Recent Advancements in Low-VOC Polyurethane Dispersions for Wood Flooring Applications

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Outline

❑ASTM definition of URETHANE COATINGS

❑Clear Varnish Volatile Organic Content (VOC) limits for wood coatings

❑Polyurethane Overview
- Raw Materials
- Solvent-borne (SB) v/s Waterborne (WB) Polyurethane
- Methods:
  - Solvent-NMP
  - Acetone
  - Pre-polymer mixing
  - Ketamine/Ketazine Process

❑Solvent-borne Low VOC Oil Modified Urethane (SB-OMU) for wood flooring applications
  - High solids
  - VOC exempt solvents
  - 275 g/L SB-OMU

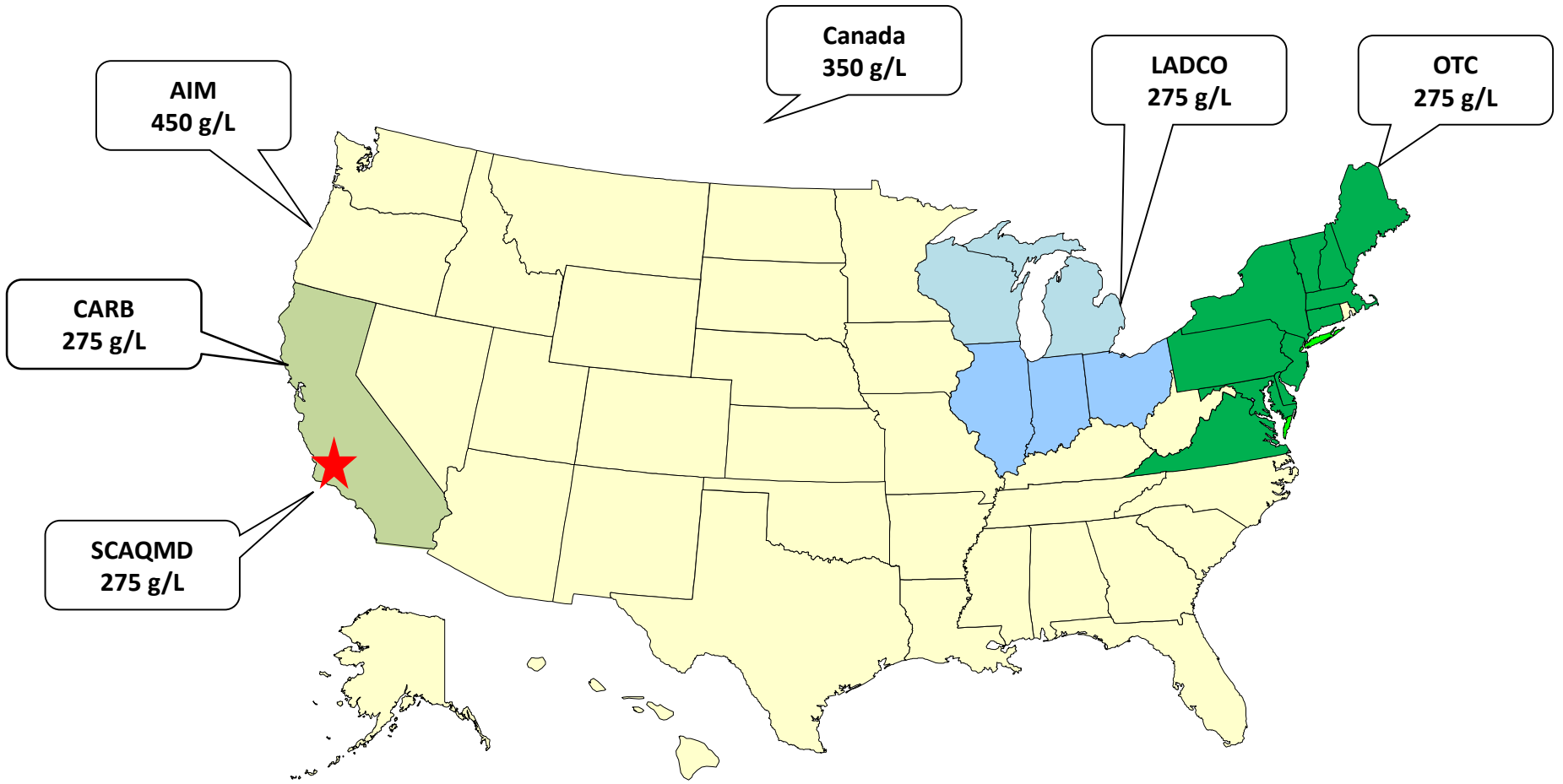
❑NMP free Waterborne Oil-Modified Urethanes (WB-OMU) for wood flooring applications
- High Solids
- Low VOC <100g/L

Classification: Urethane Coatings

- ASTM D16 Classification
  - ***Type I: One-package pre-reacted urethane***
    - ***Fatty acid modified urethanes, oxidative cure***
  - ***Type II: One-package moisture cured***
    - ***Moisture curable, cured by NCO Rx with atmospheric moisture***
  - Type III: One-package heat cured
    - Blocked urethane, cured by NCO / compound containing active H groups
  - Type IV: Two-package catalyst
    - Prepolymer crosslinking with monomeric polyol or polyamine
  - Type V: Two-package polyol
    - Prepolymer or other polyisocyanate crosslinking with polyols
  - ***Type VI: One-package non-reactive lacquer***
    - ***Solution urethane coatings, lacquer dried***

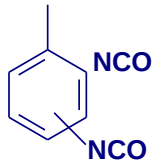
UV curable urethane, urethane powder, ***water-borne urethane (PUD)***

Clear Varnish VOC Limits: Wood Coatings

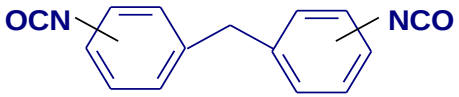


Polyurethane Overview: Raw Materials

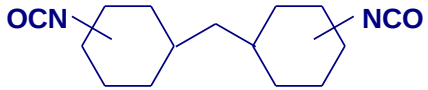
- Key Raw Materials
  - Diisocyanates
    - Toluene diisocyanates (TDI)-Aromatic
    - Methane diphenylisocyanate (MDI)-Aromatic
    - Isophorone diisocyanate (IPDI)-Aliphatic
    - Methylene bis (4-cyclohexylisocyanate) (H12MDI or HMDI)-Aliphatic
  - Polyols
    - Polyester diols
    - Polyether diols
    - Fatty acid intermediates



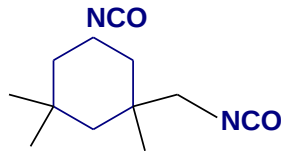
TDI



MDI



HMDI



IPDI

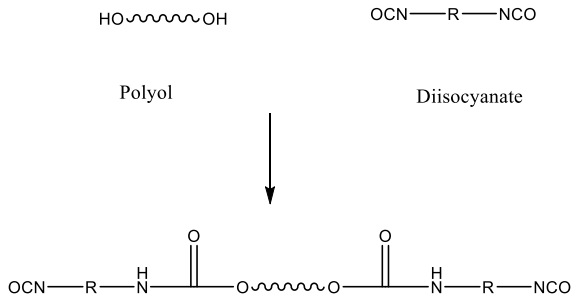
Polyurethane Overview

- Structure Property Relationships

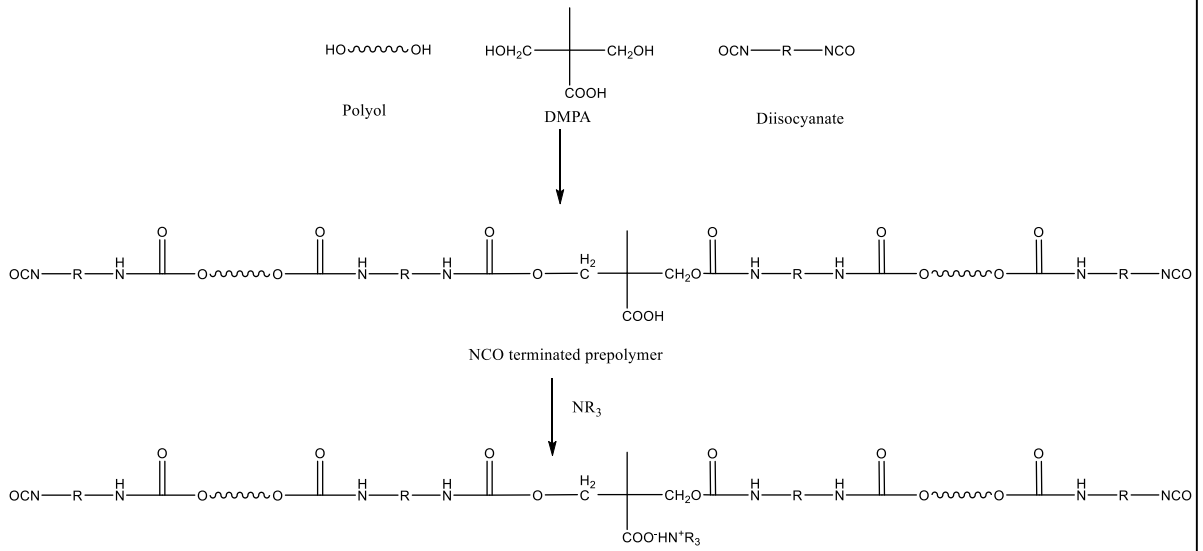
Structural Element	Chemical	Weathering	Flexibility	Hardness	Abrasion	Heat	Water
Aliphatic hydrocarbon chains	Good	Excellent	Good	Good	Good	Good	V. Good
Aromatic hydrocarbon chains	Excellent	Poor	Fair	Excellent	Excellent	V. Good	Excellent
Alkoxy groups	Fair	Good	Excellent	Poor	Good	Poor	Poor
Ester linkages	Poor	Good	Excellent	Fair	Good	Poor	Good
Urea linkages	Good	Poor	Poor	Excellent	Fair	Good	Good
Urethane linkages	Good	Good	Good	Good	Excellent	Good	Good
Allophonate groups	Fair	Excellent	Fair	Good	Good	Fair	Good
Amide linkages	Fair	Poor	Good	Good	Good	Fair	Fair
Linearity	Good	V. Good	Excellent	Fair	Fair	Poor	Depends
Low molecular weight	Poor	Poor	Fair	Fair	Good	Poor	Poor
High molecular weight	Good	Good	Good	Good	Good	Fair	V. Good
High crosslink density	Excellent	Fair	Poor	Excellent	V. Good	V. Good	Good

Polyurethane Overview: SB vs WB

❑Solvent borne Polyurethane

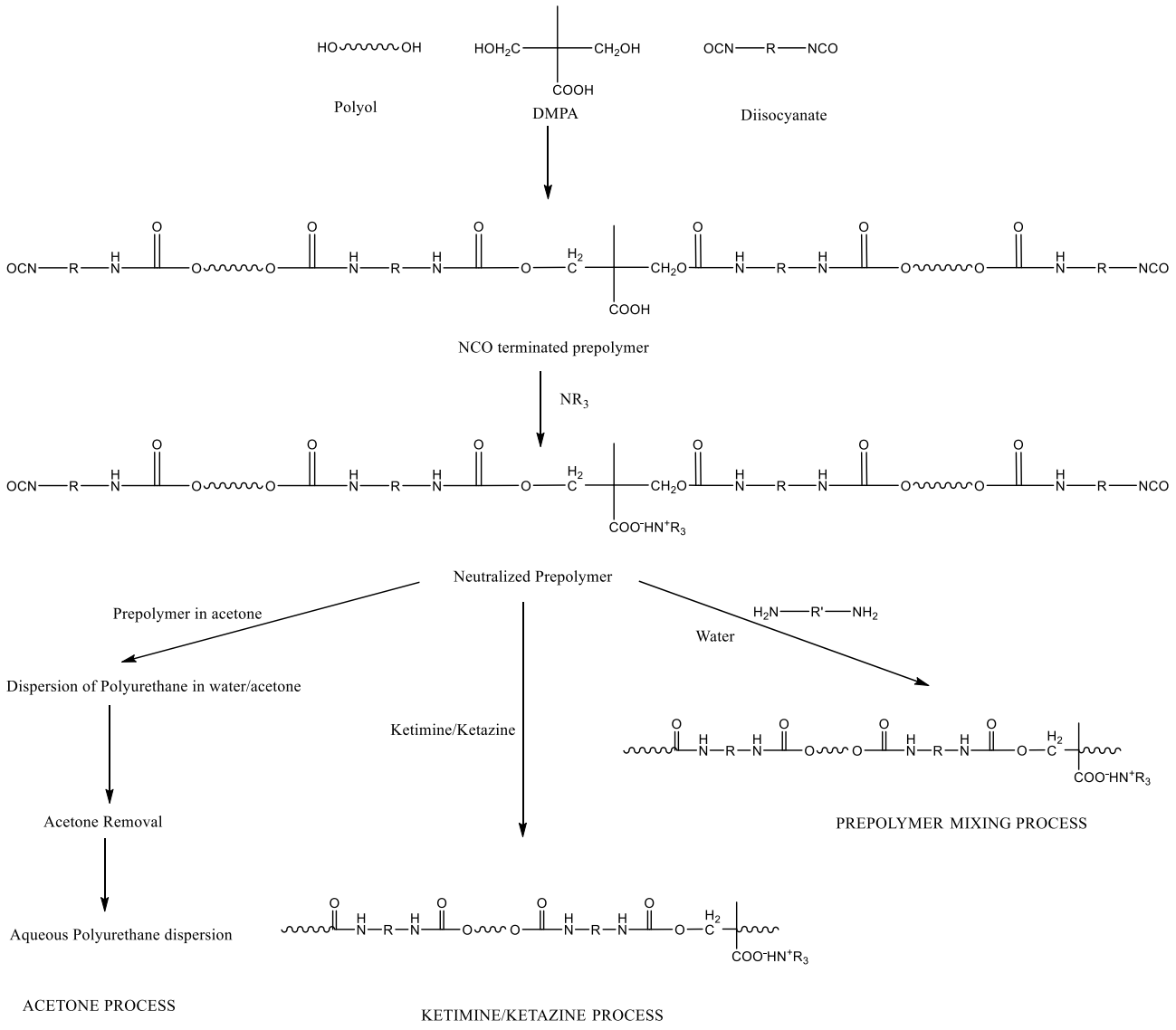


❑Water-borne Polyurethane



Polyurethane Overview: Methods

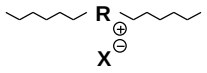
- Methods
  - Solvent-NMP
  - Acetone Process
    - Control the viscosity of the prepolymer
    - Inert and miscible in water
    - Low boiling point
  - Ketamine/Ketazine Process
  - Prepolymer mixing Process
    - Used for low mol.wt./viscosity of prepolymer
    - Eliminates co-solvent
    - High degree of crystallinity



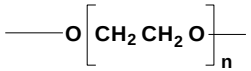
Polyurethane Overview: Methods

- Hydrophilic Group

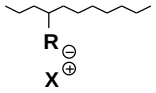
	Cationic	Non-ionic	Anionic
Film Clarity	+	+	+
Shear Stability	–	+	–
Thermal Stability	+	–	+
Water Resistance	+	–	+
Low pH Stability	+	+	–
High pH Stability	–	+	+
Hardness	+	–/+	+
Color Stability	–	+	+



Cationic



Non-ionic



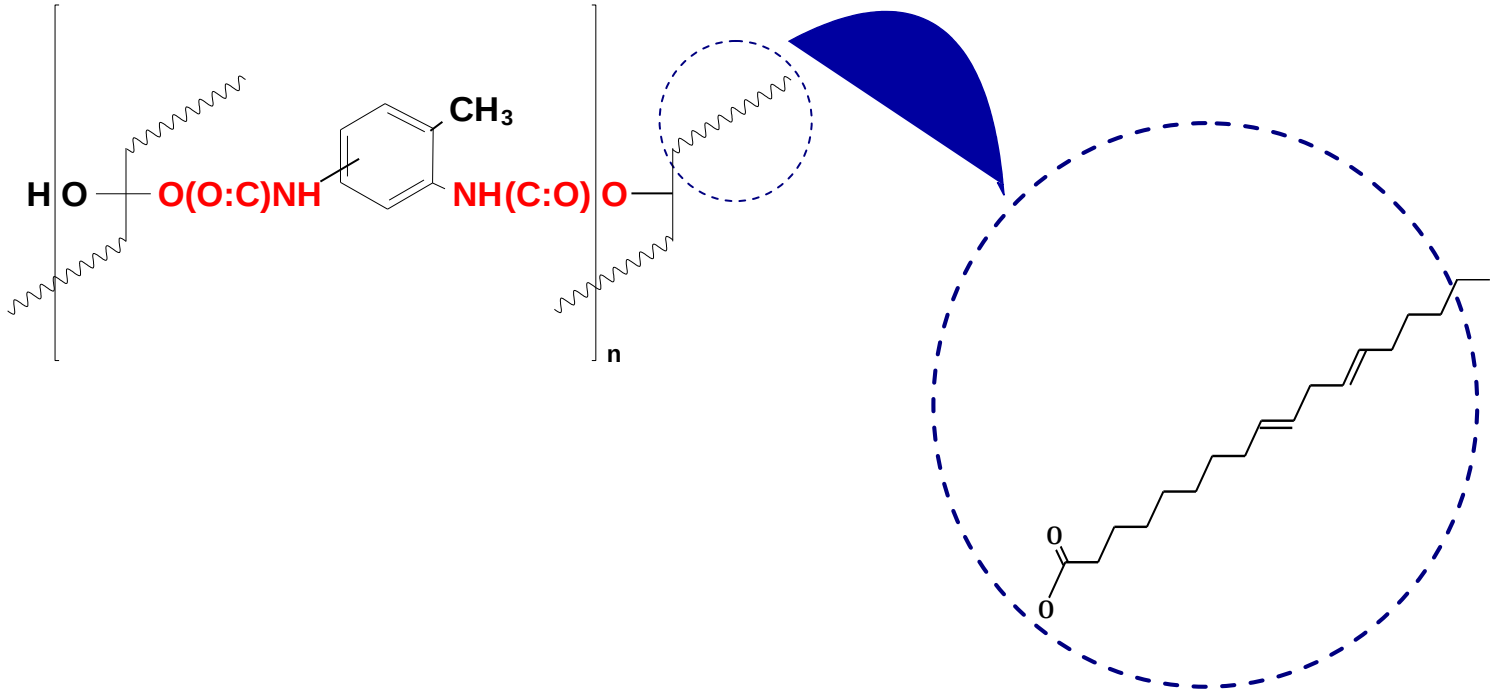
Anionic

Polyurethane Overview: Methods

- Waterborne PUD characteristics:
  - Anionic or non-ionic colloidal dispersions
  - Good freeze-thaw stability
  - Typically PUD contain NMP solvent
  - Low VOC
  - Non-flammable
  - High MW and fast Drying
  - Low Tg
  - Wide range of performance properties
  - Compatible with acrylic emulsions
  - Crosslinkable with crosslinkers
  - Self crosslinking types available

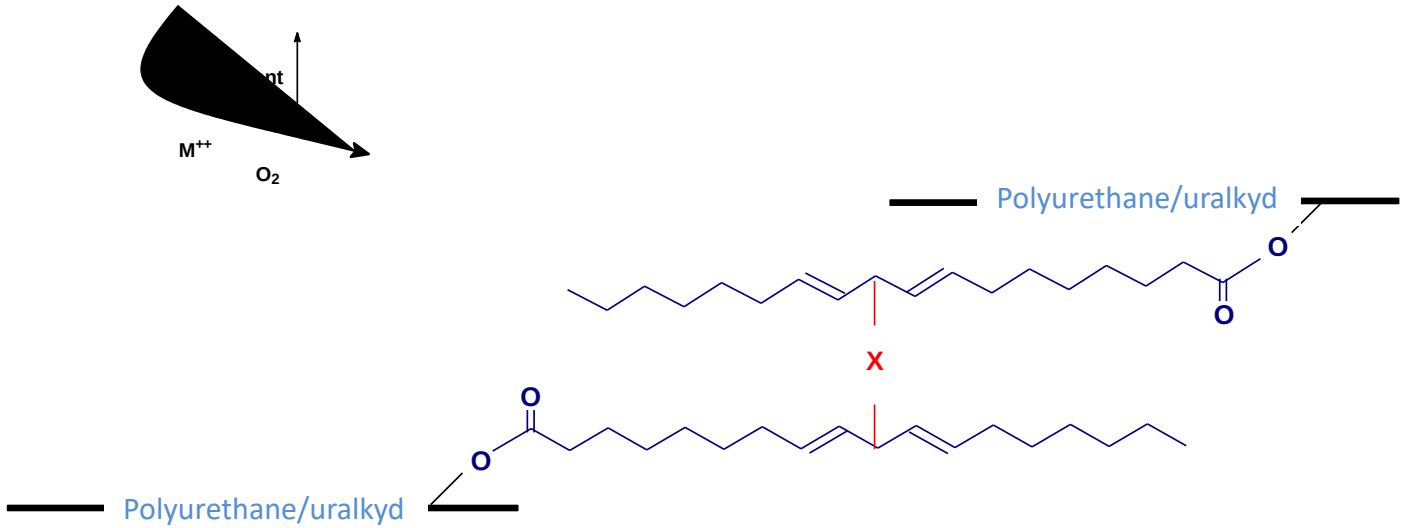
Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

- Generic OMU Polymer Structure:



Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

- Crosslinking:



X = carbon-carbon or carbon oxygen bond

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

- Solvent-borne
  - Low VOC Option – High Solids

	Designed VOC, g/l		
	Conventional 550	Conventional 450	High Solids 350
Solvent	LAMS (1)	LAMS (1)	LAMS (1)
Solids, %	40	49	62
Viscosity, cps	79	108	111
Molecular Weight (Mn)	7000	6000	3500
VOC, g/l	523	445	348
Gardner Dry Hard, (Hr: min)(2)	1:30	2:45	6:00
Sward Hardness	48	36	14

(1) Low Aromatic Mineral Spirits
(2) All contain 200 ppm cobalt on resin solids

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

- Solvent-borne
  - Low VOC Option – Exempt Solvents

	Conventional 450	High Solids 350	Exempt Solvent 350
Solvent	LAMS (1)	LAMS (1)	LAMS/PCBTF (2)
Solids, %	49	62	46
Viscosity, cps	108	111	109
Molecular Weight (Mn)	6000	3500	6000
VOC, g/l	445	348	358
Gardner Dry Time Hr:Min	2:45	6:00	4:30
Sward Hardness	36	14	38

(1) Low aromatics Mineral Spirits
(2) P-Chloro benzo trifluoride
(3) All contain 200 ppm cobalt on resin solids

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

- Solvent-borne Summary
  - Low VOC Options
    - High solids OMU
      - Low molecular weight
      - 350 g/l VOC
      - Softer
      - Less durable
    - Exempt solvent OMU
      - High molecular weight
      - VOC ≤ 350 g/l
      - Better performance vs. high solids

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

- Typical Resin Wet Properties

	275 g/L Solvent borne OMU
Appearance	Clear
Solvent (1)	LAMS
Solids, % Weight	75.0
Solids, % Volume	74.4
Gardner Color	4+
Viscosity, Stokes	50.7
Viscosity, G-H Letter	Z3+1/4
Density, #/gal	7.88
VOC, #/gal	2.02
VOC, g/l	240

(1) Low Aromatic Mineral Spirits

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

Film Performance [1]	275 g/L Solvent borne OMU	Commercial 350 g/L Benchmark #1	Commercial 350 g/L Benchmark #2
Gardner Dry Time, hr:min [2]			
Set	1:30	1:00	1:00
Hard	3:30	6:30	16:00
Through	7:00	10:00	>24:00
Sandability	Overnight	Overnight	Overnight
Sward Hardness [2]			
7 Day	26	28	24
Konig Hardness			
7 Day	57	58	64
Pencil Hardness	HB	HB	HB
Impact Resistance, Direct / Reverse	160 / 160	160 / 160	160 / 160
Mandrel Bend, 1/8”	Pass	Pass	Pass
Taber Abrasion, mg loss [3]	134	119	112

(1) Except where noted, film applied with #40 WWR to B1000 panel, air dried 7 days
(2) Film applied by 3 mil Bird bar to glass plate
(3) Taber, CS-17 wheels, 1 kg load, 1000 cycles

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

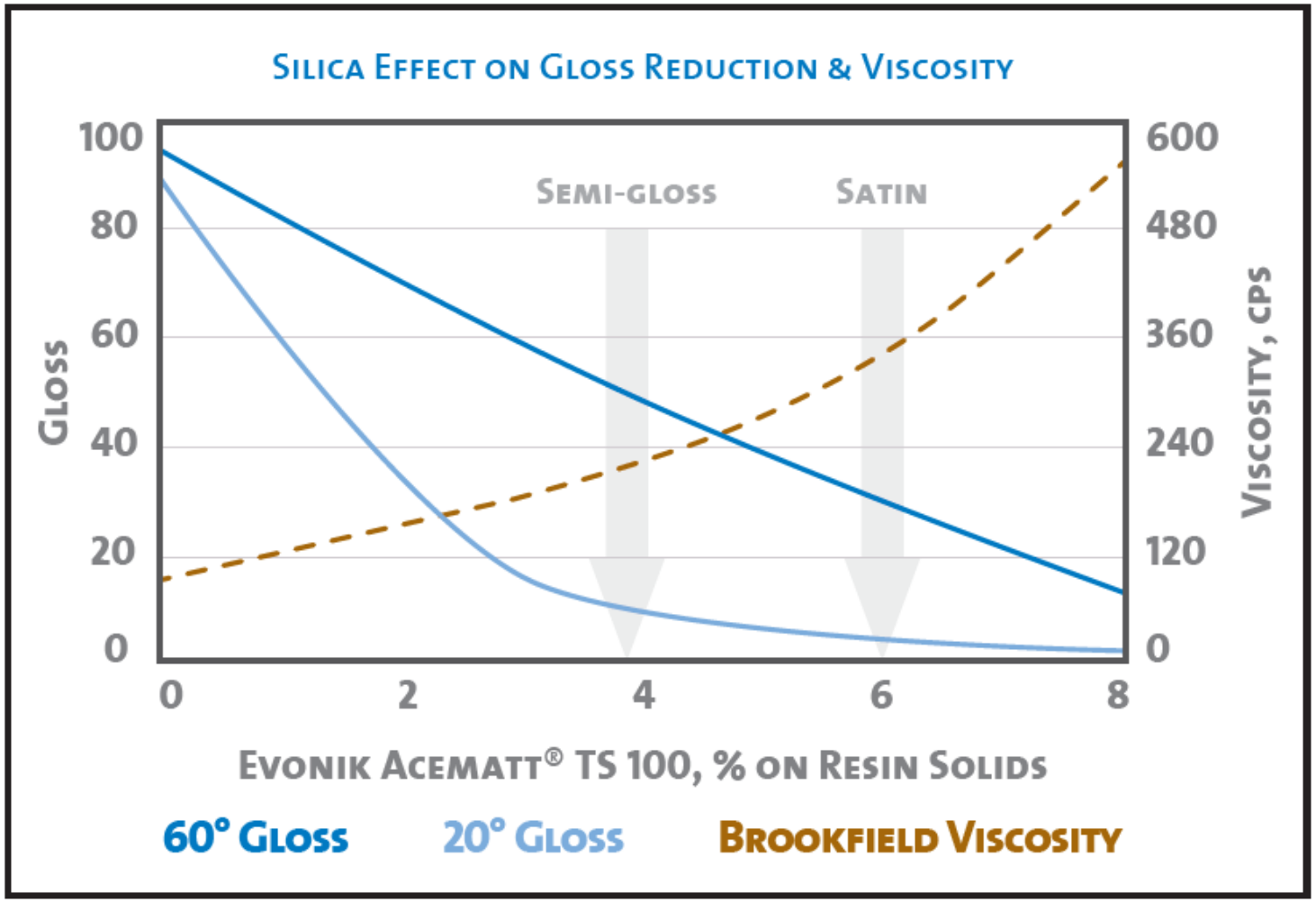
Film Performance [1]	275 g/L SB-OMU	Commercial 350 g/L Benchmark #1	Commercial 350 g/L Benchmark #2
Mar Resistance, Grams [4]	150	100	<50
Mar Resistance, Days [5]	1	1	1
Varnish Film Color [6]			
"L" Value	91.14	90.79	88.69
"a" Value	-3.66	-2.74	-3.36
"b" Value	13.26	13.73	19.77
Yellowness Index	21.79	23.40	33.53
Gloss 60° / 20° [6]	93 / 86	95 / 86	93 / 87
Stain Resistance, Average [7]	3.00	3.15	2.92
Solvent Resistance, 200 Double Rubs			
Ethanol	>200	>200	>200
Isopropanol	>200	>200	>200
Methyl Ethyl Ketone	155	190	160
Xylene	>200	>200	>200

(1) Except where noted, film applied with #40 WWR to B1000 panel, air dried 7 days
(4) Hoffman Tester, loop stylus, weight needed to mar film
(5) Time to achieve, finger nail scratch
(6) Film applied by 3 mil Bird bar to Leneta chart
(7) ASTM D1308, 24 hr exposure, covered, rating 0-5 no effect

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

Film Performance	275g/L solvent borne OMU	Target Achieved	Commercial Benchmark #1	Commercial Benchmark #2
VOC, g/L	275	✓	350	350
Gardner Dry Time, hr:min	7:00	✓	10:00	>24:00
Sward Hardness, 7 Day	26	✓	28	24
Konig Hardness, 7 Day	57	✓	58	64
Taber Abrasion, mg loss	134	✓	119	112
Mar Resistance, Grams	150	✓	100	<50
Stain Resistance, Average	3.00	✓	3.15	2.92
Thick Film Through Cure, 20 Wet Mils	Pass	✓	Pass	Fail
COF, Flattening Efficiency, 1 Day Sanding, Recoatability	Equal	✓	Equal	Equal

Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

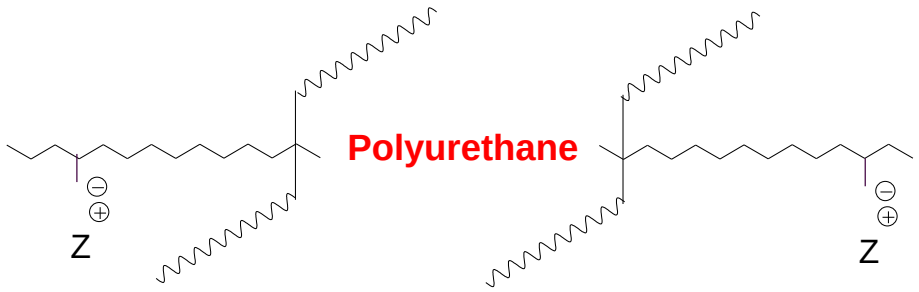


Solvent-borne Low VOC Oil Modified Urethanes (OMUs)

- Summary
  - Meets 275 g/L VOC limits and application requirements
  - Performance properties comparable to 350 g/L VOC systems
  - Good rate of dry
  - High gloss capability
  - Good response to flatting agents
  - Good stain resistance
  - Can be formulated with Volatile Methyl Siloxane (VMS) or p-Chlorobenzotrifluoride (PCBTF; commonly referred to as OXSOL® 100)
  - For VOC lower than 275 g/l, suggest going to water-borne approach

NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

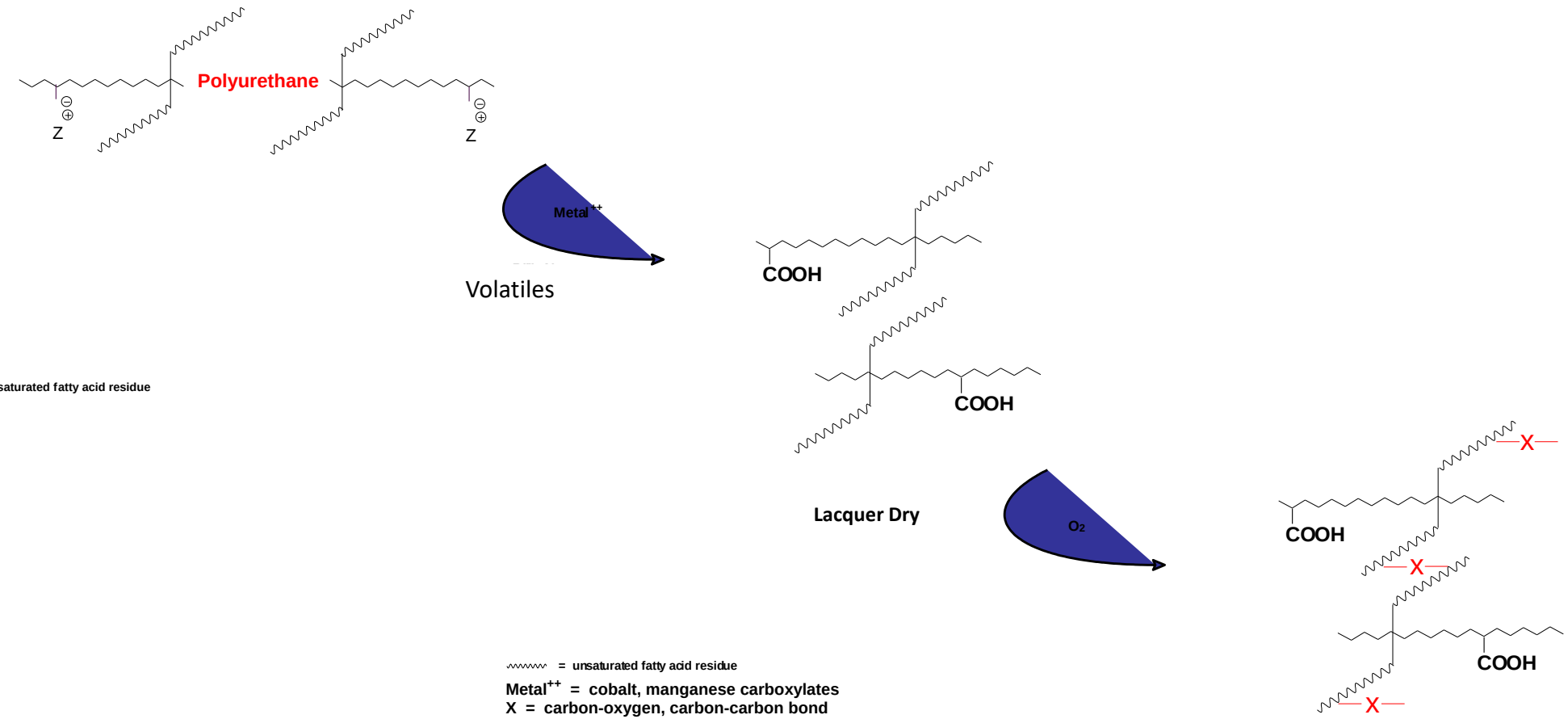
- Polymer Structure:



= **unsaturated fatty acid residue**

NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

- Oxidative Crosslinking



NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

- Commercially available Waterborne OMUs

	NMP Containing Conventional Solids WB OMU	NMP Free Conventional Solids WB OMU	NMP Containing High Solids WB OMU	Competitive WB OMU I	Competitive WB OMU II	Competitive WB OMU III	Competitive WB OMU IV
Cosolvent	NMP	DPM	NMP	Butyl Carbitol	NMP	DMM	NMP
Solids, %	33	36	45	35	33	33	31
Resin VOC, g/L	188	45	140	30	100	213	290
Varnish VOC, g/L	188	175	140	250	190	213	290

- Film performance of early generation water-borne oil modified urethanes equivalent to 450 g/L VOC solvent-borne urethanes, but with some differences:
  - Advantages:
    - Lower VOC
    - Faster dry
    - Water clean-up
  - Disadvantages
    - Contain NMP
    - Lower solids

- High solids waterborne OMU overcomes the shortcomings of earlier generations of water-borne oil modified urethanes

NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

- Typical Resin Properties

	High solids WB-OMU
Appearance	Hazy
Cosolvent (1)	TPM*
Solids, % Weight	43.0
Solids, % Volume	40.3
pH	8.2
Viscosity, Stokes	0.5-50
Viscosity, G-H Letter	A-S
Density, #/gal	8.60
VOC, #/gal	0.78
VOC, g/L	93

(1) Tripropylene Glocol Mono Methyl Ether

NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

Varnish Formula & Analysis	High Solids WB-OMU
Varnish Formula, Grams	
High solids waterborne OMU	200.00
Borchi OXY-Coat 1101	0.84
Total	**200.84**
Varnish Analysis	
Non-volatile, %	45.8
pH	8.05
Viscosity, Stokes	5.94
Viscosity, G-H Letter	T+1/2
Density, #/Gallon	8.619
VOC, #/gal	0.79
VOC, g/L	95

❑ Formulating Notes

- Add drier to the dispersion gradually under moderate agitation and allow it to sweat in for seven days prior to use to ensure optimum film performance.
- Adjust solids as needed with water, filter (50µ) and package with minimum head space.
- Add defoamer, surfactant or flatting agent as needed.

NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

- Dry Time & Gloss

Film Performance [1]	High Solids WB-OMU	1st Gen. OMU	2nd Gen. OMU	3rd Gen. OMU
Resin Cosolvent as Supplied	TPM	NMP	None	NMP
Additional Cosolvent	None	None	DPM	None
Varnish VOC, g/L	95	187	175	142
Gardner Dry Time, hr:min [2]				
Set	0:05	0:15	0:10	0:10
Hard	0:18	0:35	0:35	0:30
Through	0:20	1:00	0:55	1:05
Zapon Tack Free Time, hr:min [2]				
200g	0:15	1:00	0:55	1:00
500g	0:16	1:10	1:00	1:05
Gloss 60° / 20° [3]	93 / 85	91 / 74	93 / 83	92 / 84

(1) Except where noted, film applied with #60 WWR to B1000 panel, air dried 7 days
(2) Film applied by 3 mil Bird bar to glass plate
(3) Film applied by 3 mil Bird bar to Leneta chart

NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

- Hardness & Abrasion Resistance

Film Performance [1]	High solids WB-OMU	1st Gen. OMU	2nd Gen. OMU	3rd Gen. OMU
Sward Hardness [2]				
1 Day	24	32	32	20
7 Day	32	38	38	34
Konig Hardness				
1 Day	43	84	72	48
7 Day	75	96	98	77
Pencil Hardness				
7 Day	HB	HB	HB	HB
Impact Resistance, Direct / Reverse	160 / 160	160 / 160	160 / 160	160 / 160
Mandrel Bend, 1/8''	Pass	Pass	Pass	Pass
Taber Abrasion, mg loss [4]	66	46	41	62
Mar Resistance, Grams [5]	700	700	200	200
Mar Resistance, Days [6]	< 2	< 1	< 1	< 2

(1) Except where noted, film applied with #60 WWR to B1000 panel, air dried 7 days
(2) Film applied by 3 mil Bird bar to glass plate
(4) Taber, CS-17 wheels, 1 kg load, 1000 cycles
(5) Hoffman Tester, loop stylus, weight needed to mar film
(6) Time to achieve, finger nail scratch

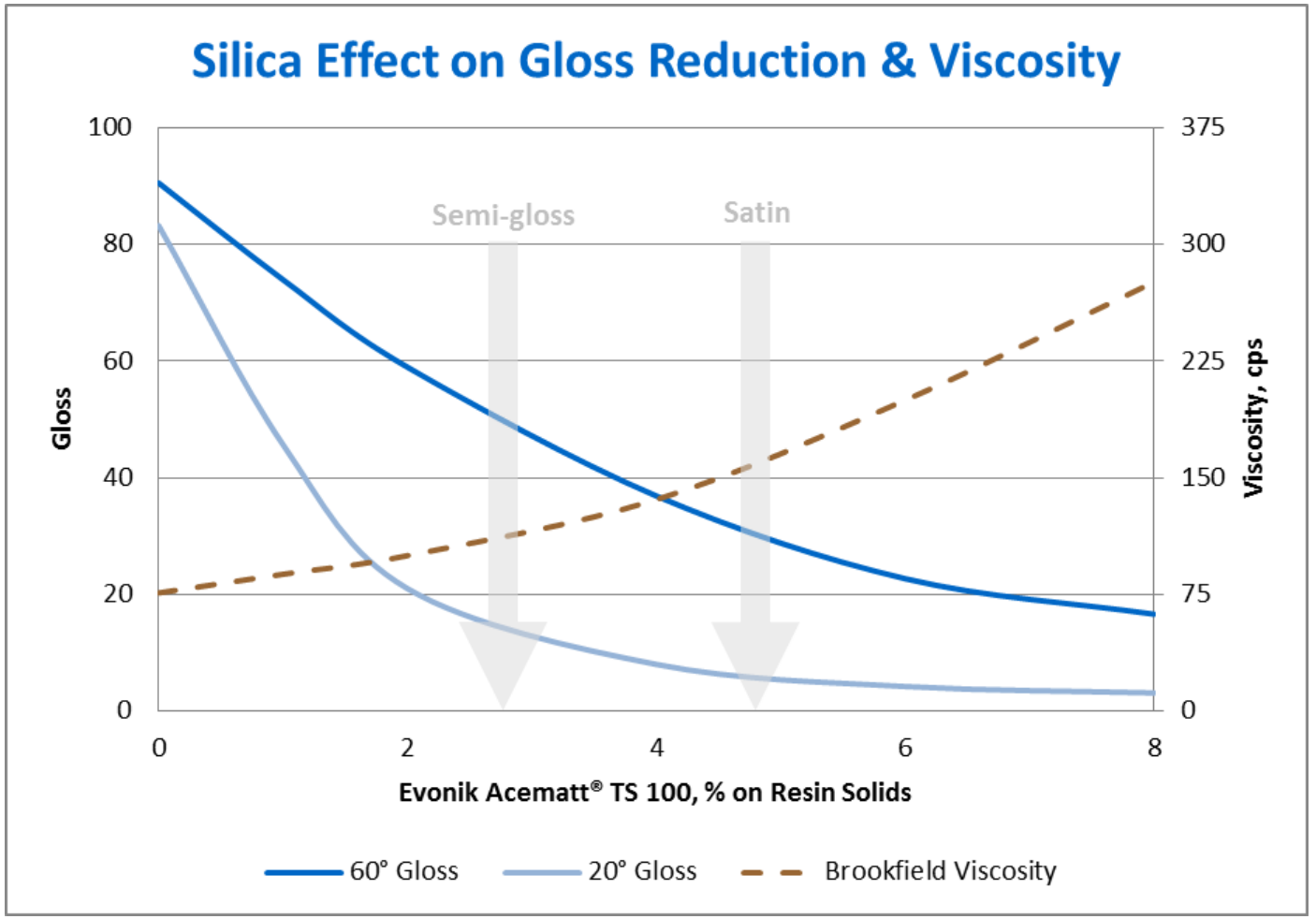
NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

❑ Stain & Solvent Resistance

Film Performance [1]	High solids waterborne OMU	1st Gen. OMU	2nd Gen. OMU	3rd Gen. OMU
Stain Resistance, Average [7]	3.88	4.15	4.08	4.04
Solvent Resistance, 200 Double Rubs				
Ethanol	> 200	> 200	> 200	> 200
Isopropanol	> 200	> 200	> 200	> 200
Methyl Ethyl Ketone	> 200	> 200	> 200	> 200
Xylene	> 200	> 200	> 200	> 200

(1) Except where noted, film applied with #60 WWR to B1000 panel, air dried 7 days
(7) ASTM D1308, 4 hr exposure, covered, rating 0-5 no effect

NMP free Waterborne Oil-Modified Urethanes (WB-OMU)



NMP free Waterborne Oil-Modified Urethanes (WB-OMU)

❑ Summary

- WB OMU with performance similar to conventional SB OMU
- NMP free and high solids (43%) via unique process control
- Very low VOC (<100 g/L)
- Self-crosslinkable with good storage stability
- Fast dry
- High gloss & easily flattened
- Excellent mar resistance
- Excellent chemical resistance and solvent resistance
- Major raw material is from renewable resource
- Applications: Clear wood floor coatings; Floor finishes, furniture, trim.

Thank You!

Obrigado!

Danke! Merci!

شُكْرًا

Gracias! धन्यवाद !

Takk! 谢谢 ! Grazie!

Děkujeme! Dank!