto compounds were studied to explore the influence of the substitution pattern explaining differences in the reactivity of the systems.

Photo-DSC measurements, in which the DSC was synchronized with the light source, were carried out to study the reactivity of the systems in both nitrogen and air surrounding to analyse the system`s sensitivity towards oxygen inhibition. The attained conversions are also determined by this method. This gives a clear pattern about the reactivity of the components in the different monomers.

Some mercapto compounds exist in a tautomeric equilibrium between the thiol and the thione that depends on the surrounding medium. ^{1}H-NMR-measurements helped to quantify the amount of thione and thiol of the mercapto compound in the monomer chosen. Experiments showed a higher reactivity of those compounds forming a higher amount of thione, while classical hydrogen donors, such as aliphatic thiols, exhibit the lowest reactivity in the photo-DSC measurements.



Scheme 1

The lophyl radicals produced by irradiation recombine back to the corresponding HABI in absence of an appropriate reactant - the heterocyclic mercapto compound. This decreases the efficiency. Recombination rate constants were determined in the monomers used to obtain a quantity about reactivity and possible recombinations in the solvent cage affecting sensitivity. Thus, these investigations provide information about the behaviour of the lophyl radicals in the particular systems and elucidate both influences of the surrounding medium and the different substituents on the reactivity of these PIS.

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P39

Effects of different nano-sized TiO_2 additives on their UV protective performance in transparent polymer coatings

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[2]Industrial Paint Research Ltd., Budapest

Rutil phase titanium dioxide nanoparticles, which were synthesized by a novel method, increase the life span of polypropylene and polyester surfaces.

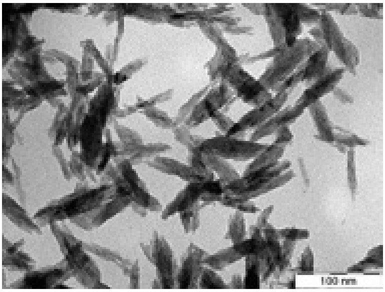
Polyesters and polypropylenes are widely used polymers; both are strong, inexpensive, light weight but UV sensitive, they need additives to inhibit photo-degradation.

Titanium dioxide nanocrystals were investigated intensively and numerous commercial applications have been developed utilizing its high refractive index and UV filter effectiveness in polymer matrix without significant loss of transparency.

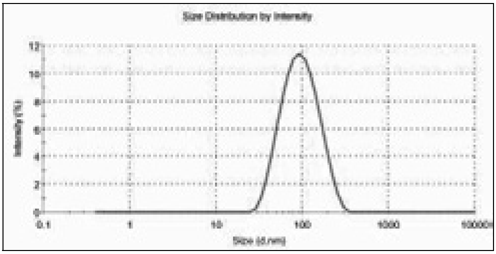
TiO_2 semiconductor nanoparticles behave particular by their size and geometry (quantum-size effect), their high surface area requires tunable surface properties to provide adequate wettability in coatings.

In the present work, detailed studies have been carried out for the investigation of new application of high-quality TiO_2 nanoparticulate products as functional additives in UV protective coatings. The emphasis was on the comparison of the performance of TiO_2 particles with different sizes, morphology and particularly with different aspect ratios.

Firstly we tested the stability and pressure-induced changes of untreated clear coat matrix at wide pH range and different TiO_2 nanoparticle loading by zeta potential measurements, than analysed the complex microstructure by Scanning Electron Microscopy. Finally we checked the UV shielding effectiveness of films containing nanoparticles by colour, gloss-change measurements after accelerated weathering.



Morphology of synthetised pure rutile TiO_2 nanocrystals prepared from inorganic titanium precursor



Size distribution of synthetised rutile nano TiO_2 particles measured by Dynamic Light Scattering method.

The aim of the study was to specify the correlation between the morphology and UV-protecting behaviour of pure rutil phase TiO_2 nanoadditives containing waterborne clear coatings to protect polypropylene and polyester surfaces against UV degradation.