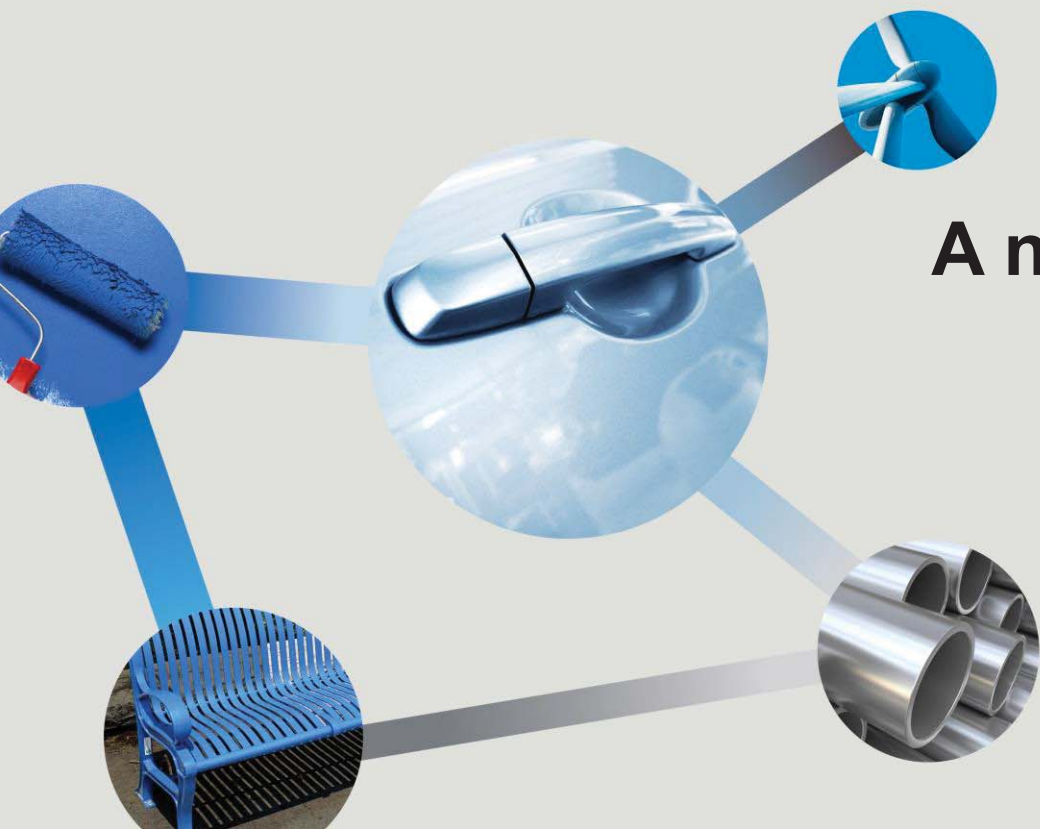


Ramspec 2014

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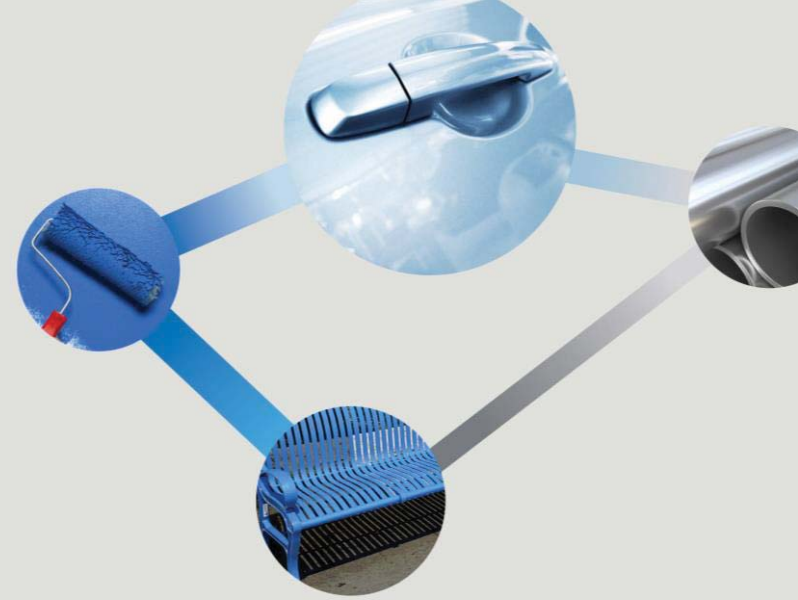


**A new generation of acrylic
binders**

Adriaan Sanderse, Dirk Mestach

Nuplex Resins BV

The Netherlands



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Focused on developing **solutions** for architectural, performance and industrial coatings and delivering **tailored service**

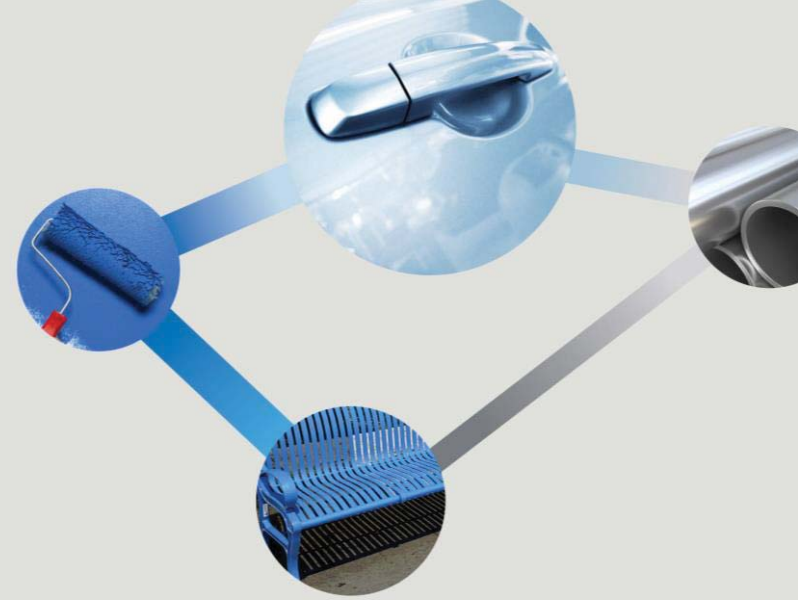
- Leading positions in a range of market segments
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Compliant decorative coatings

Decorative coatings and Indoor Air Quality

- Paints Directive 2004/42/EC: focus on the volatile organic compounds* (VOC) present in the liquid coating.
- Paint will continue to emit VOC for a long time after having been applied.
 - For paints and coatings that are being used indoors, this can lead to reduced indoor air quality (IAQ).
- Total VOC (TVOC): ISO 16000
 - all compounds between n-hexane and n-hexadecane



* initial boiling point less than or equal to 250 °C (482 °F) measured at a standard atmospheric pressure of 101.3 kPa.



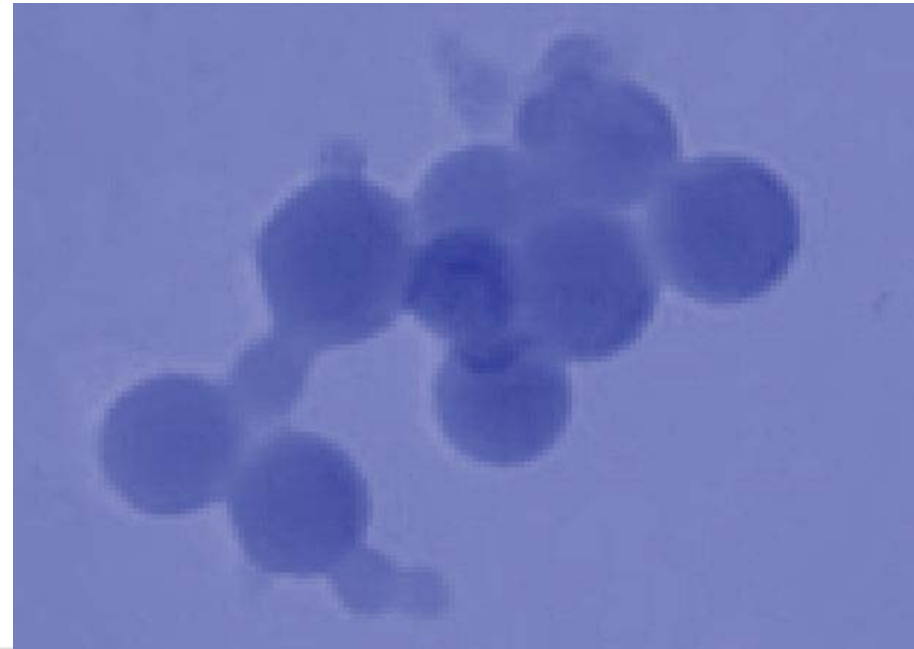
Waterborne binders for coatings with low (T)VOC

- How to get good hardness and yet sufficient film-formation at low temperatures
 - how to separate the glass-transition temperature (T_g) of the polymer from the minimal film-formation temperature (MFFT)
- Acrylic dispersions:
 - Homogeneous morphology: $MFFT \approx T_g$
 - Heterogeneous morphology:
 - core-shell morphology
 - gradient morphology

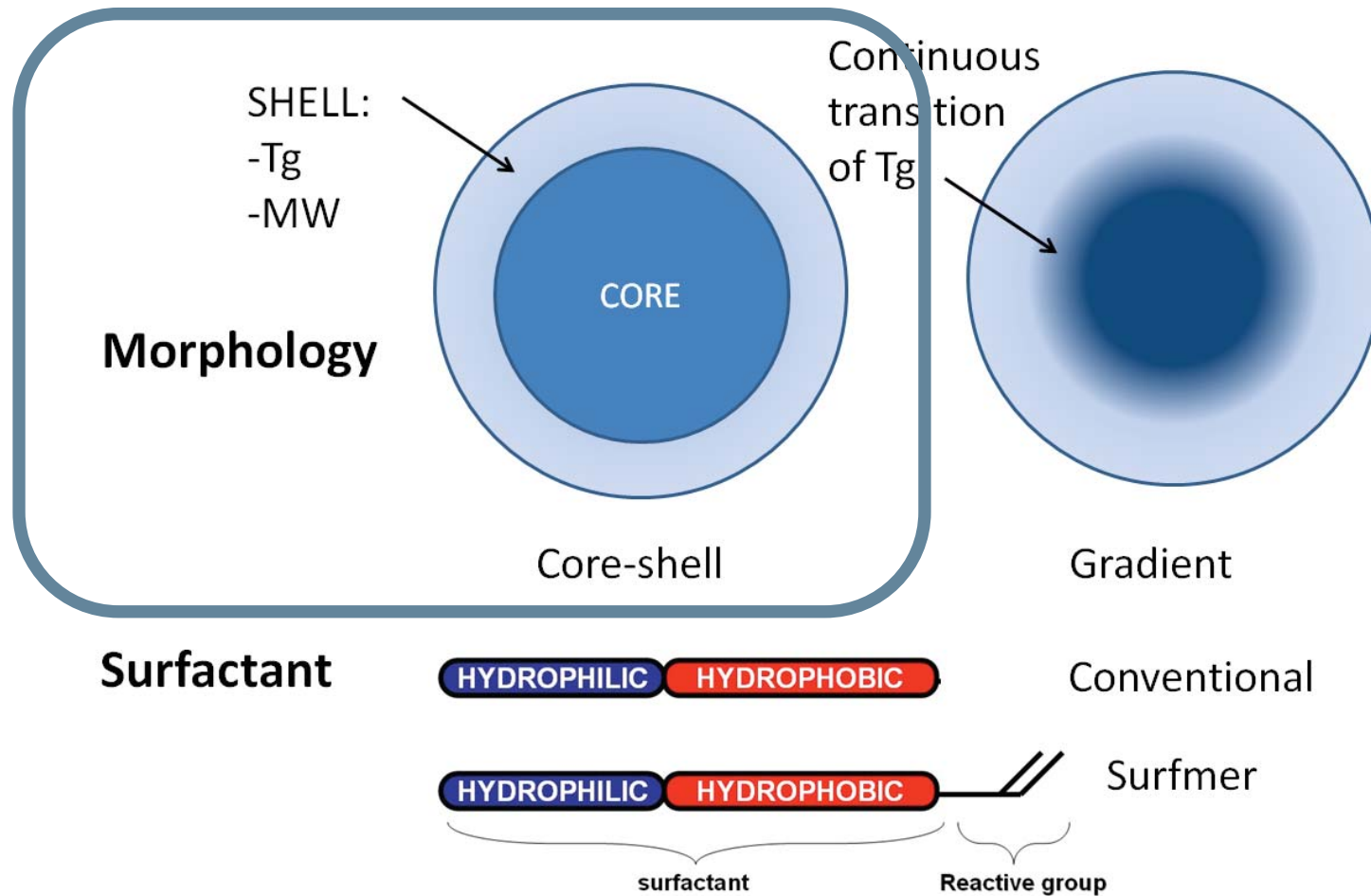


Stabilization of acrylic dispersions

- Conventional surfactants:
 - Can migrate: reduced chemical resistance and surface hardness
- Reactive surfactants:
 - Chemically bound to the polymer
 - Non-migratory:
 - Improved water-resistance
 - Improved blocking resistance
- Polymeric surfactants:
 - Low molecular weight
 - High acid value

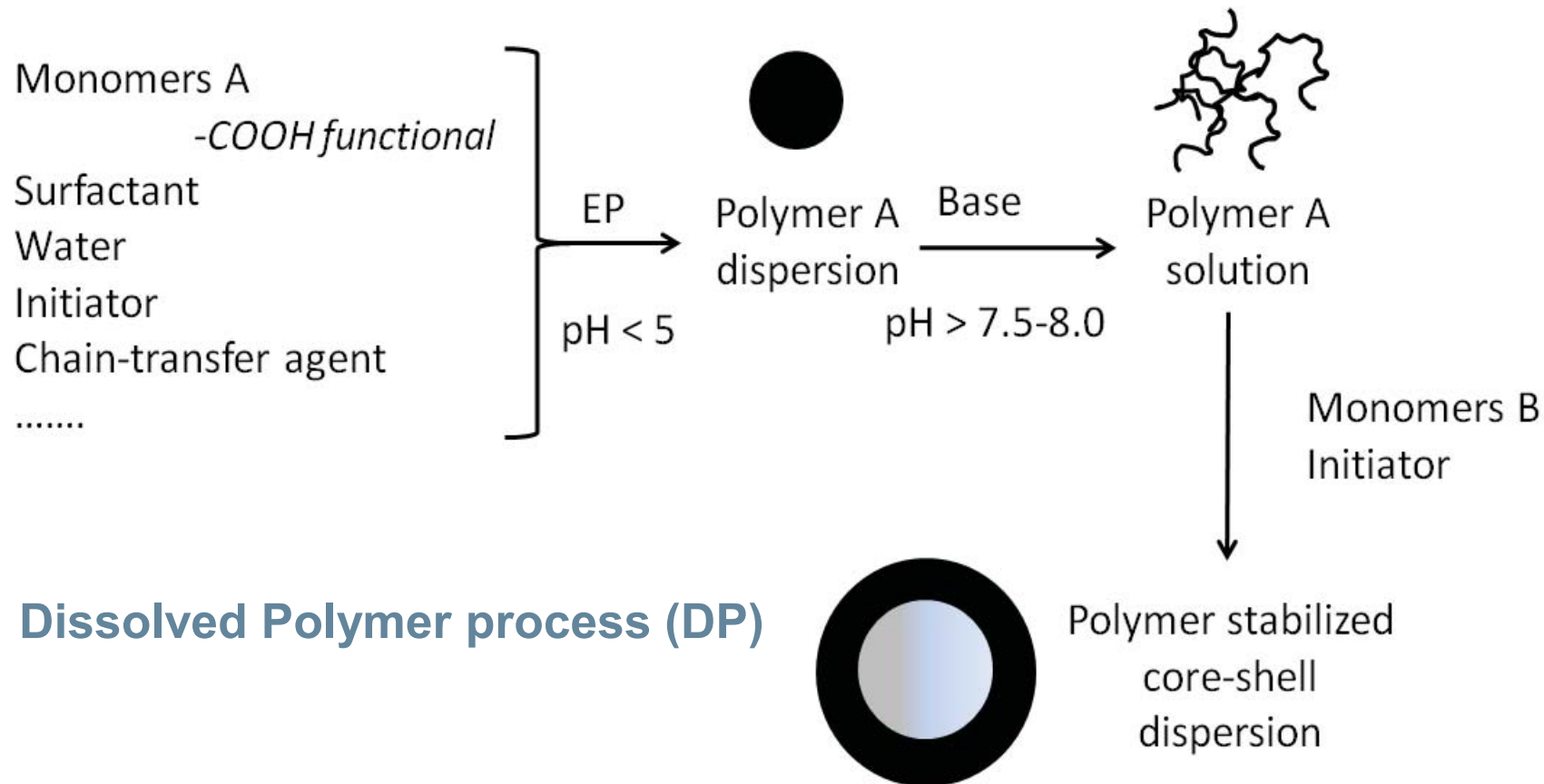


Morphology control and particle stabilization in emulsion polymerization



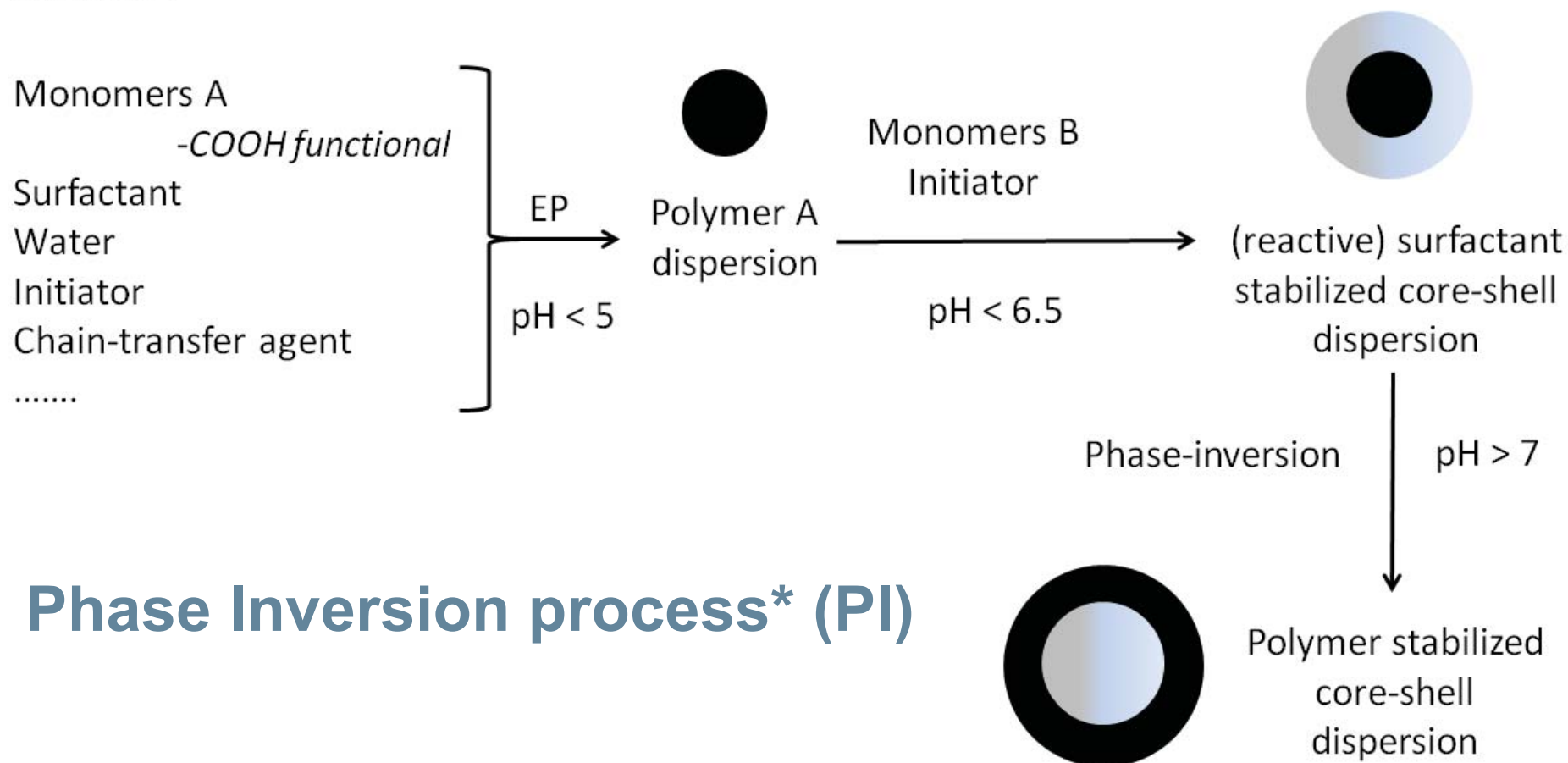
Conventional polymer stabilized acrylic dispersion

Scheme 1



Novel polymer stabilized acrylic dispersion

Scheme 2



Phase Inversion process* (PI)

* EP12712685, US14111198, WOEP12056522

Main advantages of the novel polymerization route

- Molecular weight of the stabilizing polymer can be much higher
 - Acid value of the product can be lower
 - Functional monomers that interact with acid groups can be used
 - Particle size can be very low
 - Neutral pH is possible
-
- Better (wet) adhesion on closed substrates (aged paint layers, glass, ceramic tiles,...)
 - Improved early water resistance
 - Improved (early) block resistance
 - Reduced dirt pick-up
 - Very good chemical and hand grease resistance
 - Visco-stable paint
 - Excellent in-can clarity
 - No discoloration of wood (e.g. oak)



Experimental binders

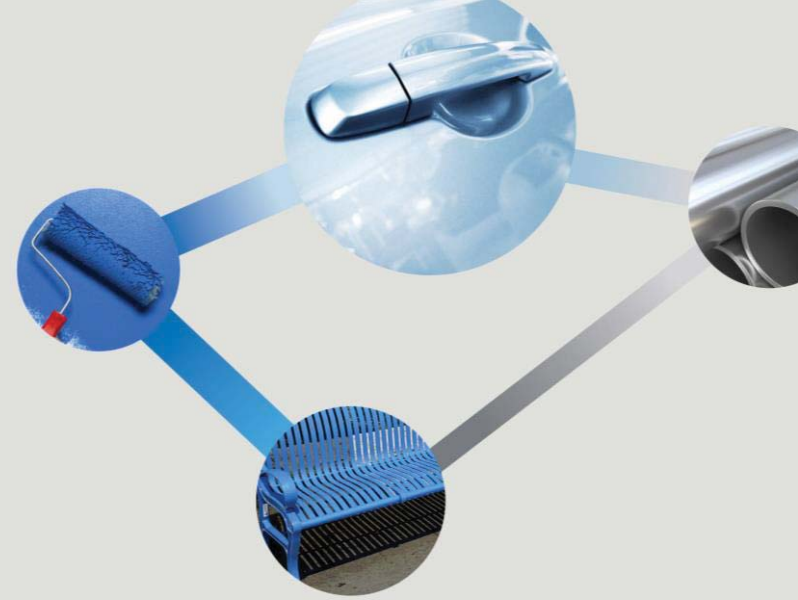
		Stabilizing polymer			Binder		
Process		Molecular weight	Acid value	wt %	MFFT	Solids content (%)	pH
DP	Binder A	low	high	35	< 5	44	7.5
PI	Binder B	high	low	35	< 5	44	8.2
DP	Binder C	low	high	52	23	40	8.3
PI	Binder D	high	low	52	36	42	8.5

Comparative testing of polymer stabilized acrylic dispersions

- **Binders A & B:**
 - Interior / exterior application

- **Binders C & D:**
 - Interior application

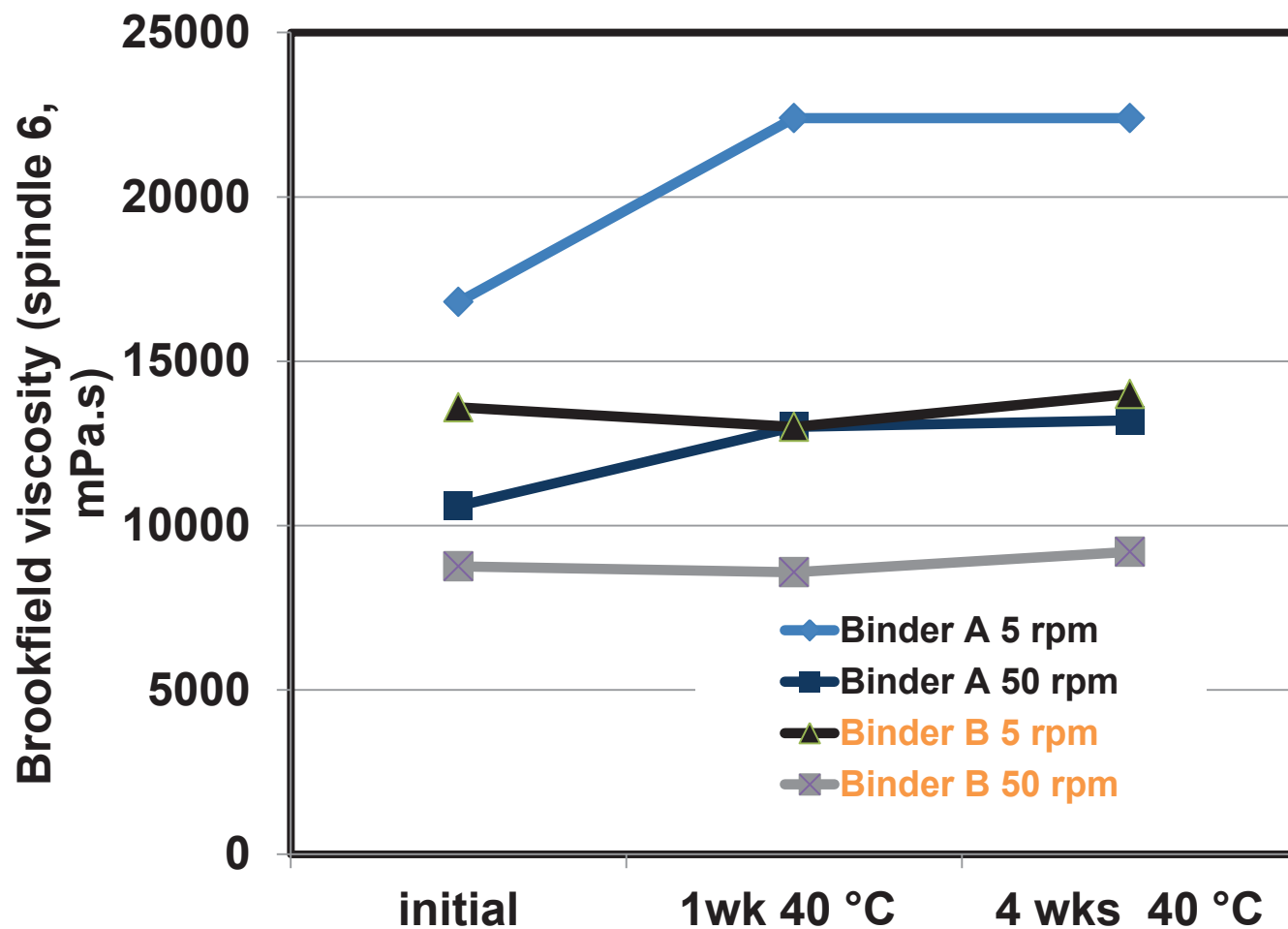




Interior / exterior application

Binders A and B

Viscosity stability of clear varnishes



Component	Weight (g)
Binder A/B	50.0
Demi water	10.0
Butyl diglycol	1.0
Modified poly dimethyl siloxanes solution (VOC-free)	0.5
Polyurethane based, non-ionic liquid thickener (50 % active) / demi water 1 : 1	0.4

Development of blocking resistance as a function of drying time

(4h at 50 °C 1 kg/cm²)

Wet layer thickness (micron)	Drying time (23 °C, 50% RH)	Blocking resistance	
		Binder A	Binder B
250	2 h	0	8
	4 h	6	8
	24 h	8	8

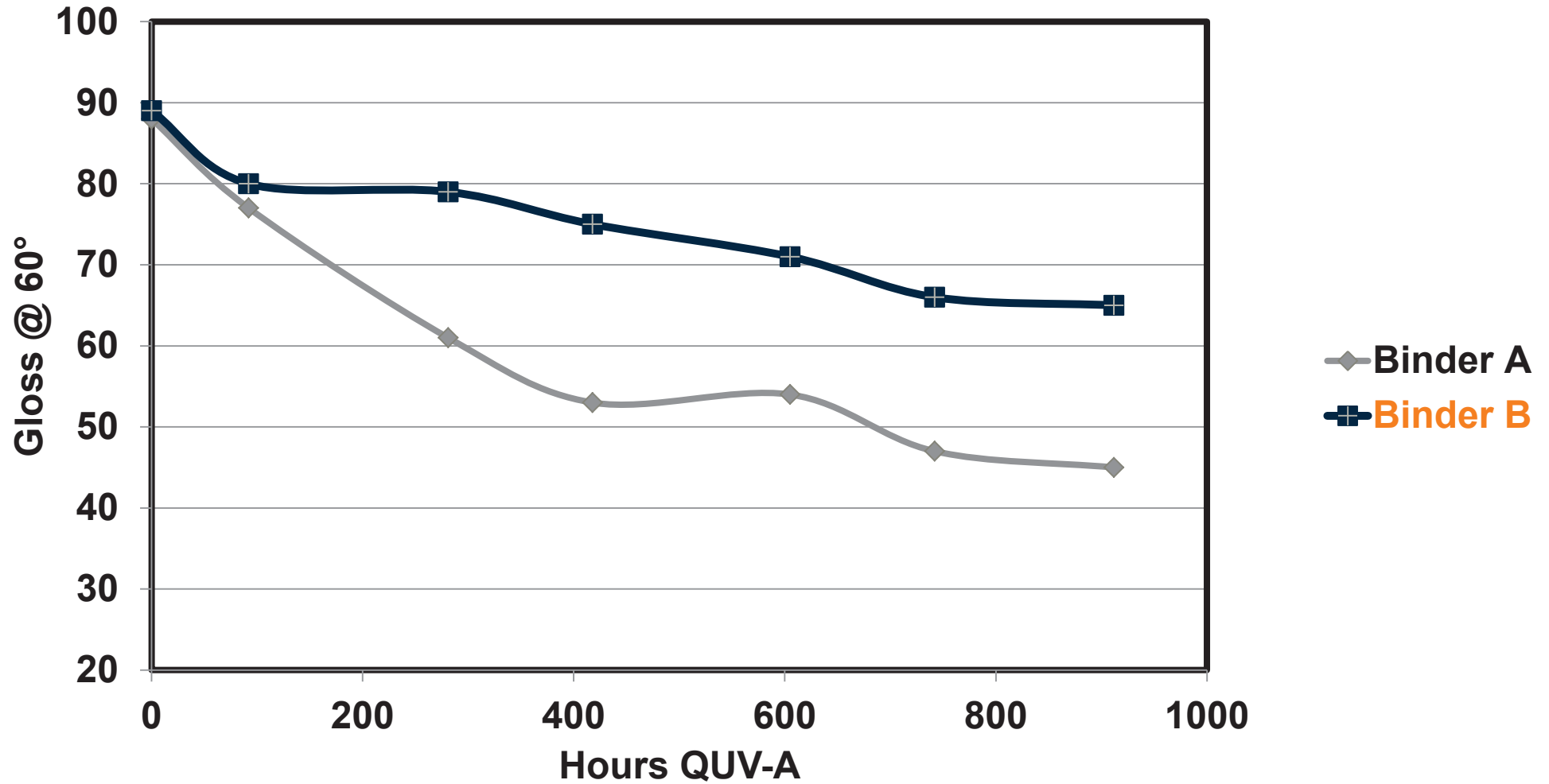
Blocking: 0: poor, 10: good

Properties of clear varnishes

Property		Binder A	Binder B
Film-formation on glass at 4 °C		5	5
Early water resistance Drying time	1 h	2/5	5/5
	2 h	0/0	5/5
	3 h	0/0	5/5
	4 h	0/0	5/5
	5 h	0/0	5/5
	24 h	0/0	5/5
König hardness (s)		49	43
Vapor test		2	5
Scratch resistance		0	1
Gloss 20-60°		70-84	65-82

Ranking: 0: poor, 5: good

Loss of gloss of wood-stains



Interior / exterior low emission satin gloss white trim paint based on binder B

Mill base

Component	Weight (g)
Water	55
Polymeric wetting and dispersing additive	12
Defoamer	5
Titanium dioxide	232

Binder B	100
Mill base	45.5
Flow additive	0.8
2-ethyl hexyl benzoate	2
Defoamer	1.5
Micronized wax	1.8
Water	28
Newtonian rheology modifier	3

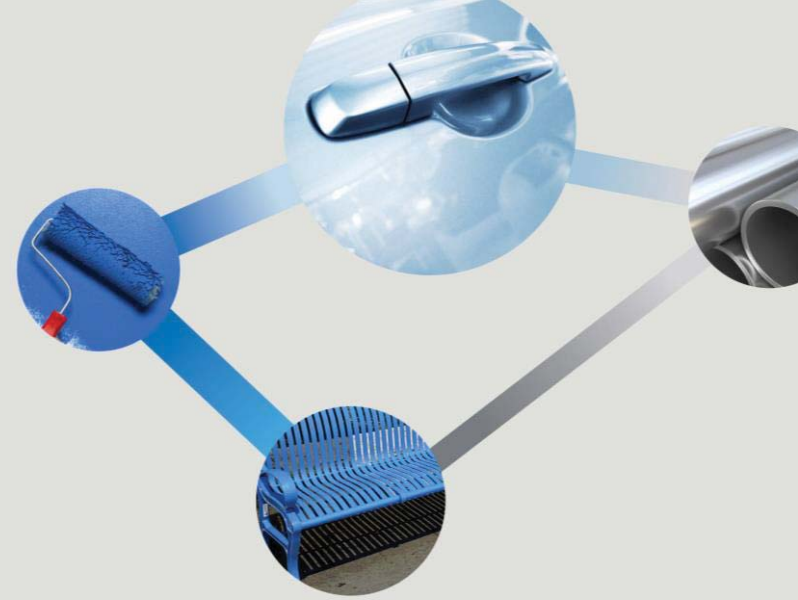
Properties

Property	Value
VOC (incl. water)	< 5 g/l
Weight solids	44.2 %
Density	1.2 kg/l
PVC	16.4 %
Viscosity	7600 mPa.s
High shear	2.1 Poise

Performance of low emission satin gloss white trim paint based on binder B

Property	Value
Syneresis	OK
Flow / leveling	4-5
Defoaming	4-5
Brushability	++
Open time first layer	15-20 m
Open time second layer after drying at room temperature for 4 h	15 m
Recoatability	++
Early blocking 150µm	8
Hardness (König)	30 s
Gloss 20-60°	14-49 GU

Ranking: 0: poor, 5: good



Interior application

Binders C & D

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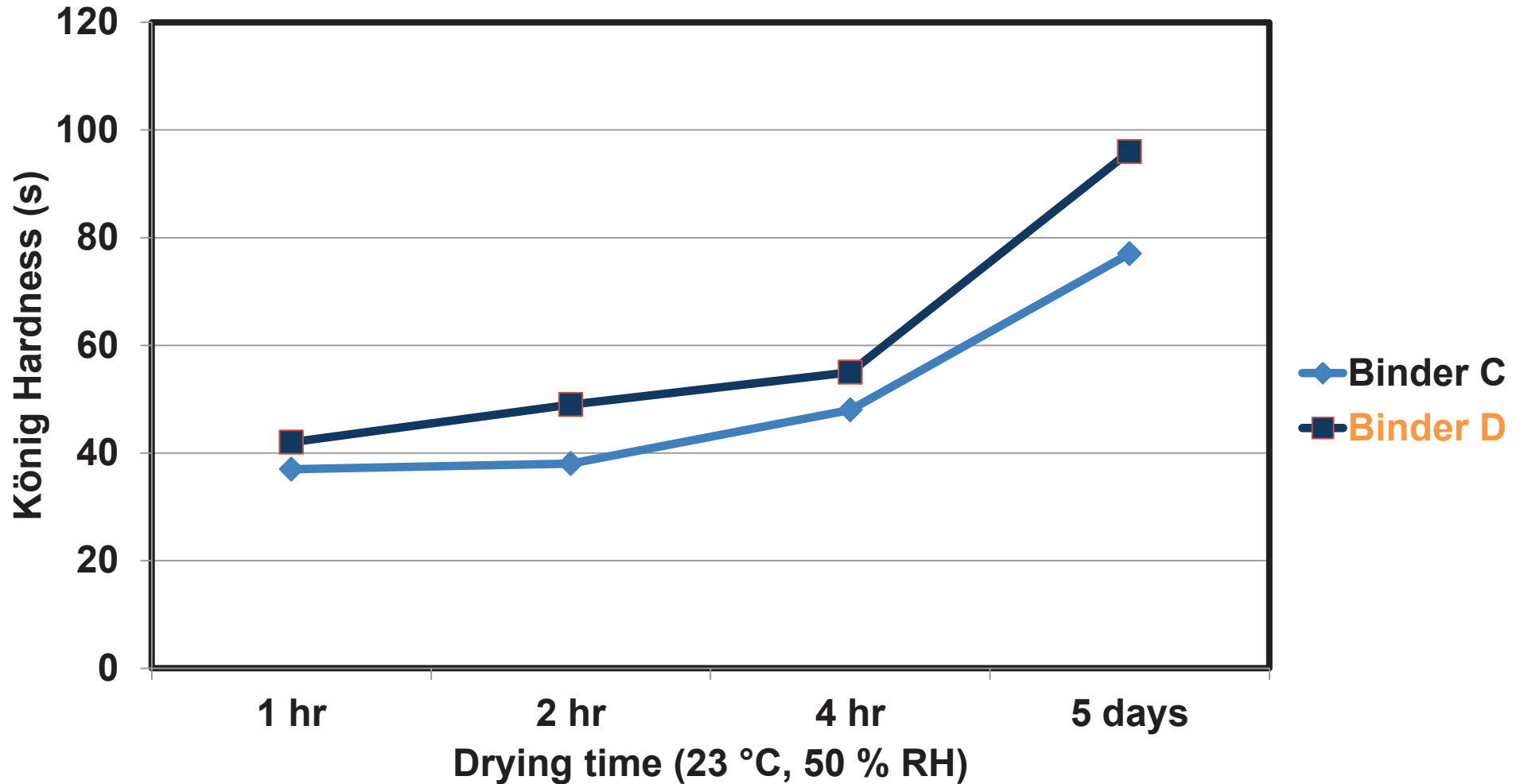
Satin gloss interior white paints

Mill base

Ingredient	Weight (g)
Propylene glycol	25
Demi water	52
Solution of a high molecular weight block copolymer with pigment affinic groups (40 % active)	14
Modified polydimethyl siloxane (10 % in 2-butoxyethanol)	5
TiO ₂ (Rutile, aluminium and zirconium surface treatment)	232

Ingredient	Weight (g)
Binder C or D	100
Pigment paste	48.8
2,2,4-trimethyl-1,3-pentaandiolmonoisobutyrat	4.0
Dipropylene glycol methyl ether	4.0
100% organo-modified silicones defoamer	1.5
Silica matting agent	1.5
Demi water	28.0
Ammonia (25 %)	Until pH 9.5
Alkali soluble acrylic based associative thickener	5.0

Satin gloss interior white paint – hardness development



Properties of a satin gloss brushing paint based on binder D

Property	Value
pH	8.5
High shear viscosity (Poise)	2.2
Brookfield viscosity (spindle 06, 5-50 rpm, mPa.s)	
Initial	3600 - 2760
After 5 days at 40°C	3000 - 2200
Viscosity difference	-17%
Syneresis	OK
Flow / leveling	4 - 5
Defoaming	4 - 5
Brushability	++
Open time (m)	12 - 14

Ranking: 0: poor, 5: good

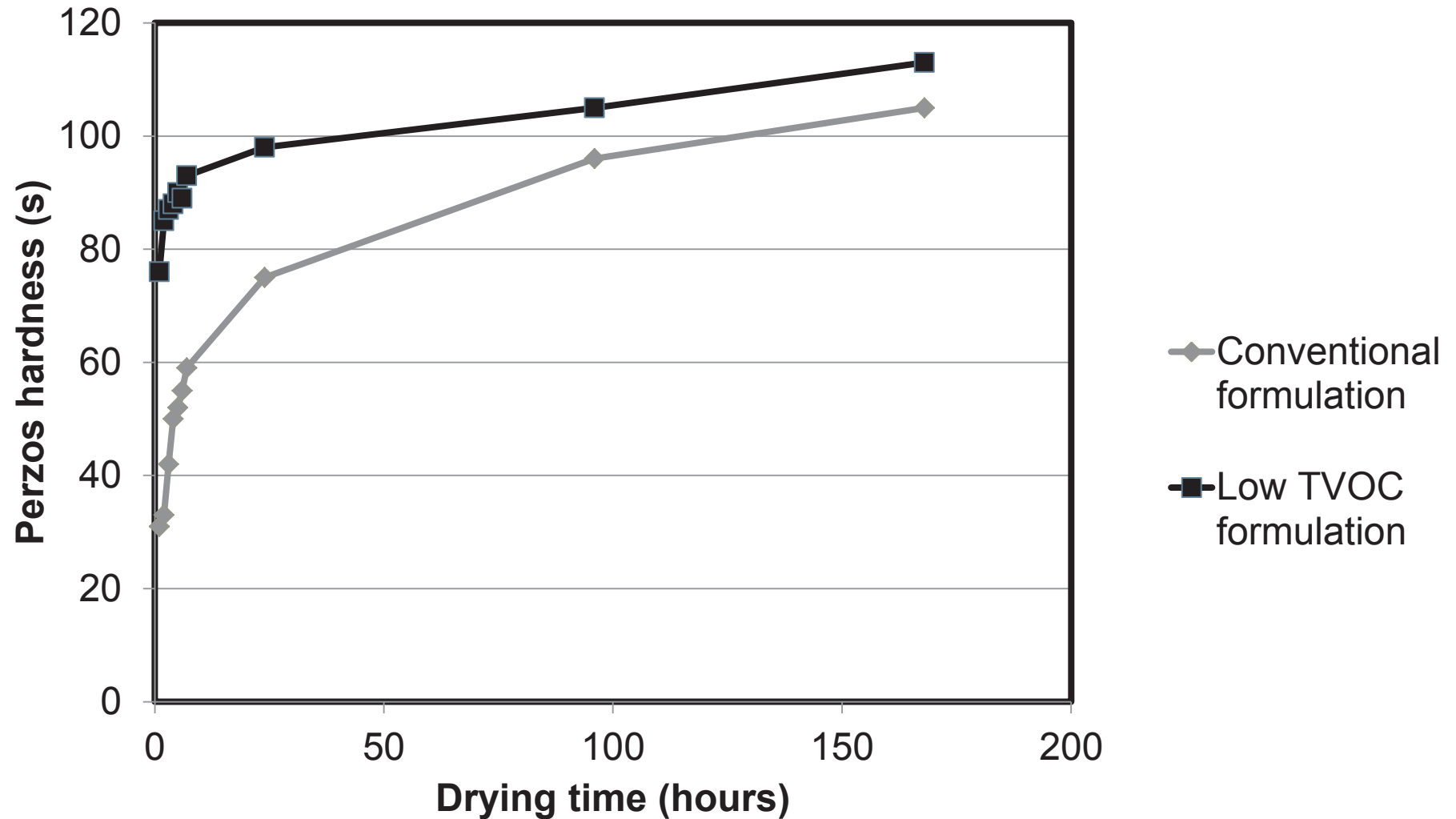
Low emission interior furniture varnishes based on binder D

Ingredients	Conventional formulation	Low TVOC formulation
Binder D	87.77	89.00
Demi water	7.42	7.53
Butyl Glycol / Butyl di glycol / Dipropylenglycol-n-butylether (3:0.5:0.5)	2.63	-
Alkyl Benzoate Plasticizer	-	1.78
Modified polysiloxane defoamer*	1.00	0.36
Acetylenic diol surface active agent *	0.35	0.36
Polyurethane-based thickener	0.22	0.36
Slip additive based on an emulsion of a high molecular weight polydimethylsiloxane	0.60	0.61

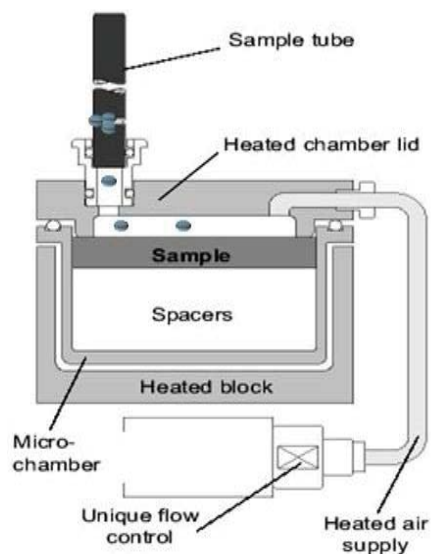
* Contains dipropylenglycol-n-methyl ether

Coalescent content on solid resin (%)	3.00	2.41
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Hardness development furniture varnishes based on binder D



Micro emission chamber set-up

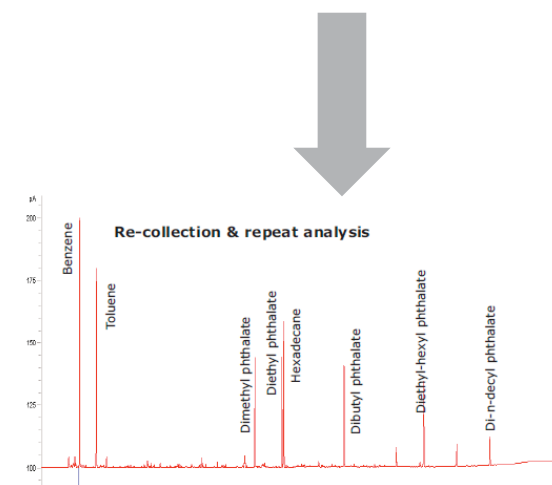


Tenax column

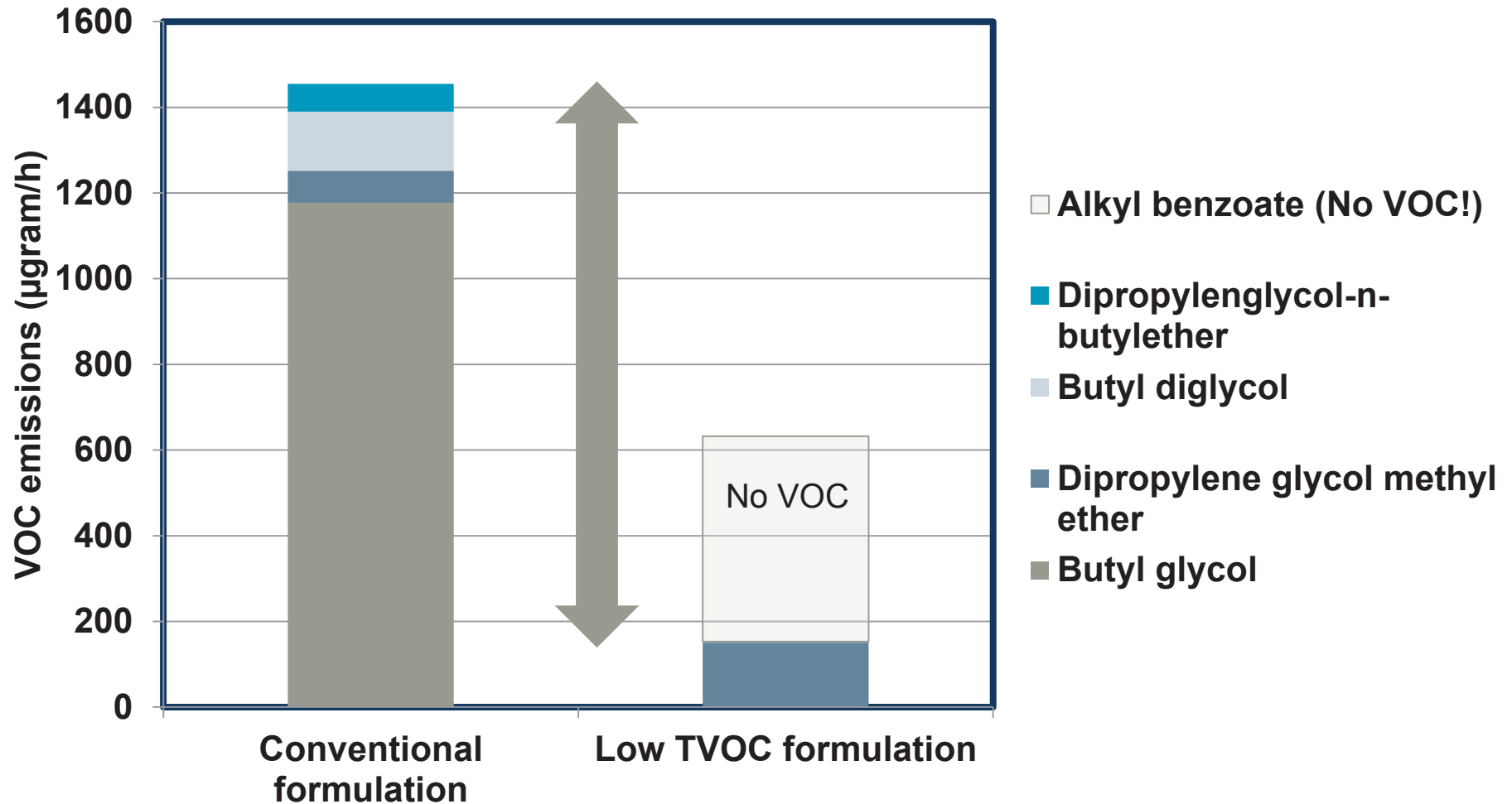


Thermal desorption and cold trap

GC-MS



TVOC emission rates after 48 hours of varnishes based on binder D



Conclusions

- A novel emulsion polymerization process has been developed, based on phase-inversion technology.
- This process can overcome the deficiencies of the dissolved polymer stabilizer process.
- Benefits of the new process have been demonstrated with regards to coating properties.
- Significant reduction of longer term emissions is possible with acrylic polymer dispersions synthesized using the novel phase inversion process.
- Both binders are commercially available:
 - Binder B: ***Setaqua ECO 6791***
 - Binder D: ***Setaqua ECO 6788***

Acknowledgements

- Ankie van Gorkum
- Jessica Rommens
- Andrew Teasdale
- Wouter Kloosterman
- Aschwin van der Horst
- Jacqueline Slaakweg
- Afke Kroes
- Rob Adolphs

Thank you for your attention