Coatings Trends & Technologies SUMMIT

Innovative TEA-free Polyurethane Dispersions For Industrial Wood Coatings

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Outline

Waterborne PUDs

- History and Morphology
- Chemistry
- Manufacturing
- Properties
- Triethyl amine (TEA) free PUDs

Industrial Wood Coatings

- Markets
- Project Plan
- Specifications and Test Methods
- Products Evaluated
- Carbodiimide Chemistry and Crosslinking Mechanism
- Formulations
- Panel Preparation
- Data
- Summary

Introduction: PU History and Morphology

1930
- Otto Bayer invented PU
- ☼ Isocyanate/PUs
- ☼ Urethane lacquers

1940s
- ☼ Rigid PU foams
- ☼ Isocyanate/alkyds

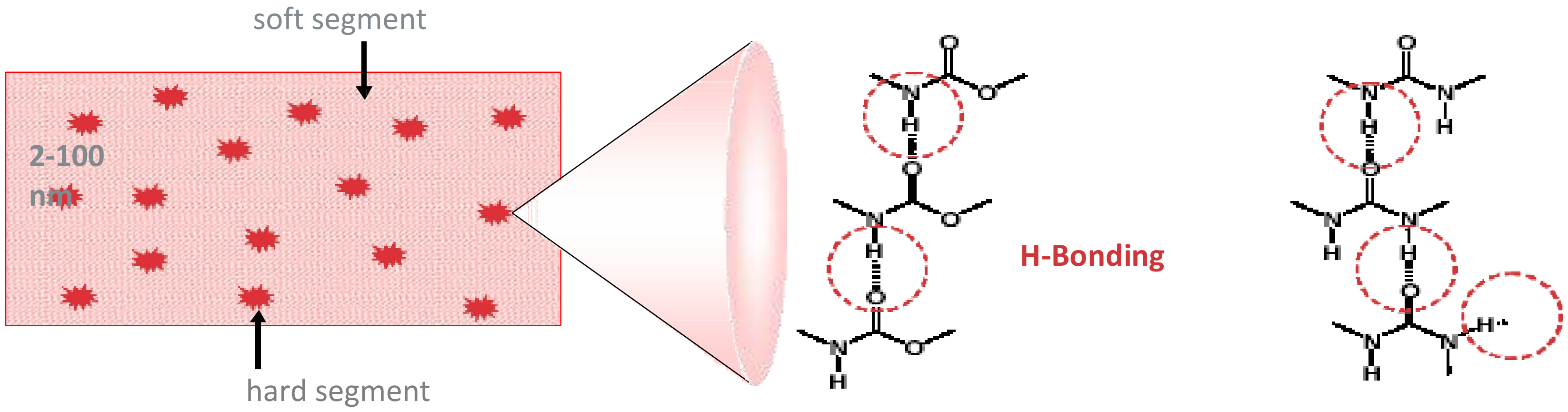
1950s
- ☼Flexible PU foam
- ☼Urethane elastomers
- ☼Aromatic prepolymers

1960s
- ☼ Polyisocyanate alkyd enamels

1970s
- ☼ PUDs
- ☼ RIM

1980s
- ☼ 2-component PUs

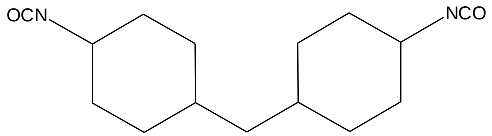
1990s
- ☼ 1-K Blocked Iso systems
- ☼ 2-K WB PU coatings



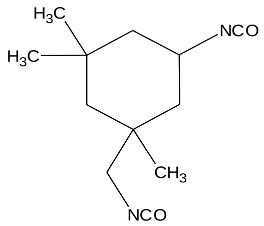
- ¤ acts as crosslinking point
- ¤ will release under strain
- ¤ allows flow to relieve stress
- ¤ allows self healing of defects

Traditional PUD Building Blocks for Coatings

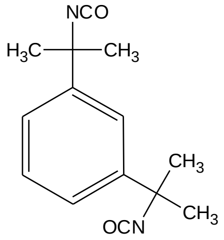
Isocyanates



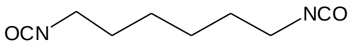
$H_{12}MDI$



IPDI

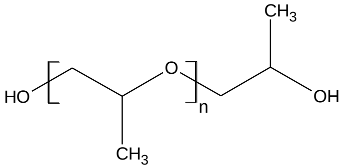


TMXDI

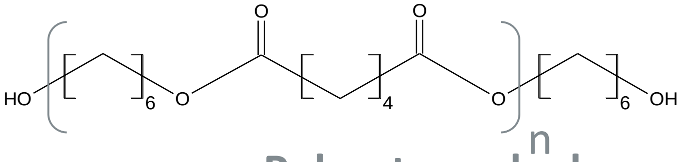


HDI

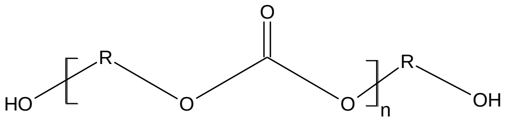
Polyols/Co-reactants



Polyether polyol



Polyester polyol



Polycarbonate polyol

Aqueous Polyurethane Dispersions - Chemistry

Pre-polymer preparation

- A polyol is reacted with a stoichiometric excess of isocyanate to produce a pre-polymer.
- Dimethylpropionic acid (DMPA), an anionic stabilizing agent, is used to build functionality into the polymer chain.

Neutralization

- An amine, typically TEA or DMEA, is used for neutralization.

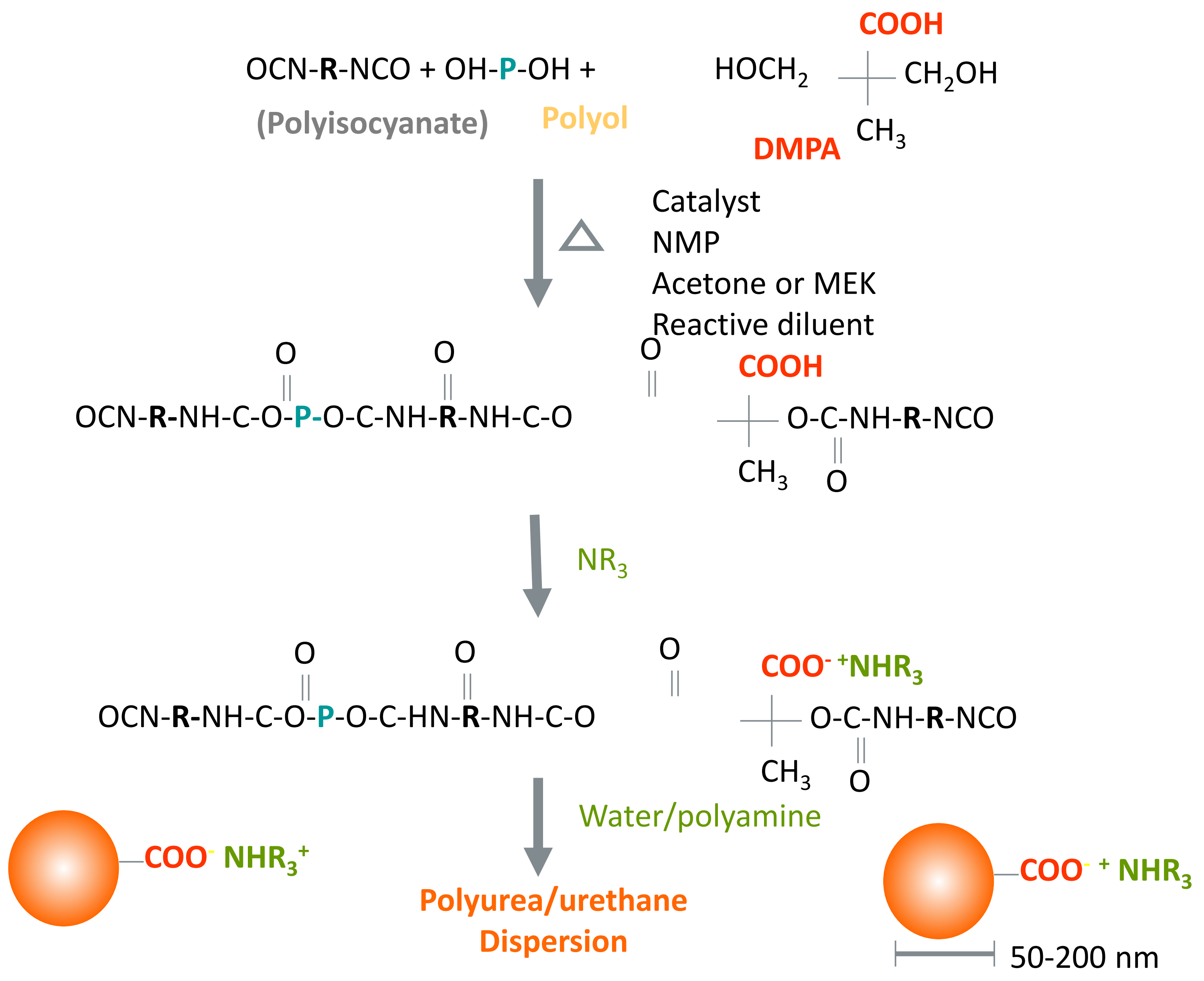
Dispersion

- The pre-polymer is dispersed in water.

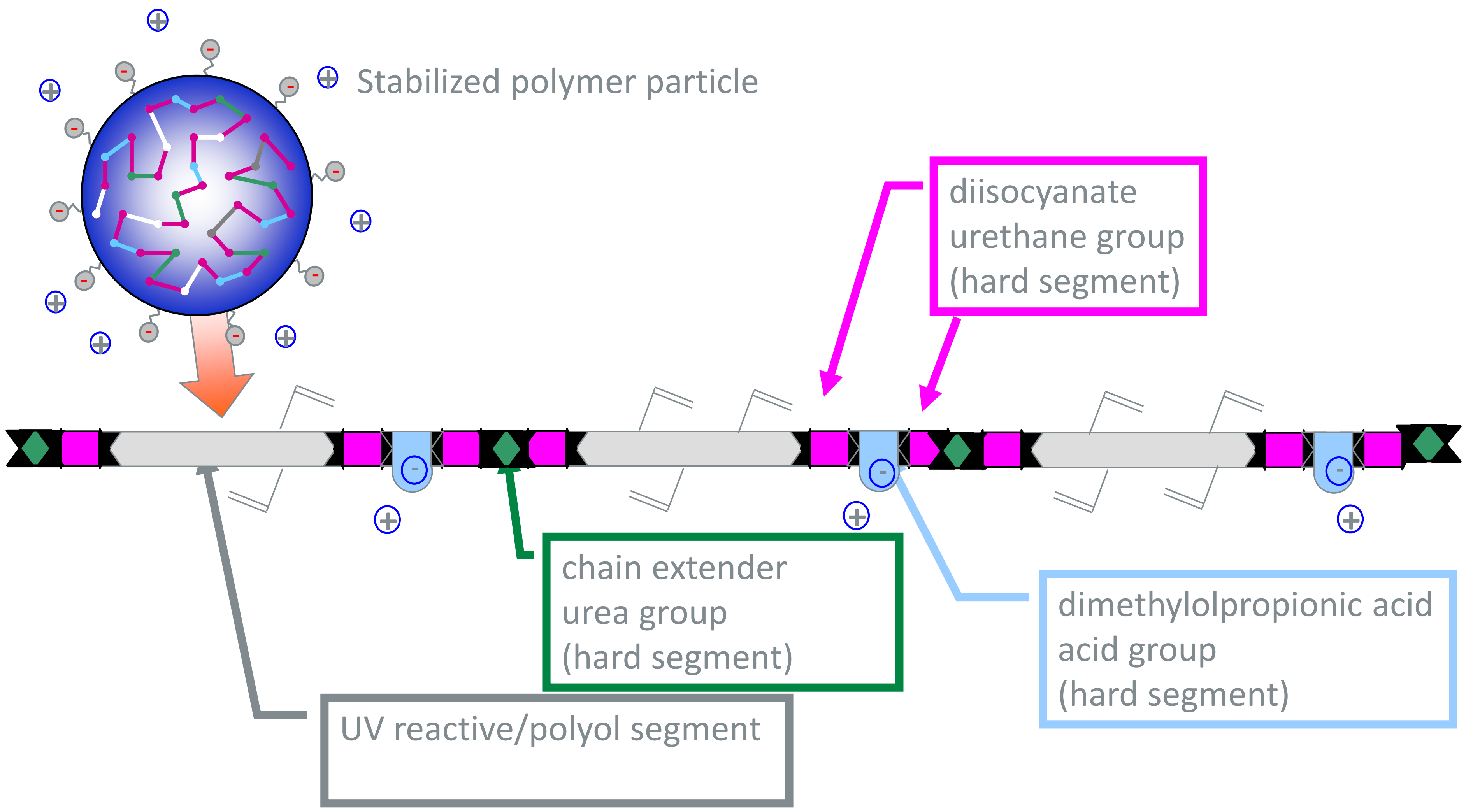
Chain Extension

- Molecular weight is increased.

PUD Chemistry



UV Curable Polyurethane Dispersions: Polymer Structure



Ion Bearing Molecules

Dimethyl Propionic acid

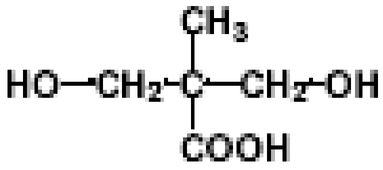
- Typically used with tertiary amines
- Looses hydrophilicity upon amine evaporation Relatively high Tg component
- Insoluble in PU component

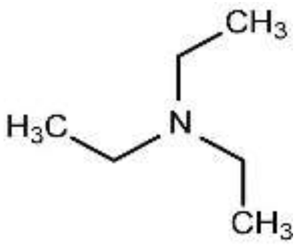
Sodium Sulfonate Diols

- Na salt remains in film Relatively low Tg component
- Improved solution stability of polyesters

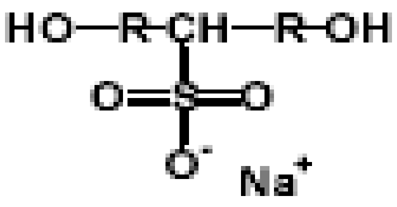
Tertiary amine diol

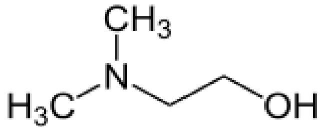
- Typically used with HCl or AcCOOH
- Commonly used for paper and leather application



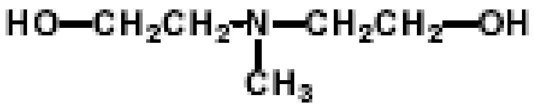


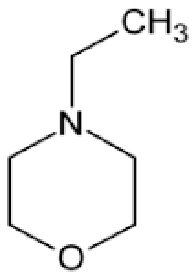
TEA





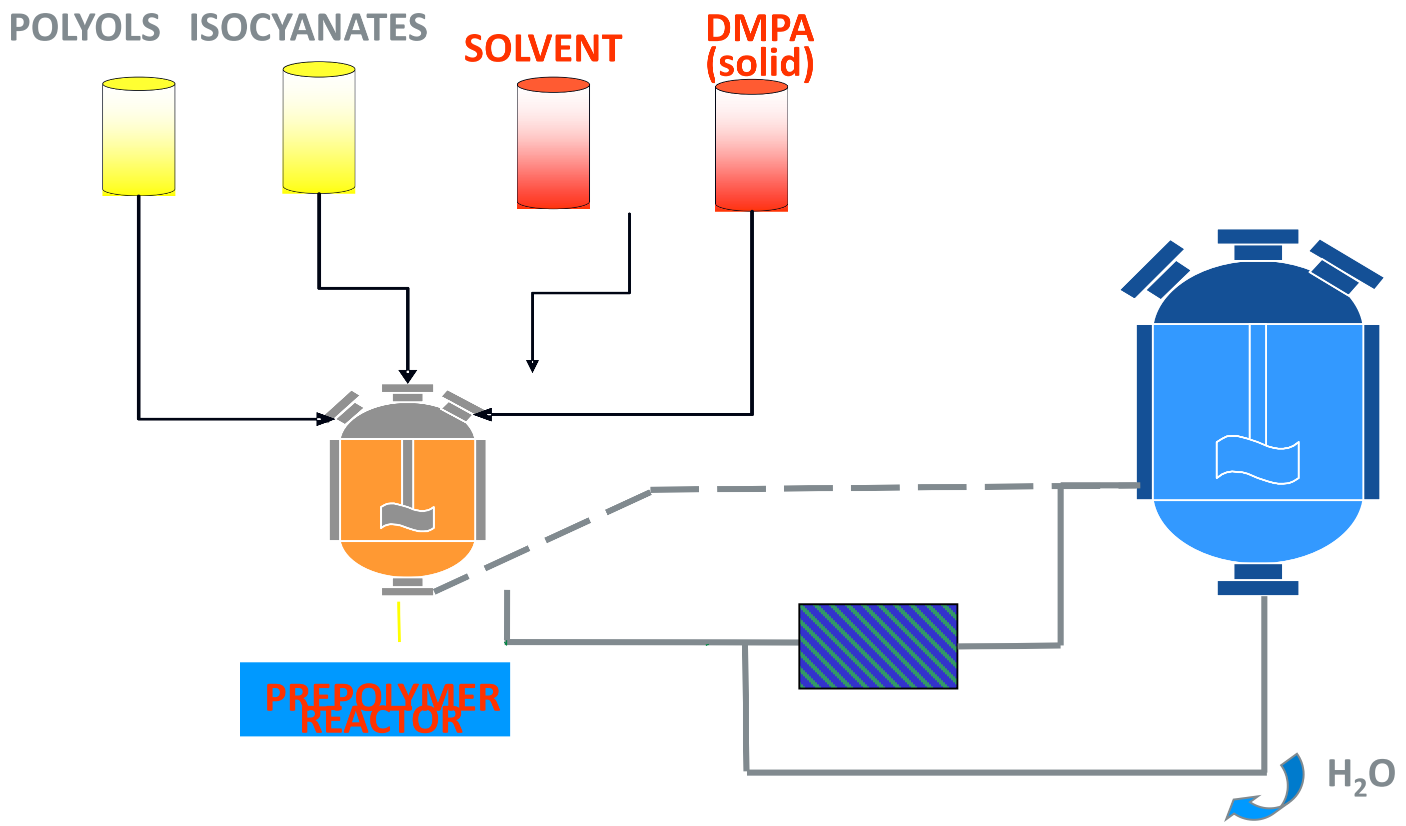
DMEA

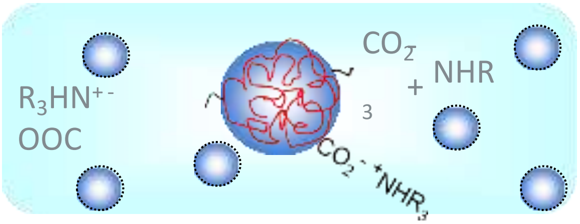


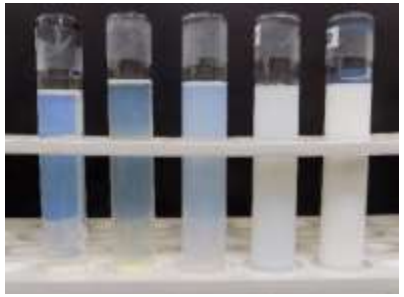


NEM

PUD Manufacturing





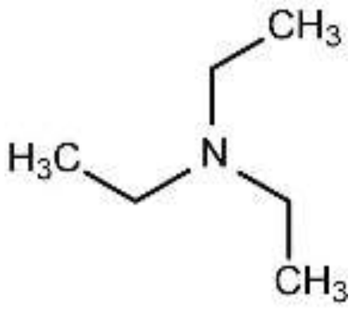


Properties of Polyurethane Dispersions

- Abrasion Resistance
- Flexibility
- Scratch and Mar Resistance
- Hardness
- Toughness
- Weatherability
- Functionality - Crosslinkable

TEA free PUDs Background: The case for TEA free

- Triethyl amine is the most common neutralizing agent for PUDs.



- According to GHS labeling it is flammable, harmful and toxic to the skin and eyes.

- Due to this classification, resulting binders and paints with TEA >1% have classification:

- TEA has a significant impact on emissions and indoor air quality.

Industrial Wood Coatings

Markets:

- Kitchen cabinets
- Furniture
- Flooring
- Doors
- Decorative moldings/Trim

Industrial Spray Lines

Experimental – Phase 1

- Five high performance TEA-free, WB PUDs were developed for wood coatings.
- Both 1K and 2K clear formulas were examined. The 2K coatings were crosslinked with carbodiimide.
- The coatings were evaluated according to Kitchen Cabinet Manufacturer's Association (KCMA), Architectural Woodworking Standards and office furniture manufacturer's specifications.

Kitchen Cabinet Manufacturer's Association (KCMA)

Purpose:

- To establish a nationally recognized performance
- Standard for kitchen and vanity cabinets.

Finish Requirements:

- Shrinkage and Heat Resistance
- Hot and Cold Check Resistance
- Chemical Resistance
- Detergent and Water Resistance

Architectural Woodwork Standards

Purpose:

- To provide design professionals with logical and
- simple means to comprehensively specify elements
- of architectural woodwork.

Finish Requirements:

- Chemical Resistance
- Wear Index
- Cold Check
- Adhesion

Individual Office Furniture Manufacturer’s Specifications

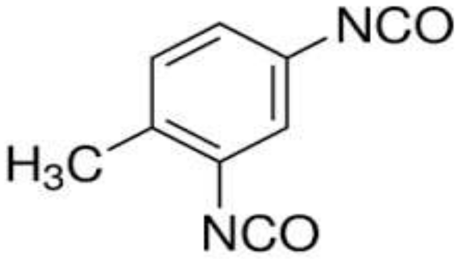
- Chemical/Stain Resistance
- Green Print Resistance
- Toughness/Adhesion
- Plasticizer Resistance
- Hot print Resistance
- Hot/Cold Check Resistance
- Ballpoint Pen Indentation
- Boiling Water Resistance
- Impact Resistance
- Resistance to fading or chalking
- Resistance to yellowing

Products Evaluated

Product	MFFT	Solids Content	Chemistry	Stabilization
WB PUD 1	25^{o}C	40%	Polyester PUD	Ammonium Hydroxide
WB PUD 2	20^{o}C	35%	Urethane acrylic copolymer 44% biobased carbon content	N-Ethyldiisopropylamine
WB PUD 3	5^{o}C	35%	Polyester/Polycarbonate PUD	Dimethylethanolamine
WB PUD 4	40^{o}C	35%	Polyester PUD	Dimethylethanolamine
WB PUD 5	0^{o}C	36%	WB UV Curable PUD	Sodium Sulfate Diol

Carbodiimide Chemistry

Diisocyanate



+

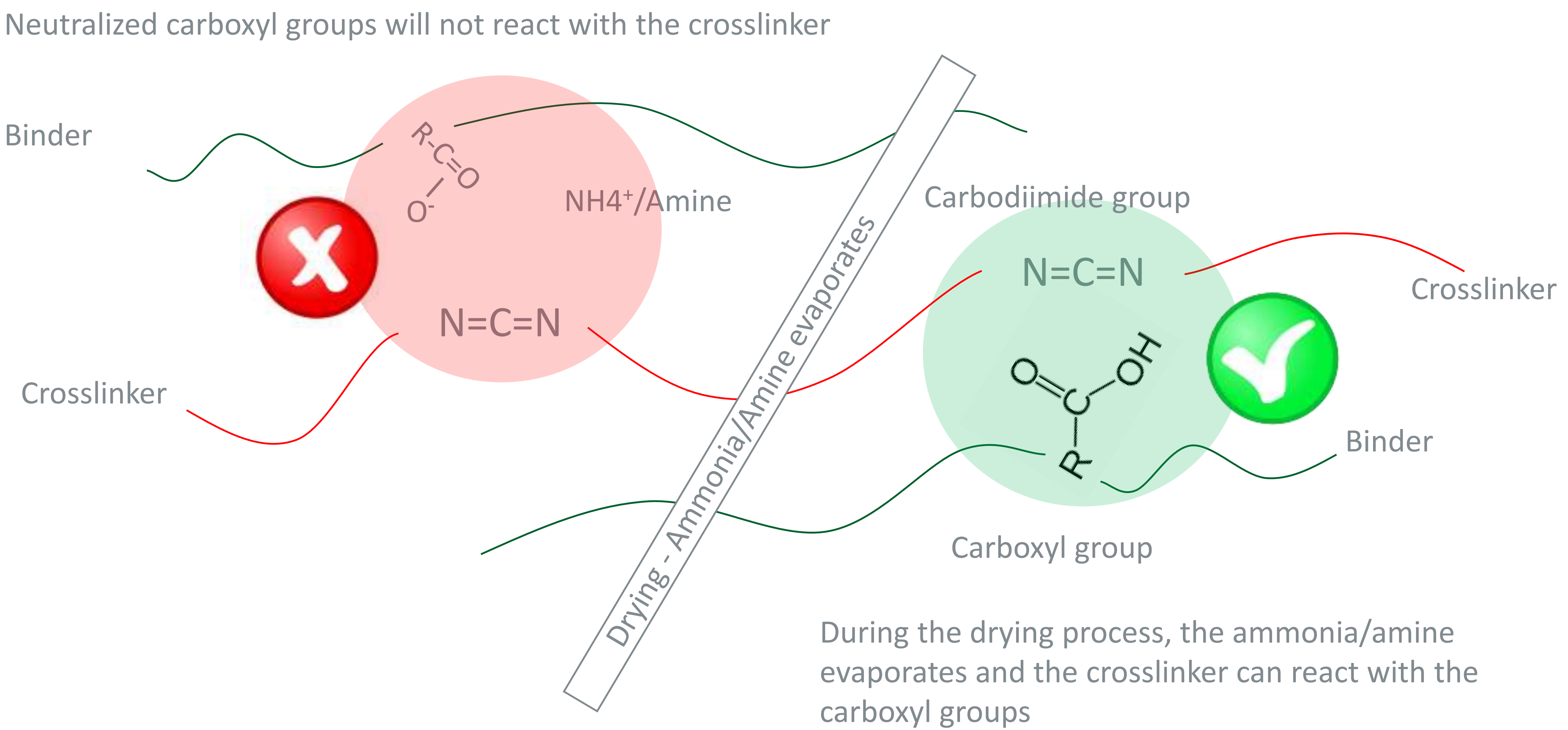
Catalyst

$- CO_2$

Polycarbodiimide

-R-N=C=N-R-[N=C=N]-R-N=C=N-R-

Carbodiimide Crosslinking Mechanism



During the drying process, the ammonia/amine evaporates and the crosslinker can react with the carboxyl groups

Formulations

	PUD 1	PUD 1 Carbodiimide	PUD 2	PUD 2 Carbodiimide	PUD 3	PUD 3 Carbodiimide	PUD 4	PUD 4 Carbodiimide	PUD 5
WB PUD 1	227.78	227.78	0	0	0	0	0	0	0
WB PUD 2	0	0	257.8	257.8	0	0	0	0	0
WB PUD 3	0	0	0	0	257.82	257.82	0	0	0
WB PUD 4	0	0	0	0	0	0	257.79	257.79	0
WB PUD 5	0	0	0	0	0	0	0	0	243.48
Defoamer	0.33	0.33	0.37	0.37	0.37	0.37	0.37	0.37	0.35
Surfactant	1.63	1.63	1.84	1.84	1.84	1.84	1.84	1.84	1.74
Water	38.86	38.86	9.33	9.33	15.66	15.66	9.99	9.99	33.35
Coalescing Solvent	7.24	7.24	5.75	5.75	2.58	2.58	5.43	5.43	0
Coalescing Solvent	7.24	7.24	5.75	5.75	2.58	2.58	5.43	5.43	0
Wax Emulsion	16.27	16.27	18.41	18.41	18.42	18.42	18.41	18.41	17.39
Rheology Modifier	0.65	0.65	0.74	0.74	0.74	0.74	0.74	0.74	0.7
Photoinitiator	0	0	0	0	0	0	0	0	3
Carbodiimide	0	19.15	0	19.15	0	19.15	0	19.15	0
Weight Solids (%)	32.63	31.87	32.63	31.87	32.62	31.88	32.63	31.87	32.63
Volume Solids (%)	30	29.16	29.61	28.8	29.71	28.89	29.67	28.85	29.81
VOC (g/l)	150	145.6	150	145.7	100	97.01	150	145.8	12.97

Panel Preparation

Evaluations on Leneta Cards:

- 3 mil draw down on 3B-H Leneta card.
- Test for : Block Resistance

Evaluations on Wood Panels:

- Two coats over 18 X 18 inch stained birch plywood panel. UV coatings cured with mercury bulb at 800 mJ/cm^2. Wait 7 days before testing unless otherwise indicated in the test method.
- For Door Edge Soak – same as above except use a 4 X 4 inch oak panel and coat all sides.

Test for:

- Chemical resistance
- Plasticizer resistance
- Print resistance
- Boiling water resistance
- Scrape adhesion
- Ball Point Pen Indentation
- Door Edge Soak
- Hot and Cold Check

Chemical/Stain Resistance

Test method:

- Apply enough chemical/stain to create a ¼ - ½ inch diameter spot on the test panel.
- Cover with a watch glass.
- Allow chemical/stain to dwell according to specification.
- Remove chemical/stain and wash the surface of the panel with water.
- Rate each chemical/stain on a scale of 0 to 5 with 0 being complete destruction of the film and 5 being no effect on the film.

Chemical Resistance - KCMA Chemicals

	PUD 1	PUD 1 Carbodiimide	PUD 2	PUD 2 Carbodiimide	PUD 3	PUD 3 Carbodiimide	PUD 4	PUD 4 Carbodiimide	PUD 5
Vinegar	4	5	5	5	2	2	2	3	5
Lemon Juice	5	5	5	5	5	5	3	3	5
Orange Juice	5	5	5	5	5	5	5	5	5
Grape Juice	5	5	5	5	4.5	4.5	5	5	5
Ketchup	5	5	5	5	4	4	5	5	5
Coffee	5	5	5	5	5	5	5	5	5
Olive Oil	5	5	5	5	5	5	5	5	5
100-proof Vodka	5	5	4.5	5	0	3	0	4	5
Detergent Solution	5	5	5	5	4.5	4.5	5	5	5
Mustard	4.5	4.5	4.5	4.5	3	3	4	4	5
Total	**48.5**	**49.5**	**49**	**49.5**	**38**	**41**	**39**	**44**	**50**

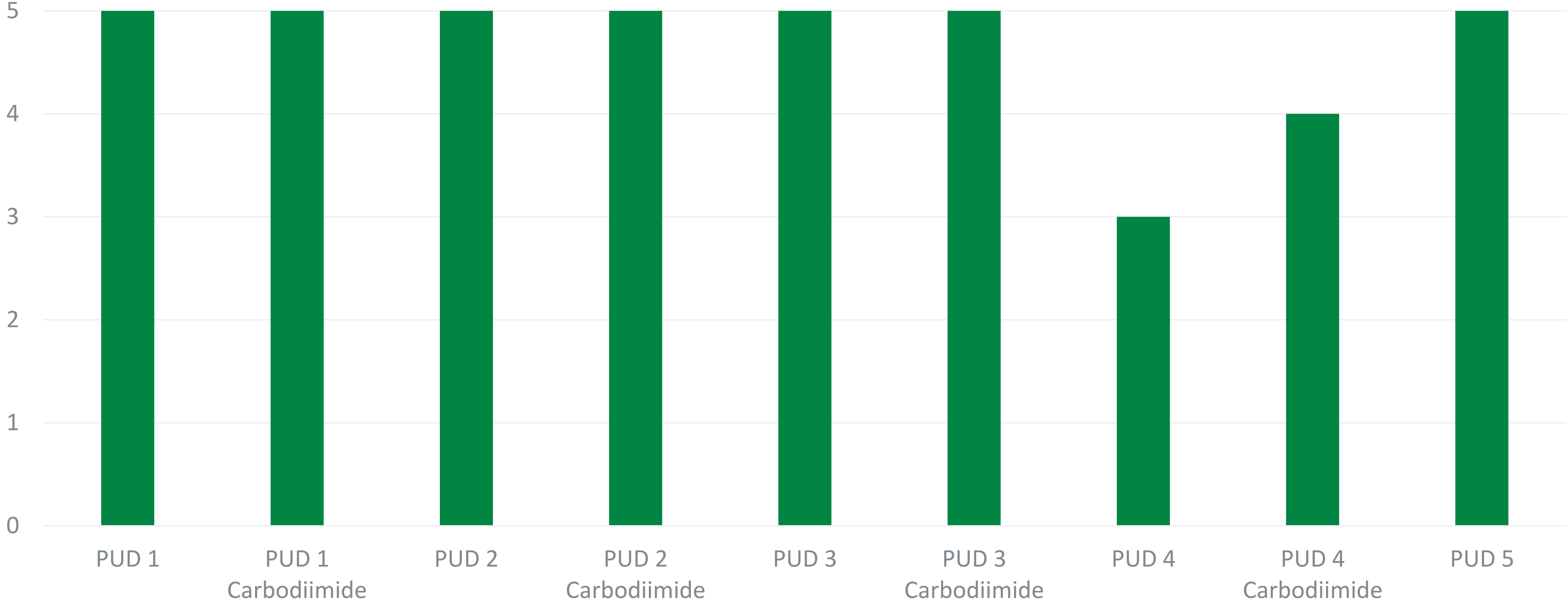
Chemical Resistance - Other Chemicals

	PUD 1	PUD 1 Carbodiimide	PUD 2	PUD 2 Carbodiimide	PUD 3	PUD 3 Carbodiimide	PUD 4	PUD 4 Carbodiimide	PUD 5
Pine Sol	4	4	5	5	3	3	3	3	5
Formula 409	4	5	4	5	3	4	4	5	5
Water	4	5	5	5	5	5	5	5	5
Acetone	5	5	4	5	3	3	0	3	5
Mineral Spirits	5	5	5	5	5	5	5	5	5
Betadine	5	5	4	4	4	4	4	4	4.5
Total	27	29	27	29	23	24	21	25	29.5

	PUD 1	PUD 1 Carbodiimide	PUD 2	PUD 2 Carbodiimide	PUD 3	PUD 3 Carbodiimide	PUD 4	PUD 4 Carbodiimide	PUD 5
Total Chemical Score (80 possible)	75.5	78.5	76	78.5	61	65	60	69	79.5

Boiling Water Resistance

Apply 10 ml boiling water to the test panel. Place a ceramic cup full of boiling water on top of the 10 ml of water. Wait 1 hour. Remove the cup and wipe with a paper towel. Wait 24 hours. Evaluate for whitening.



BYK Balanced Beam Scrape Adhesion and Mar Tester

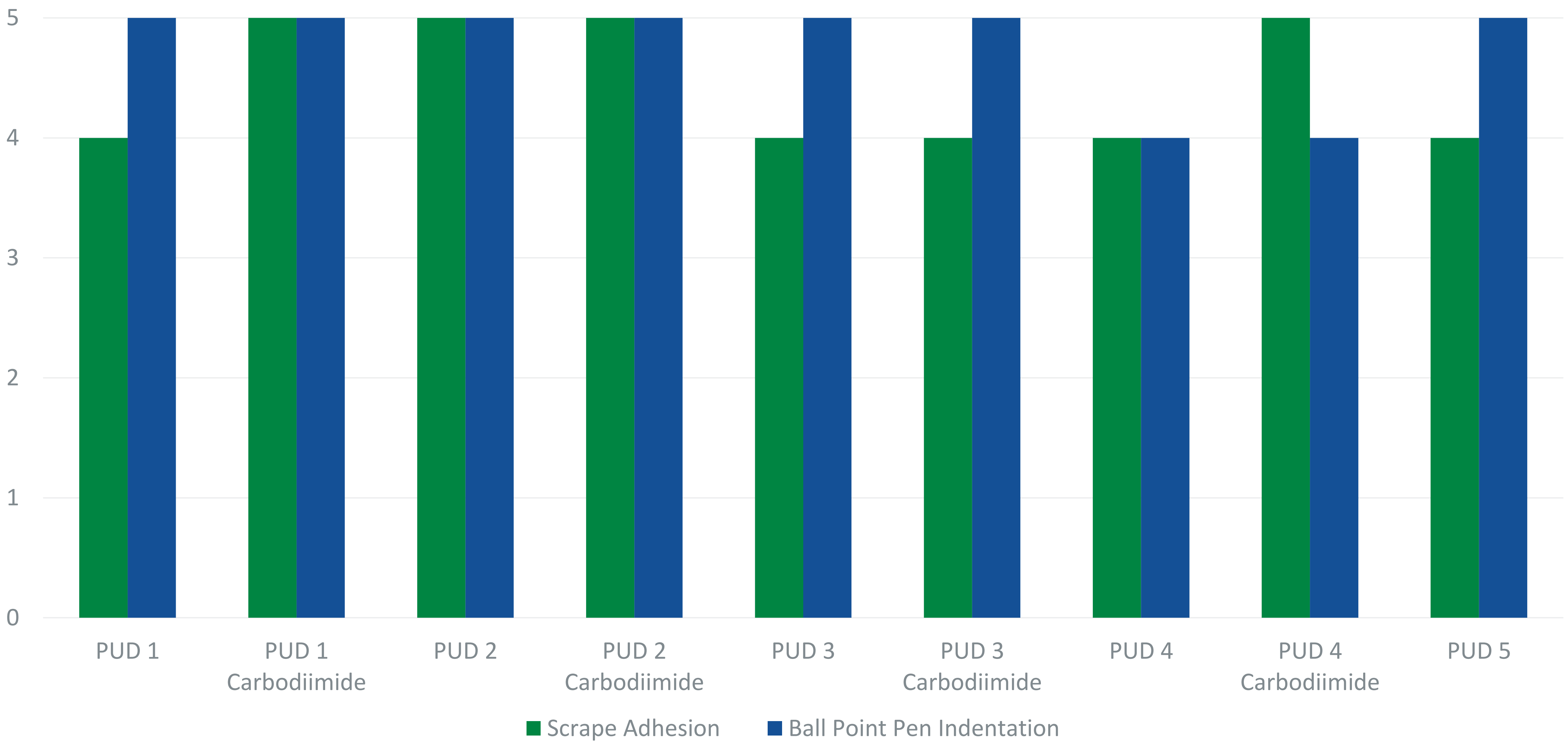
Scrape Adhesion

- Cut a 4X7 inch piece from each test panel. Test adhesion with 5000 grams of weight using the loop stylus. Rate on a scale of 0 to 5.

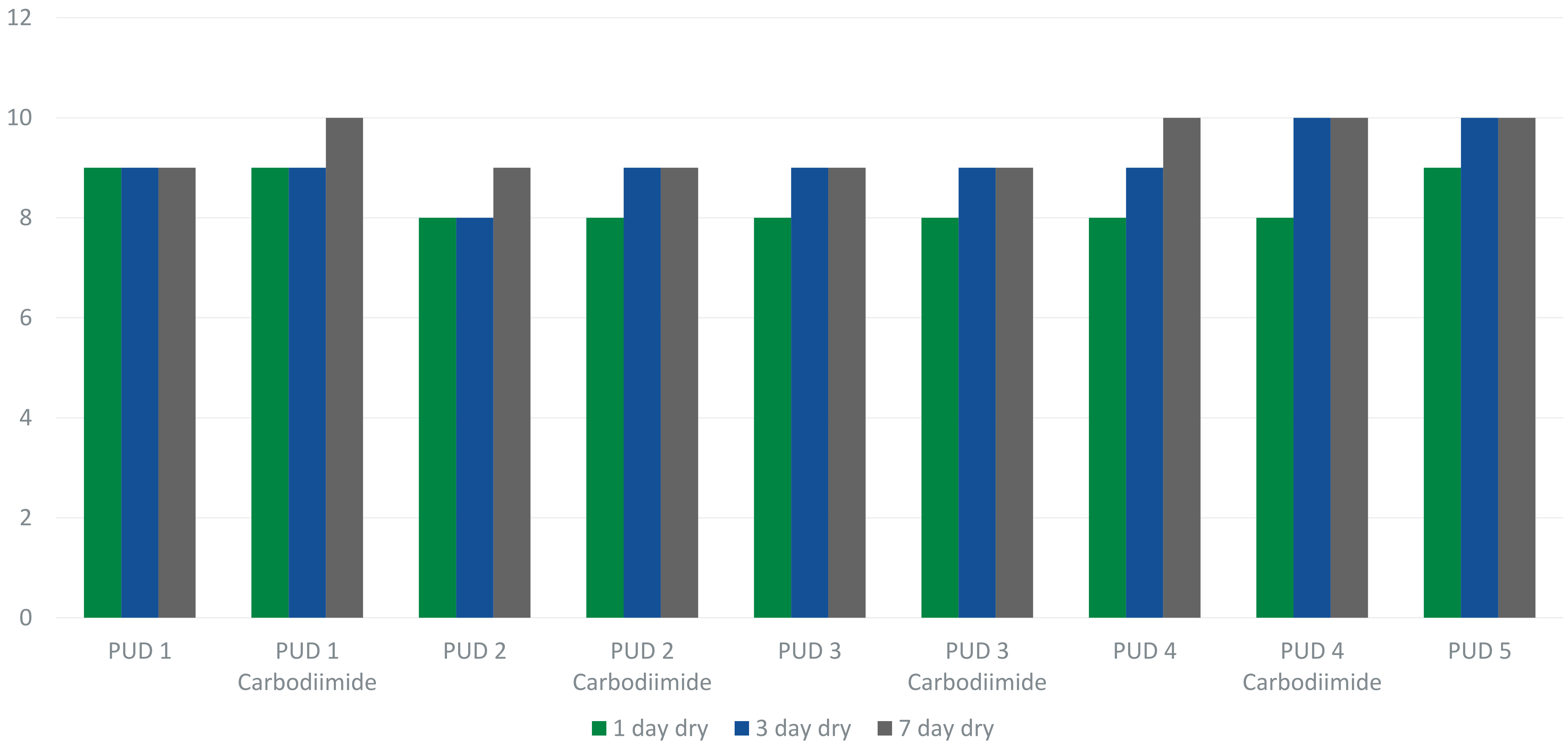
Ball Point Pen Indentation

- Cut a 4X7 inch piece from each test panel. Test with the small pen attachment (#5785) and 300 grams of weight. Rate on a scale of 0 to 5.

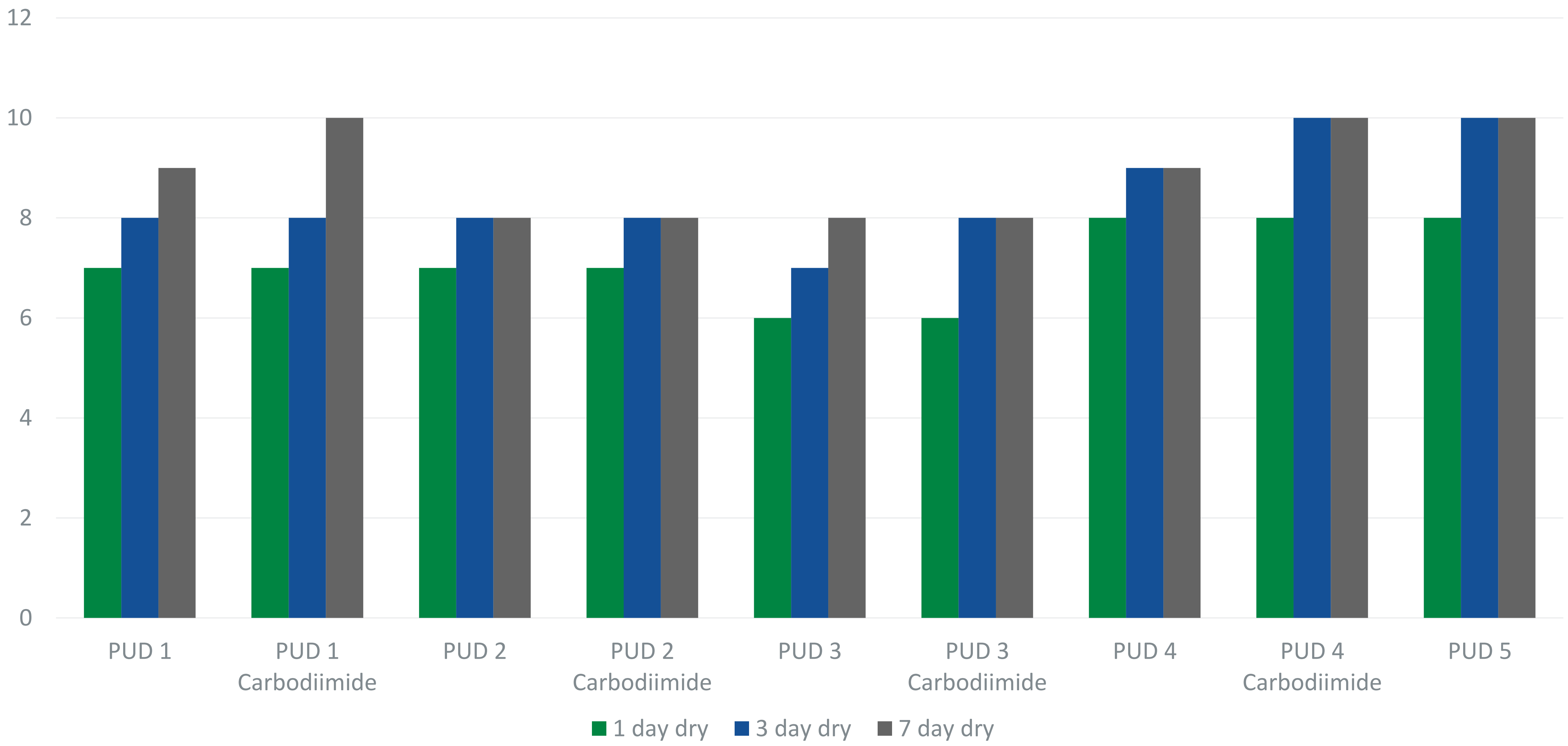
BYK Balanced Beam Scrape Adhesion and Mar Tester



Block Resistance – Room Temperature



Block Resistance – Elevated Temperature (50C)



Other Test Methods – All Coatings Passed

Green Print Resistance

After curing test panel wait 1 hour the apply a 2 inch square piece of #10 cotton duck cloth to the finish. Apply a force of 2 lb/square inch directly to the duck cloth. Wait 24 hours then remove the cotton duck cloth. Evaluate for printing.

Hot Print Resistance

After curing the panel wait 14 days then apply a 2 inch square piece of cotton duck cloth to the finish. Apply a force of 1 lb/square inch directly to the duck cloth. Place the specimen in the oven at 60C for 24 hours. Allow the specimen to cool to room temperature and then remove he duck cloth. Evaluate for printing.

Plasticizer Resistance

Apply a 2 inch square piece of red vinyl to the test panel. Apply a force of ½ lb/square inch. Place the specimen in the oven at 50C for 72 hours. After cooling at room temperature for 1 hour, remove the vinyl square. Evaluate for softening and blistering.

Edge Soak

Place a cellulose sponge in a plastic container. Level container and fill with detergent solution (1% Dawn® dish soap by weight in water) to one half inch below top level of sponge. Place panel on sponge, cut side down. Permit to stand for 24 hours.

Hot and Cold Check Resistance

Cut a 4”X4” piece from each panel. Cycle as follows: Place panel in humidity cabinet at 50C and 70% humidity for one hour. Remove for 30 minutes and allow to reach original room temperature and humidity. Place in freezer at -10C for one hour. Remove and allow to reach original room temperature and humidity. Repeat for five cycles.

Experimental – Phase 2

The highest performing TEA free binders in Phase 1 have been modified with a multiphase self-crosslinking acrylic dispersion.

The performance of these acrylic urethane hybrid binders has been evaluated according to industrial wood coating specifications.

Technical Data – Acrylic Dispersion 1

Solids content [%]	47 – 49
Viscosity [mPas]	100 – 1000
pH-value	7.5 – 9.0
MFFT [°C]	approx. 0
Morphology	Multi-phase
Polymer type	Self-crosslinking Acrylic
VOC capability	Near-zero

Acrylic Modification of Polyurethane Dispersions

Advantages:

- Lower Cost
- Improve Chemical Resistance
- Improve Pigment Wetting Properties

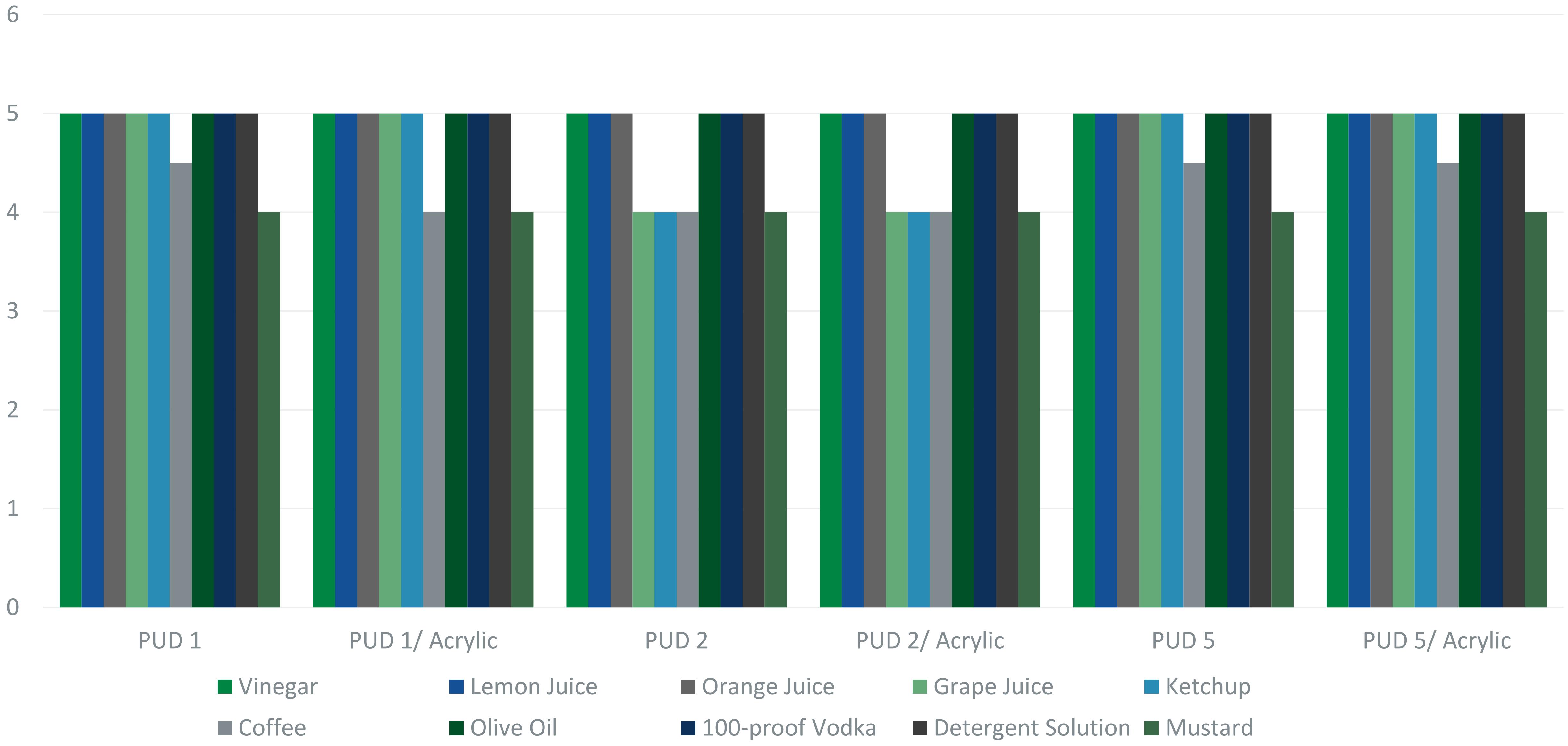
Challenges:

- Lower abrasion resistance
- Less flexibility

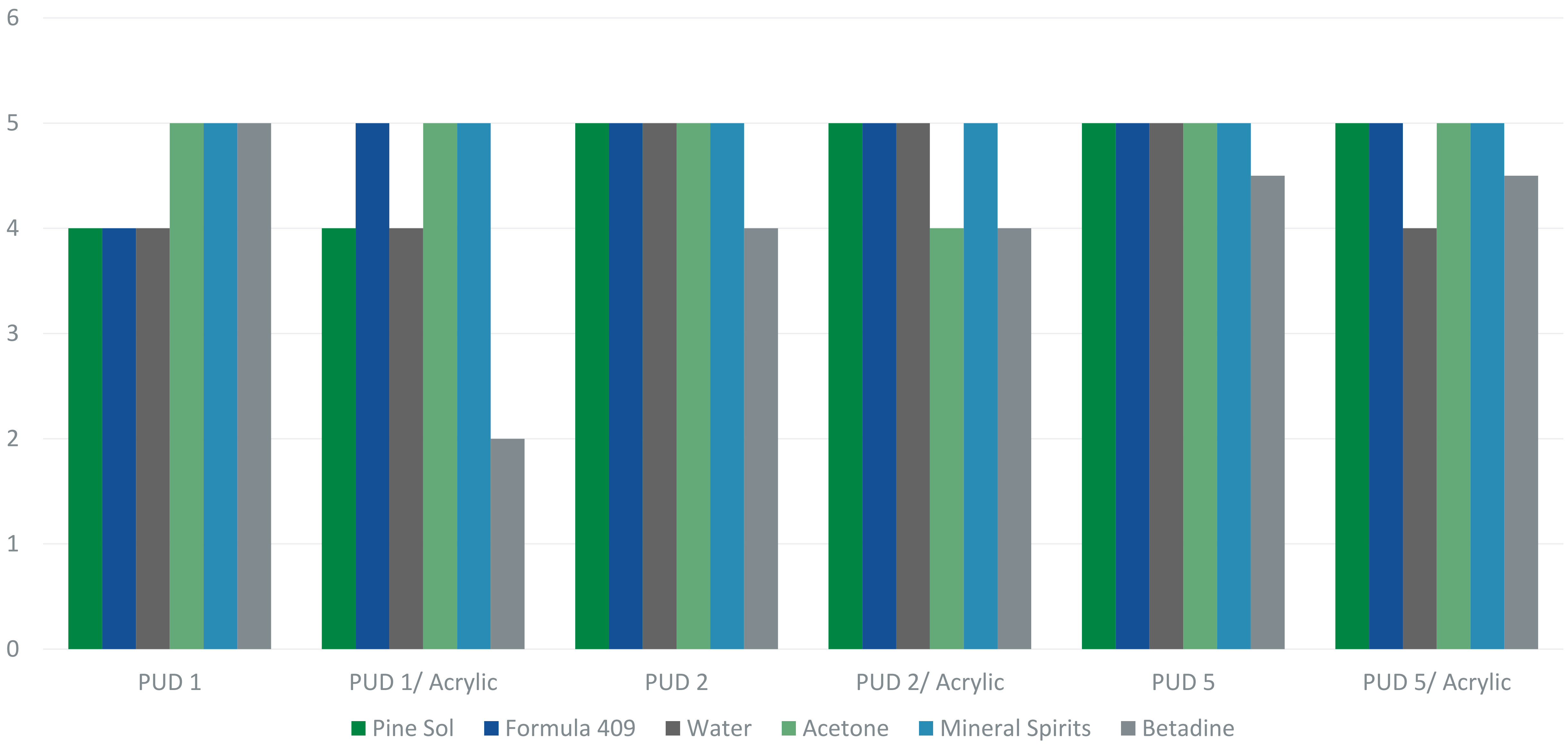
Formulations

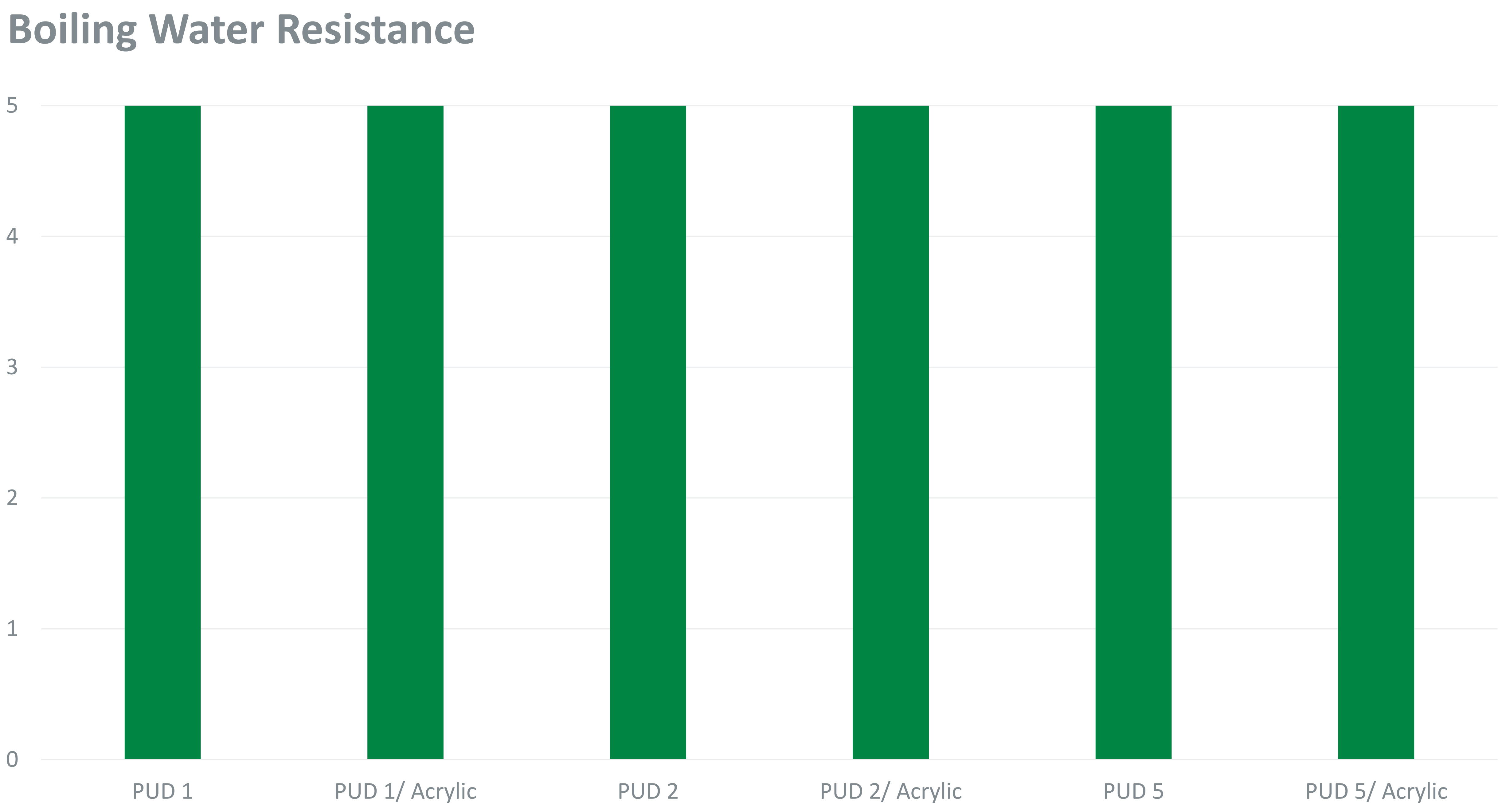
	PUD 1	PUD 1/ Acrylic	PUD 2	PUD 2/ Acrylic	PUD 5	PUD 5/ Acrylic
WB PUD 1	227.78	158.83	0	0	0	0
WB PUD 2	0	0	257.8	179.76	0	0
WB PUD 5	0	0	0	0	243.48	169.81
Acrylic Dispersion	0	56.73	0	56.17	0	54.58
Defoamer	0.33	0.32	0.37	0.37	0.35	0.35
Surfactant	1.63	1.62	1.84	1.83	1.74	1.73
Water	38.86	51.21	9.33	30.32	33.35	52.52
Coalescing Solvent	7.24	7.3	5.75	6.24	0	0
Coalescing Solvent	7.24	7.3	5.75	6.24	0	0
Wax Emulsion	16.27	16.21	18.41	18.34	17.39	17.33
Rheology Modifier	0.65	0.65	0.74	0.73	0.7	0.69
Photoinitiator	0	0	0	0	3	3
Weight Solids (%)	32.63	32.62	32.63	32.63	32.63	32.64
Volume Solids (%)	30	30.09	29.61	29.86	29.81	30.03
VOC (g/l)	150	150	150	150	12.97	12.79

Chemical Resistance – KCMA Chemicals

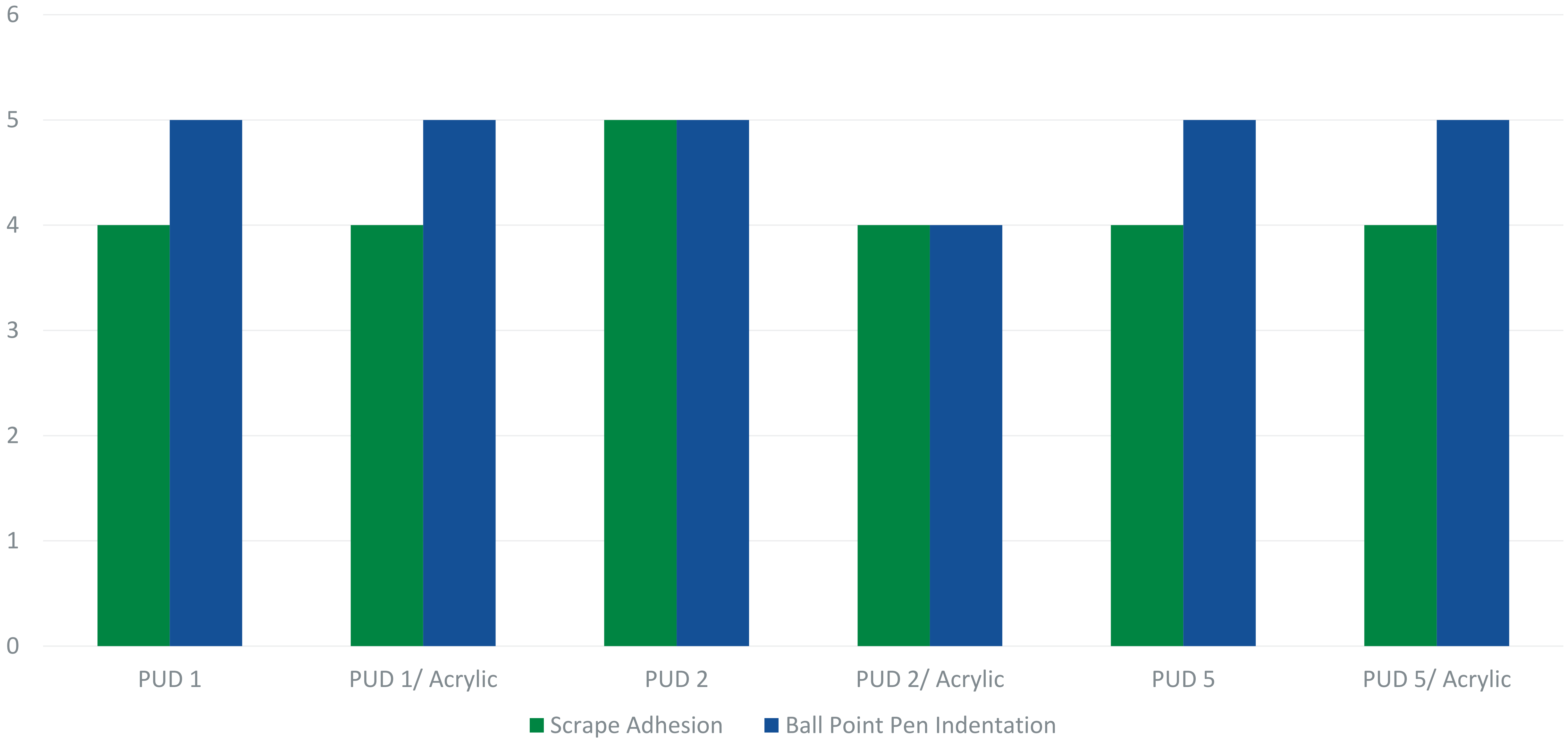


Chemical Resistance – Other Chemicals




Boiling Water Resistance
5
4
3
2
1
0
PUD 1
PUD 1/ Acrylic
PUD 2
PUD 2/ Acrylic
PUD 5
PUD 5/ Acrylic

BYK Balanced Beam Scrape Adhesion and Mar Tester



Summary

- A versatile family of TEA free polyurethane dispersions has been developed for use in industrial wood coatings.
- TEA free PUDs are less toxic and less harmful to the environment than their TEA containing counterparts.
- TEA free PUDs have excellent chemical resistance, flexibility, scratch and mar resistance and resilience.
- The UV Curable TEA free PUD has the best performance in this study.
- The addition of carbodiimide crosslinker improved the performance in all cases.
- The TEA free PUDs can be modified with an acrylic dispersion at 30% on total resin solids to create a cost-effective coating that has very good performance.

Questions?

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