

Non-Isocyanate Polyurethane Platform for Sustainable and Advanced Rain-Erosion Resistant Coatings

Project Number : WP 2602

**Vijay Mannari
Eastern Michigan University**

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14. ABSTRACT Design and develop isocyanate free customized building blocks for PU using cyclic carbonate/ amine chemistry - Develop two coating systems that meet technical and environmental requirements of SON 16 02. 1.Two component high solid coating systems (2K-HS-NIPU) 2.100% Solid UV Curable Coating systems (UV NIPU) - Test and evaluate these coatings to demonstrate performance and environmental benefits. - Identify best prototypes for extensive evaluation, including Rain Erosion Testing at WPAFB, in comparison with commercial benchmark (CAAPCO C W4) - Develop a roadmap for strategic transition plan by cooperative development with industry partners and end user DoD sites					
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Project Team

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Dr. S.M. Mirabedini – Scientist

Dr Nagraj Ireni – Post-doc.

Co-Performer

Ollie L. Scott, Wright Patterson Airforce Base (WPAFB)

WPAFB, Scientist, University of Dayton.

Testing of prototype coatings for Rain Erosion Resistance.

Chemical Dynamics, Plymouth, MI

Testing and evaluation - accelerated weathering



Background

- Project Initiated: Sept. 2016
- Statement of Need : WIPSON-16-02

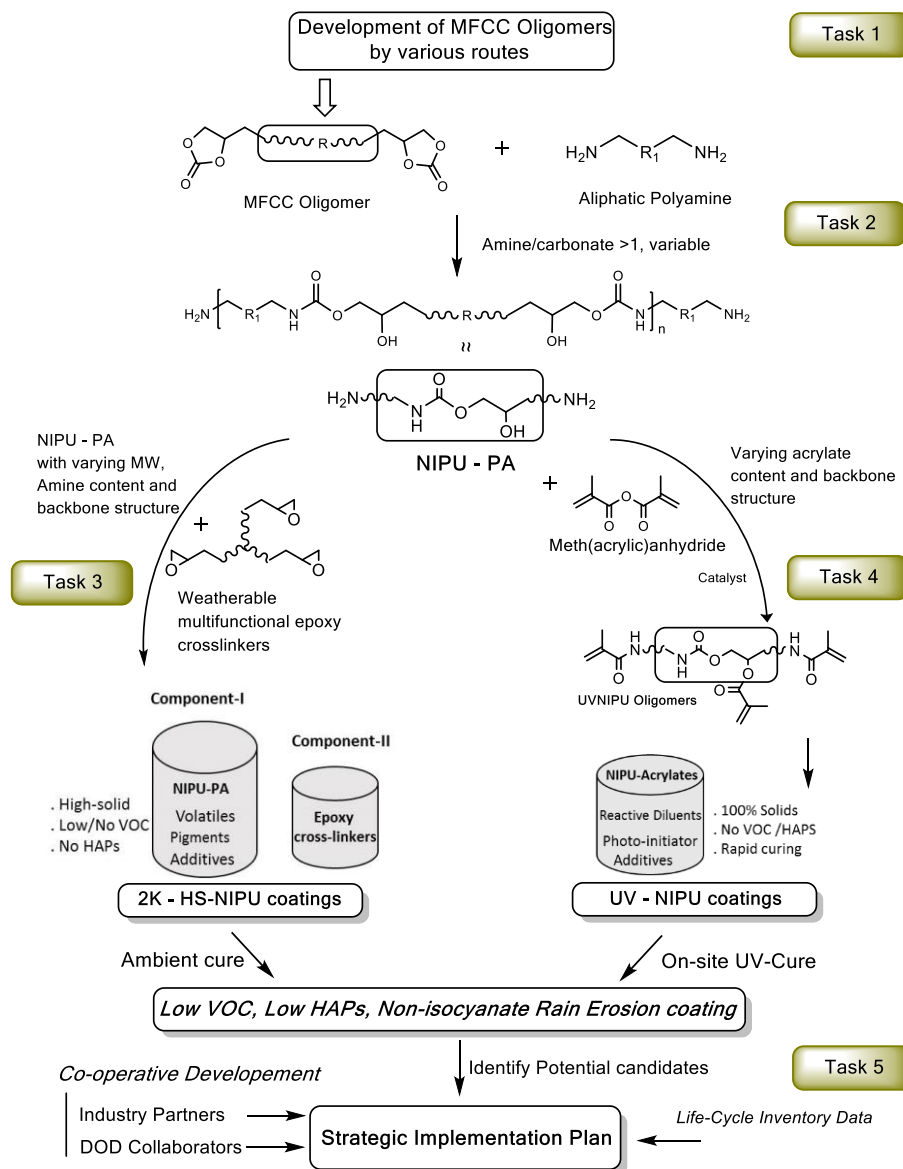
Reducing or Eliminating HAPS and VOCs and isocyanate compounds from Polyurethane Rain Erosion Coatings

- Project Title: Non-Isocyanate Polyurethane Platform for Sustainable and Advanced Rain-Erosion Resistant Coatings

Technical Objective

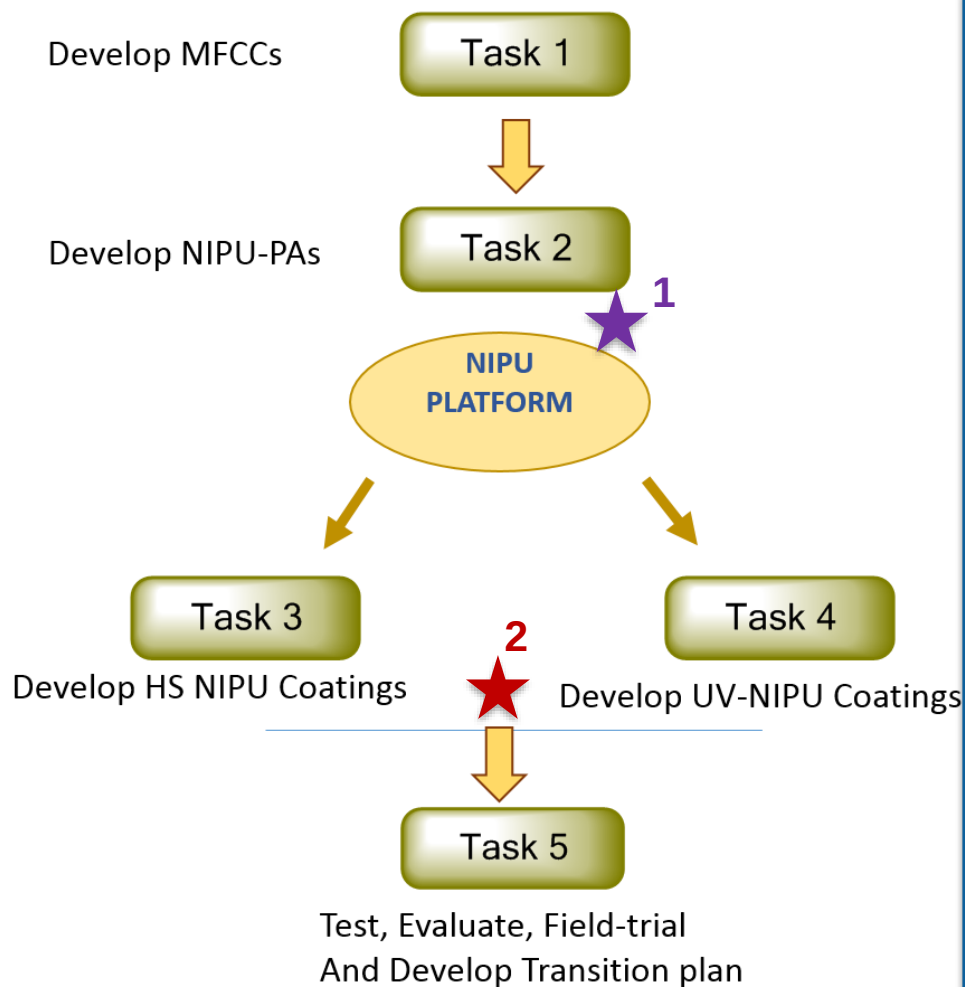
- Design and develop isocyanate –free customized building blocks for PU using cyclic carbonate/amine chemistry
- Develop two coating systems that meet technical and environmental requirements of SON -16-02.
 1. Two-component high-solid coating systems (2K-HS-NIPU)
 2. 100% Solid UV-Curable Coating systems (UV-NIPU)
- Test and evaluate these coatings to demonstrate performance and environmental benefits.
- Identify best prototypes for extensive evaluation, including Rain Erosion Testing at WPAFB, in comparison with commercial benchmark (CAAPCO-C-W4)
- Develop a roadmap for strategic transition plan by cooperative development with industry partners and end-user DoD sites

Technical Approach





Technical Approach

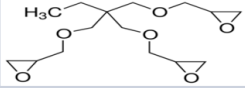
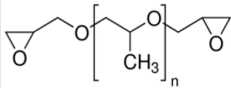
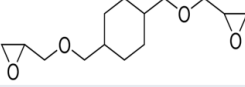
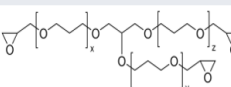
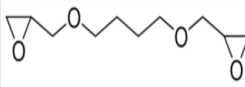
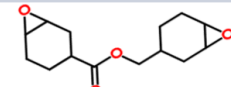
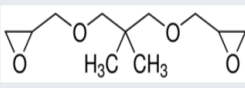
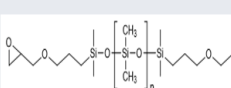


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1. Design, synthesis and characterization of multi-functional cyclic carbonates (MFCCs)
 2. Design and Synthesis of Amine-Functional NIPU Oligomers / Resins (NIPU-PA)
 3. Design and Development of Two Component High-Solid NIPU Coating Systems (2K-HS-NIPU).
 4. Design and Development of UV-Curable NIPU Coating Systems (UV-NIPU).
 5. Testing, Evaluation, and Characterization of NIPU Coatings – Transition plan.

Significant Outcomes / Results –Task 1

Design, synthesis and characterization of multi-functional cyclic carbonates (MFCCs)

❑ Identified commercial multi-functional based on final coating specs.

Commercial Name	Structure	Viscosity cP at 25 °C	Commercial Name	Structure	Viscosity cP at 25 °C
Hexion Heloxy Modifier 48	EEW 135-150 	100-200	Emeralds performance materials Erysis_GE24	EEW 310-330 	60-70
Hexion Heloxy Modifier 107	EEW 145-165 	45-75	Emeralds performance materials Erysis_GE36	EEW 620-680 	200-320
Emeralds performance materials Erysis_GE2 1	EEW 120-130 	10-18	Dow UVR 6110	EEW 135 	300
Emeralds performance materials Erysis_GE2 0	EEW 125-137 	10-18	Wacker SIRLES HP1250	EEW 660-680 	90-135

Selection
Criteria

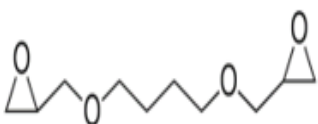
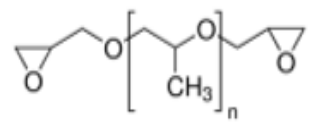
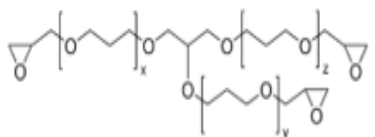


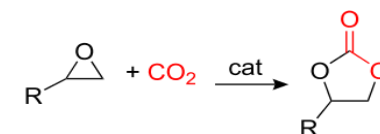
- Viscosity- VOC consideration
- Expected toughness of final coating – Erosion resistance
- Backbone structure – purely aliphatic – Exterior durability
- Functionality of cyclic carbonates - Cross-link density

Significant Outcomes / Results –Task 1

Design, synthesis and characterization of multi-functional cyclic carbonates (MFCCs)

- ❑ Successfully developed process for carbonation of selected epoxy compounds
- ❑ Of all methods tried, direct-carbonation of epoxy compounds found the best.

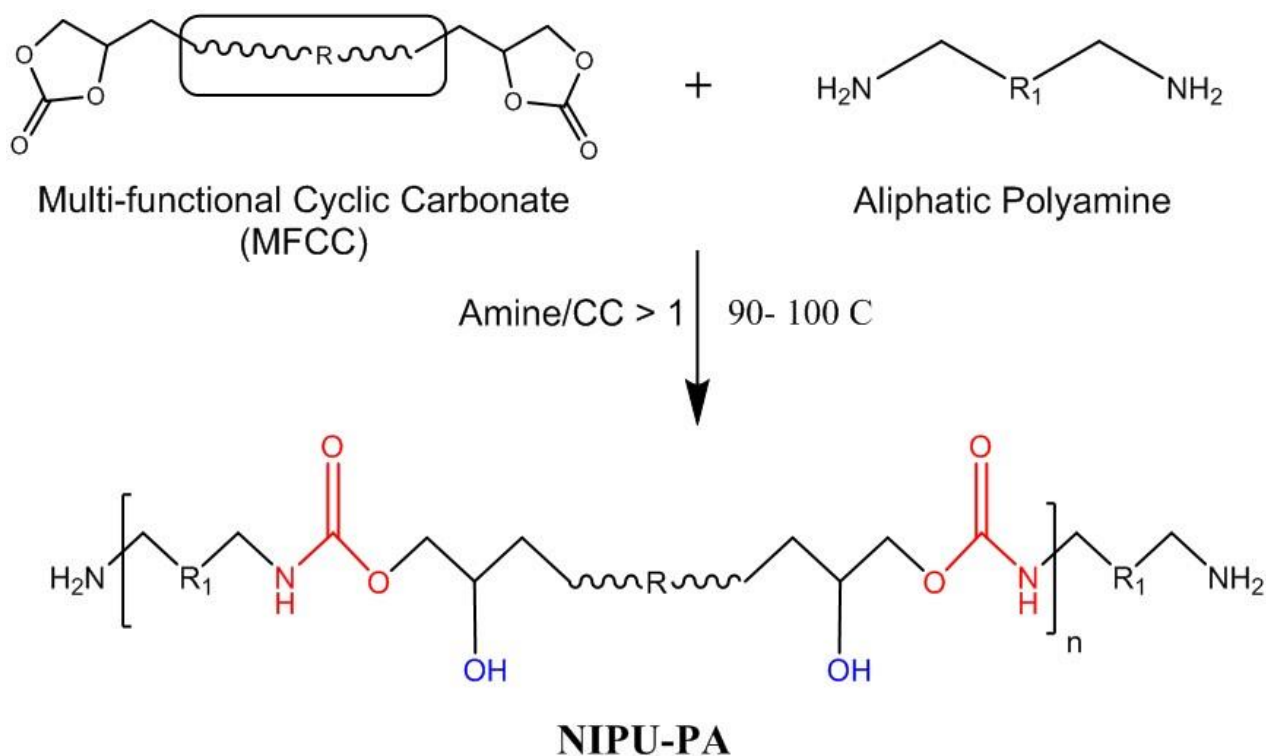
Epoxy Compound	Cyclic carbonate	Temperature (°C)	Reaction Time (h)	Conversion %
	CC1	70	24	99
	CC2	70	48	97
	CC3	70	48	96



- Using methyl-triphenyl phosphonium iodide (MePhI) as catalyst
- 1-methoxy-2-propanol as solvent

Significant Outcomes / Results- Task-2

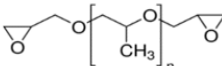
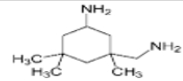
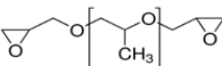
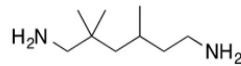
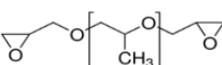
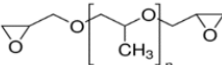
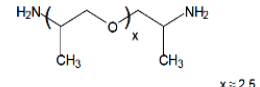
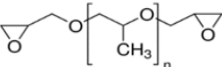
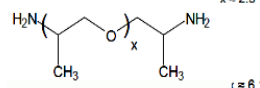
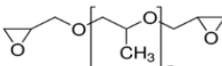
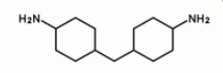
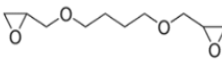
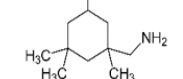
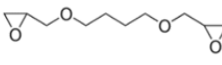
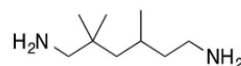
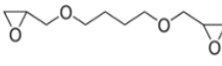
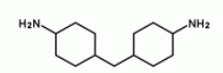
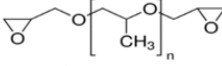
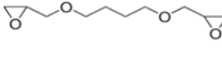
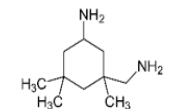
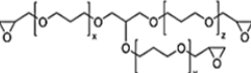
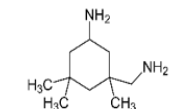
Design and Synthesis of Amine Functional NIPU Oligomers Resins (NIPU-PA)



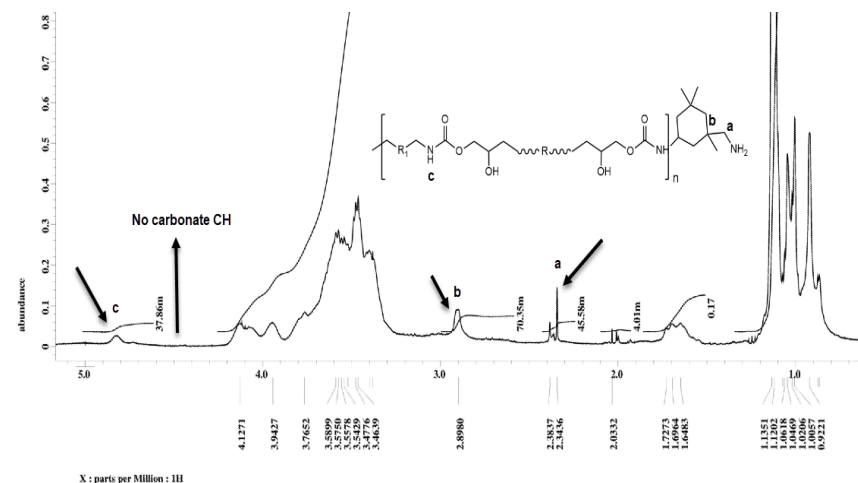
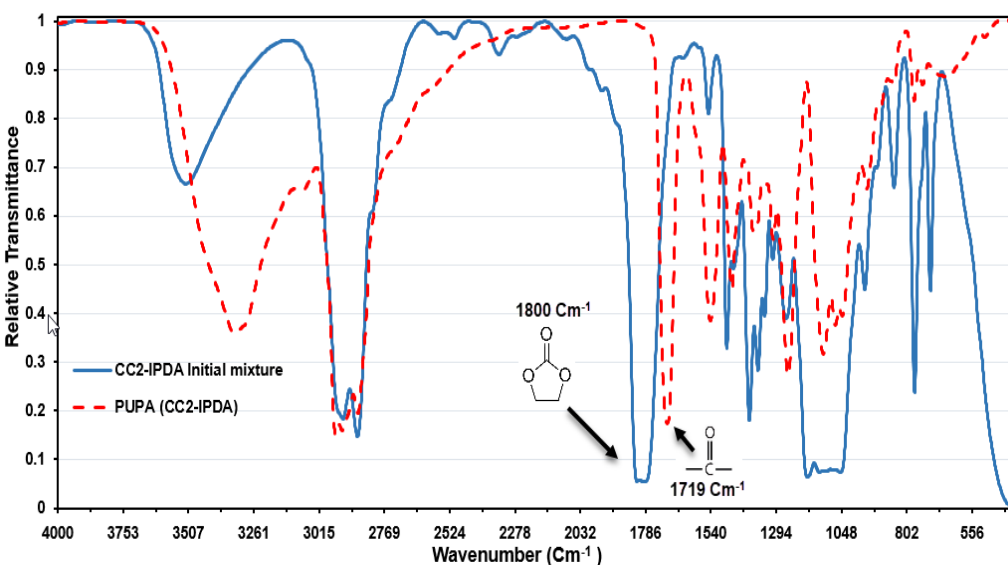
Task-2 - Results

- A variety of NIPU-PA (~15) synthesized from 4 MFCCs and various diamines and combinations. (# 2,1, 2,2).
- Reaction condition optimized for high yield and desired MW.
- Amine Hydrogen Equivalent Wt. (AHEW) was varied from 200 -1000 g.
- Aliphatic, linear, branched and cycloaliphatic amines used to vary backbone structure. All NIPU-PA characterized for AHEW, viscosity, and chemical structure.
- Reactivity, viscosity, and functional group (-NH_2) were used as criteria for shortlisting (# 2.3)

Polyurethane Polyamines PUPA (NIPU-PA) Prepared:

NIPU-PA	Cyclic carbonate	Epoxy used in making Cyclic carbonate	Amine	Reaction Time (h)	AHEW
PUPA (CC2-IPDA)	CC2			6	472
PUPA (CC2-TMD)	CC2			5	466
PUPA (CC2-1074)	CC2			8	1098
PUPA (CC2-D230)	CC2			12	526
PUPA (CC2-D400)	CC2			16	779
PUPA (CC1-PACM)	CC2			7	489
PUPA (CC1-IPDA)	CC1			4	203
PUPA (CC1-TMD)	CC1			4	255
PUPA (CC1-PACM)	CC1			5	269
PUPA (mix-IPDA)	CC1/CC2 1:1 eq.	 		5	322
PUPA (CC3-IPDA)	CC3			6	724

Characterization of NIPU-PA



FTIR and H-NMR spectra of PUPA(CC2-IPDA)

Selected NIPU-PA

Sample Name	M _n	M _w	PDI	Theoretical MW	Viscosity cps (75 wt.% at 25 °C)
PUPA (CC1-IPDA)	968	1025	1.060	1058	17200
PUPA (CC2-IPDA)	1395	1901	1.363	1902	13500
PUPA (CC3-IPDA)	3079	3557	1.15	3736	10800

Major Go/No-Go decision points

- **# 1 At the end of Task 1 & 2 . Development of NIPU Platform and PU coating building blocks.**
 - **Feasibility of synthesis in the lab and scale up / commercialization**
 - Identify the feasibility of synthesis at lab scale. (Reaction conditions, catalyst, handling/ storage, regulatory issues)
 - Potential issues in scale-up and commercialization
 - Use of VOC exempt and non-HAP solvents possible? To what extent?
 - **Architectural control**
 - Possibility of making polymers or oligomers with varying morphology
 - Ability to control structures that offer compatibility with NIPU-PA (cross-linkers), solvents, potential interactions with substrates to improve adhesion, wetting etc.
 - **Degree of conversion**
 - Are reactions capable of high (>95%) conversion in reasonable time?
 - If conversions are sub-optimum, are unreacted reactants pose problems with stability, cure-rate, and dry film exterior durability, and associated environmental issues?
 - **Control functionality and functional group contents**
 - Can we effectively vary functionality from 2 - 6?
 - Can we effectively vary functional group content?
 - What are the limits of functionality and functional group contents for each route?
 - **Viscosity of the product**
 - Lower viscosity the better (both for High-solid and UV-cure coatings)
 - How is viscosity control with VOC exempt solvent
 - Consideration of viscosity effect due to H-bonding or high MW



Passed most criteria. Low functionality of NIPU-PA was an issue, we addressed by addition of amines externally. Balanced Drying time and film performance. So “Go”

Significant Outcomes / Results-Task-3

Task 3 Design & Development of Two-Component High-Solid NIPU Coating Systems (2K-HS-NIPU)

- Commercial product – CAAPCOAT- CW-4 (CAAP Co Inc.) used as benchmark – fully-evaluated (except rain-erosion test) to develop product specifications. (# 3).
- Brainstorming – Identified “Critical Performance Properties” and designed / revised strategy for 2K-HS-NIPU formulation. (# 3.1, 3.1 & 2.0)
- Formulated and tested various 2K-HS-NIPU coating systems. And evaluated for critical tests – **Drying time, low temp flexibility, adhesion and resistance to liquids / fluids to screen samples.**
- 4 promising samples were tested and evaluated for thermo-mechanical properties and compared with benchmark.

Significant Outcomes / Results-Task-3

Task 3 Design & Development of Two-Component High-Solid NIPU Coating Systems (2K-HS-NIPU)

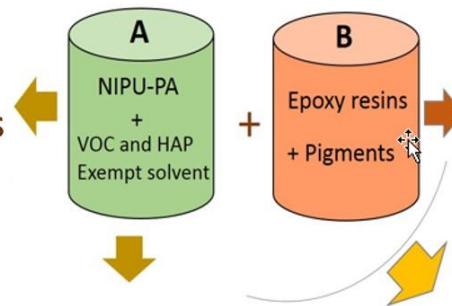
- Various NIPU-PAs tried

- Selection of NIPU-PA based on

- Coating Performance properties
- Viscosity & Compatibility
- Solvent demand
- Reactivity / curing time

- VOC and HAPs exempt solvents used as far as possible

- Viscosity VS drying time
- Compatibility with part-B
- Target %solids > 75



- Commercial Epoxy resins

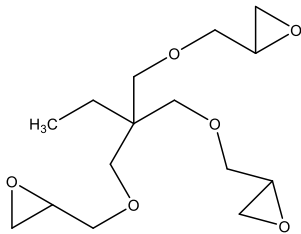
- Aliphatic / Cycloaliphatic
- Custom-made epoxy resins

- Pigments

- Outdoor durability
- Chemical resistance....

Compositions screened based on

- Coating Performance
- VOC and HAPs status
- % NVM
- Cure time / pot-life considerations



Hardener Used

CAPPCOAT C-W4 Benchmark



Representative 2K-HS-NIPU Systems – Film Prop.

Thermo-mechanical properties

Coating System	T _g (°C)	T _d 50% (°C)	Elongation at Break (%)	Tensile Strength (MPa)	Young's Modulus (MPa)
NIPU (mix,IPDA)	45	391	123	1.35	0.97
NIPU (CC2,IPDA)	16	382	195	1.71	0.73
NIPU (CC3,IPDA)	-31	433	164	0.78	0.31
NIPU (CC3,IPDA) + IPDA	-11	425	107	1.25	1.01
Benchmark CAAPCOAT C-W3	-23	401	548	9.42	1.35

- Film properties vary with varying type of NIPU-PA and Hardener
- Mechanical properties significantly lower than benchmark -



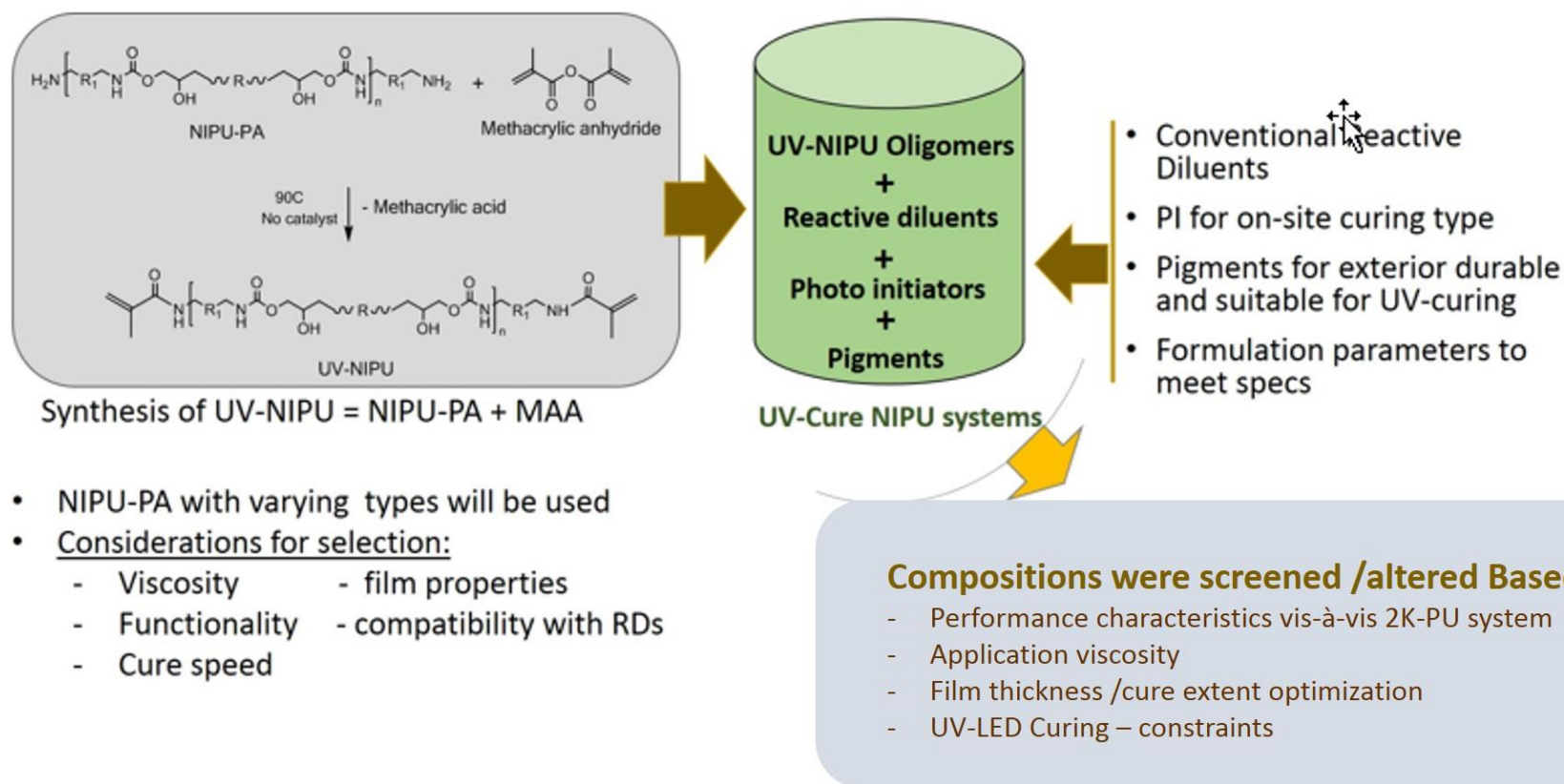
Representative 2K-HS-NIPU Systems – Film Prop.

Coating System	MEK Double Rub (25% loss)	Aromatic Fuel	Lubricating Oil	Hydraulic fluid	Flexibility (1/8" at -56 °C)	Adhesion (2-3 mils thickness)	Water Immersion	Pencil Hardness	Impact resistance		Gloss	
									Direct	Indirect	20°	60°
NIPU (mix,IPDA)	180±5	Pass	Pass	Pass	Fail	5B	Pass	3H	160	140	80	91
NIPU (CC2,IPDA)	155±5	Pass	Pass	Pass	Fail	5B	Pass	2B	160	160	77	88
NIPU (CC3,IPDA)	140±5	Pass	Pass	Pass	Pass	4B	Pass (Adhesion loss)	5B	160	160	27	72
NIPU (CC3,IPDA) + IPDA	150±5	Pass	Pass	Pass	Pass	4B	Pass	HB	160	160	80	90
Benchmark CAAPCOAT C-W4	165±5	Pass	Pass	Pass	Pass	5B	Pass	7H	160	160	28	71

- Film properties vary with varying type of NIPU-PA and Hardener

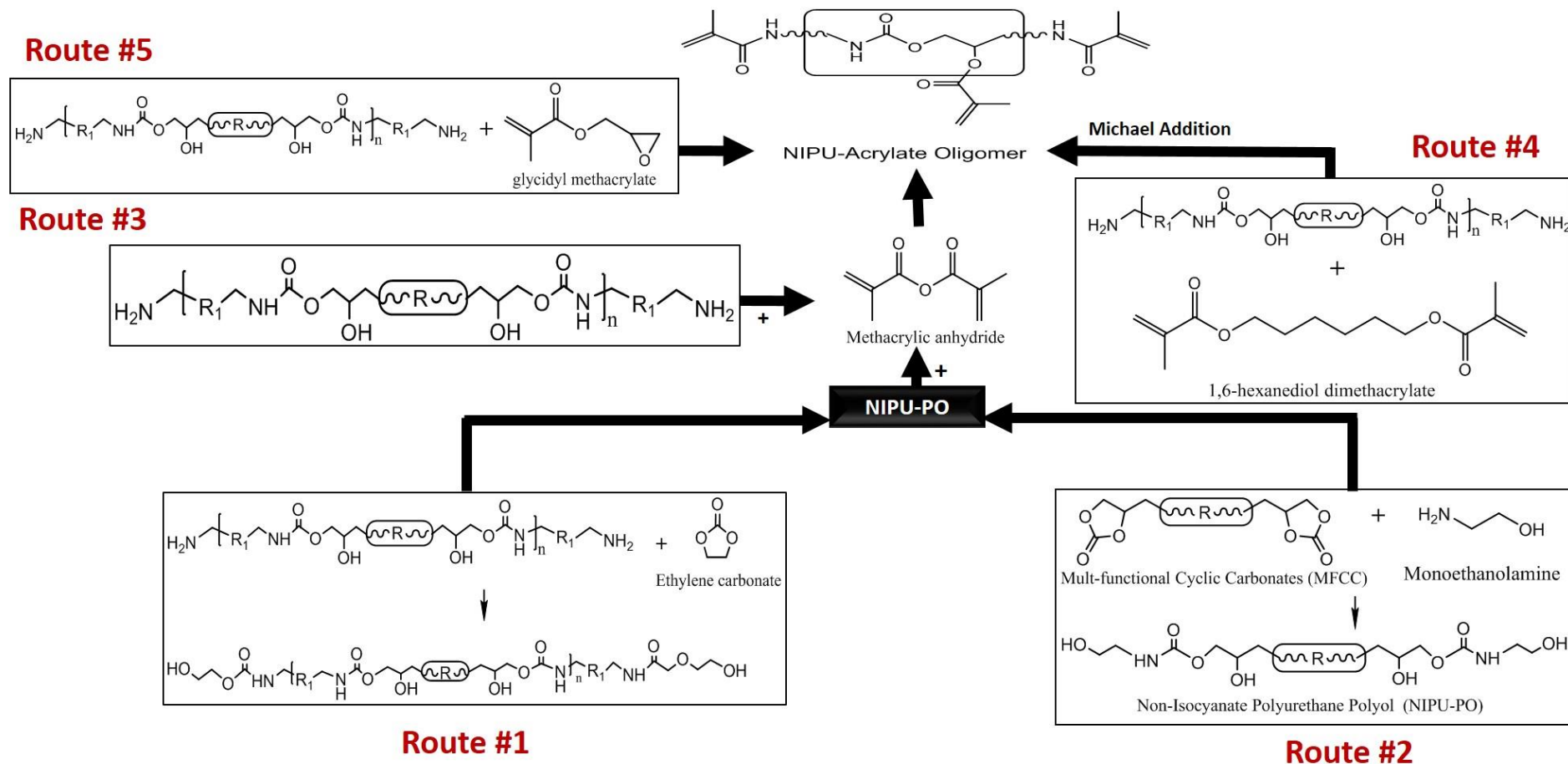
Task 4 Design & Development of UV-Curable NIPU systems (UV-NIPU)

Design Strategy – UV-Curable NIPU Coatings



Significant Outcomes / Results

Explored various synthesis routes for making UV-NIPU Rsins.



Significant Outcomes / Results

Task 4 Design and Development of UV-Curable NIPU Coating Systems (UV-NIPU).

Subtask 4.1

Urethane acrylate		Reactants			Characteristics	
Synthetic route	Name	Corresponding compounds			Reaction time (h)	Acrylate EW (gr)
		1	2	3		
Route #1	UA 1-24-1074	PUPA(24-1074)	EC	MAAH	20	2352.0
	UA 1-24-PACM	PUPA(24-PACM)	EC	MAAH	20	1135.0
Route #2	UA 1-36-EA	CC-36	Ethanol amine	MAAH	15	812.0
Route #3	UA 3-24-IPDA	PUPA(24-IPDA)	MAAH	-	5	923.0
	UA 3-36-IPDA	PUPA(36-IPDA)	MAAH	-	5	1518.0
Route #4	UA 4-24-IPDA	PUPA(24-IPDA)	HDDA	Glycidol	25	1306.0
Route #5	UA 2-24-PACM-GMA	PUPA(24-PACM)	GMA	-	20	1264.0
	UA 2-36-IPDA-GMA	PUPA(36-IPDA)	GMA	-	48	1733.0

- Selected coating compositions were tested for mechanical properties and SAE standard tests

Coating Composition				Testing				
System	UA Oligomer	ODA Wt%	HDDA Wt%	Low Temperature Flexibility	Water Immersion test	Resistance to Hydraulic Fluid	Resistance to Fuel B	Resistance to Lubricating oil
# 1	UA CC3-IPDA	10	10	Pass	Pass	Pass	Delamination	Delamination
# 2	UA CC3-IPDA + UA CC2-IPDA (1:1 eq.)	0	20	Pass	Pass	Pass	Delamination	Delamination

- 2 compositions from 27 were selected for pigmented coatings
- 2 wt.% of Irgacure 184/819 (80:20 wt%) plus 0.6% ITX were used as the photo initiator package. All Coatings were applied with 10 mil DFT using a layer-by-layer application method and were UV-cured for 3 passes using a Fusion UV system.

Significant deficiency in mechanical properties compared to reference sample



Even after modifying with using more flexible NIPU + CNT + Siloxane

Evaluation					
UVNIPU system	Tg	Tensile strength (MPa)	Elongation % @ break	Modulus (MPa)	T50% Decomposition
1	N/A	1.28	42	7	441
2	14.8	2.07	63	24	433
Ref.	-23	9.42	548	1.35	401

Major Go/No-Go decision points

- **# 2 At the end of Task 4 . Suitability of formulation 2K-HS and UV-cure coatings , and their primary properties for targeted coating system**

- **Feasibility of formulation, application, curing of 2K-HS coatings**

- Prepare prototype 2K-HS coatings and check
- Potential issues in VOC, viscosity, pigmentation need to be acceptable.
- Identified primary film properties must be met . Extent of curing in Rain-erosion coatings.

- **Feasibility of formulation, application, curing of UV-Cure coatings**

- Prepare prototype UV-Cure coatings and check
- Potential issues in viscosity, compatibility with reactive diluents, pigmentation need to be acceptable.
- Required film thickness for rain erosion coatings must be possible (challenging in UV formulation)
- Check suitability of initiator package Identified primary film properties must be met .

- **Post-formulation identification of sustainability profile**

- VOC content (if any), Possibility of making polymers or oligomers with varying morphology
- Use of RDs and their impact on toxicity / environmental profile.
- Suitable for multiple-layer applications?



2K-HS-PU



UV-NIPU

Met most criteria. High viscosity of NIPU-acrylate is an issue. Required us to use special monofunctional RDs. UV-cure coatings could not meet the flexibility / tensile strength balance so “Go” decision for 2K-NIPU and No-go for UV-cure system for subsequent development work.

Results – Task-5

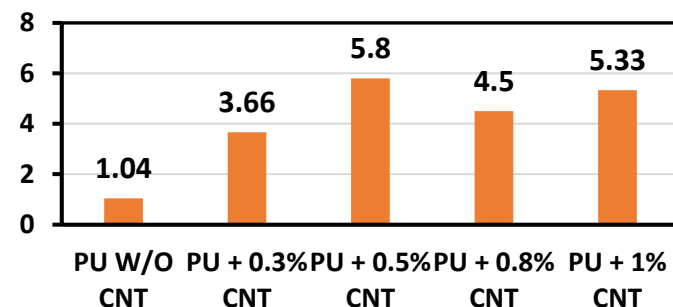
Task-5 Advanced Testing of selected 2K-HS-NIPU Coatings

- Modifications to 2K-NIPU systems with Carbon nano-tubes (CNT) was evaluated per IPR meeting action.
- Two best 2K-NIPU coatings that passed all preliminary criteria and tests were selected for advanced testing
 - ◆ Exterior durability tests (QUV) –per ASTM D4587 Cycle 2
 - Compared with conventional 2K-PU as reference
 - Test run for ~1000 hrs (CRC Test panels)
 - Appearance, Gloss, and Chalking tendency was evaluated
 - ◆ Rain erosion resistance test
 - Conducted at WPAFB Lab (U of Dayton, OH)

Decision on CNT level to use in NIPU formula

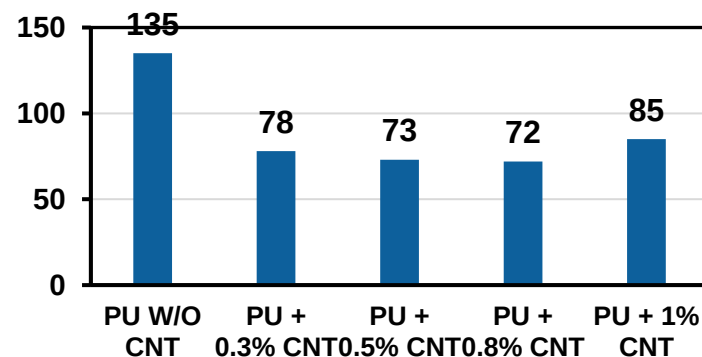
Coating System	Surface Resistivity Ohm/Sq.
PUPA (mix-IPDA-1.7) + 1:1 IPDA	3.9 E + 10
PUPA (mix-IPDA-1.7) + 1:1.25 IPDA	4 E + 10
PUPA (mix-IPDA-1.7) + 1:1.5 IPDA	5.1 E + 10
PUPA (mix-IPDA-1.7) + 1:2 IPDA	6.5 E + 10

Tensile Strength (MPa)



Coating System	Surface Resistivity Ohm/Sq.
Standard PU	2.2 E + 12
PU + 0.3% CNT	8.5 E + 5
PU + 0.5% CNT	1.8 E + 5
PU + 0.8% CNT	9.9 E + 4
PU + 1% CNT	N/A

Elongation %



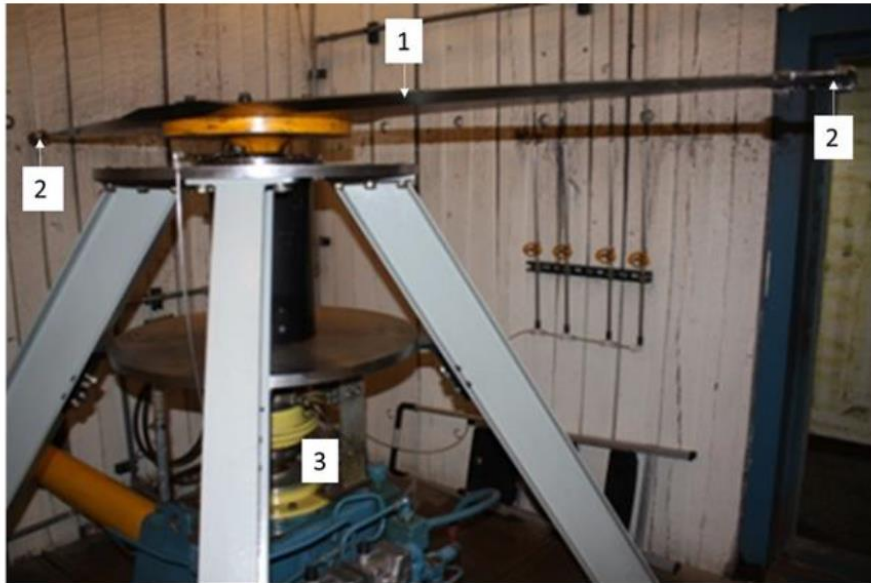
Required Surface Resistivity : No less than 0.5 E +6 no more than 1.5 E+7 ohm per square

Results

Coatings	Evaluation after Q-UV Accelerated weathering test			
	Characteristics	480 hrs.	816 hrs.	1152 hrs.
Conventional PU	Appearance	No chalking	No chalking	No chalking
	Gloss (20°/60°)	73/86	73/85	71 /81
	Δb	0.59	0.70	1.10
Coating #1	Appearance	No chalking	No chalking	No chalking
	Gloss (20°/60°)	69/83	58/82	48/79
	Δb	1.20	1.53	1.79
Coating #2	Appearance	No chalking	No chalking	No chalking
	Gloss (20°/60°)	81/89	78/89	74/88
	Δb	1.09	1.20	1.26
Coating #3	Appearance	No chalking	No chalking	No chalking
	Gloss (20°/60°)	72/83	70/81	55/76
	Δb	1.75	1.95	2.20
Coating #4	Appearance	No chalking	No chalking	No chalking
	Gloss (20°/60°)	68/83	64/82	45/72
	Δb	0.95	1.02	1.62
Coating #5	Appearance	No chalking	No chalking	No chalking
	Gloss (20°/60°)	54/74	36/53	20/34
	Δb	1.41	1.48	2.10

Rain Erosion Resistance Test

WPAFB / U of Dayton, OH



1. Double-Arm Blade 2. Mated Specimen Location 3. Vertical Drive Gear Box



Figure 2: Curved Manifold Quadrants to Simulate Rainfall



Table 1: Eastern Michigan University Test Plan

Number of Specimens	8
Geometry	Airfoil
Speed (s)	440 mph
Impingement Angle	90°
Composition	Aeroglaze 4977 wash primer, non-isocyanate polyurethane topcoat
Run-time	Maximum 60 minutes

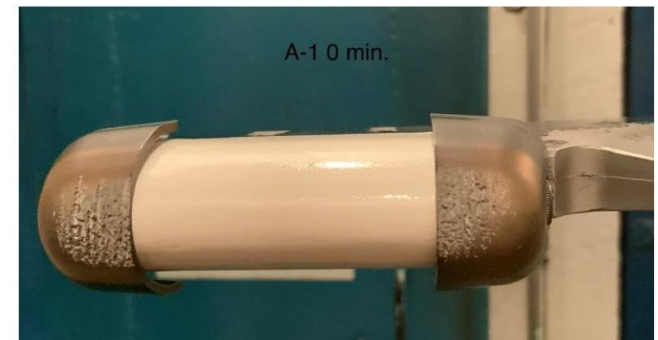


Figure 3: Test Specimen Fixed to Blade Tip at 90° Impact Angle

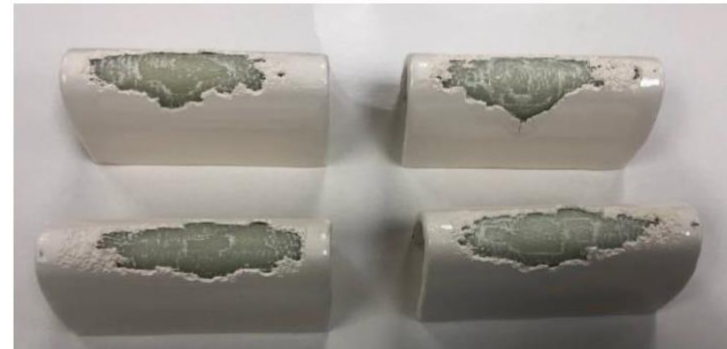
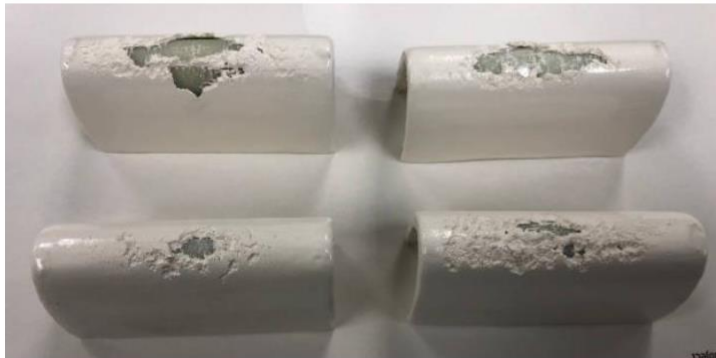
Rain Erosion Test samples

CCmix-PACM-1.2/EC2

CCAr1001-PACM-1.2/EC2



Before rain erosion test



After rain erosion test

Figure 2.16. AirFoil sample appearance coated with either CCmix-PACM or CCAr1001-PACM before and after rain erosion

Table 2: Summary of Rain Erosion Results

Sample ID	Speed (mph)	Exposure (min)	Impact Angle (90°)	Results
1-1	440	11	Airfoil	Erosion Failure
1-2	440	11	Airfoil	Erosion Failure
2-1	440	9	Airfoil	Erosion Failure
2-2	440	9	Airfoil	Erosion Failure
1-3	440	10	Airfoil	Erosion Failure
2-3	440	10	Airfoil	Erosion Failure
1-4	440	9	Airfoil	Erosion Failure
2-4	440	9	Airfoil	Erosion Failure



Figure 4: Specimen ID 1-2 after Rain Exposure at 440 MPH

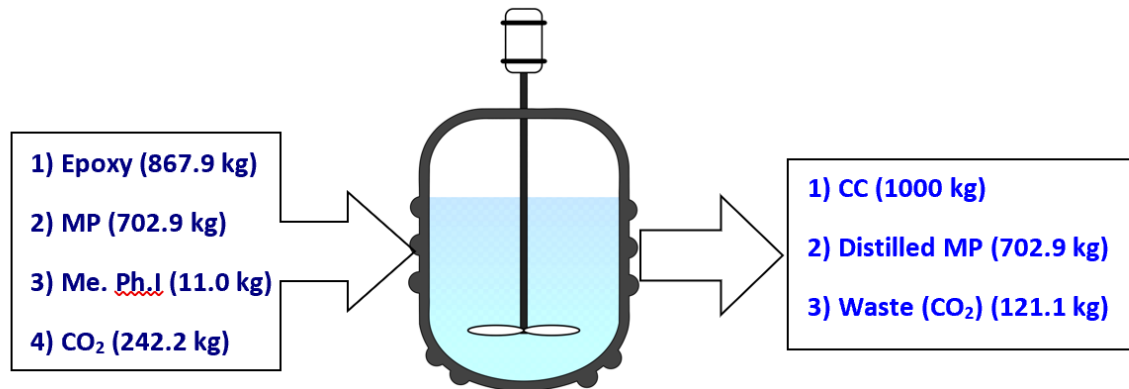
1 min. center leading edge coating penetration / 3 min. center leading edge multiple coating penetration sites / 10 min. center leading edge additional coating penetration, substrate exposed / 11 min. inboard, outboard leading edge additional (add'l) coating penetration, add'l substrate exposed / erosion failure

Life-Cycle Inventory Data

Gate-to-Gate

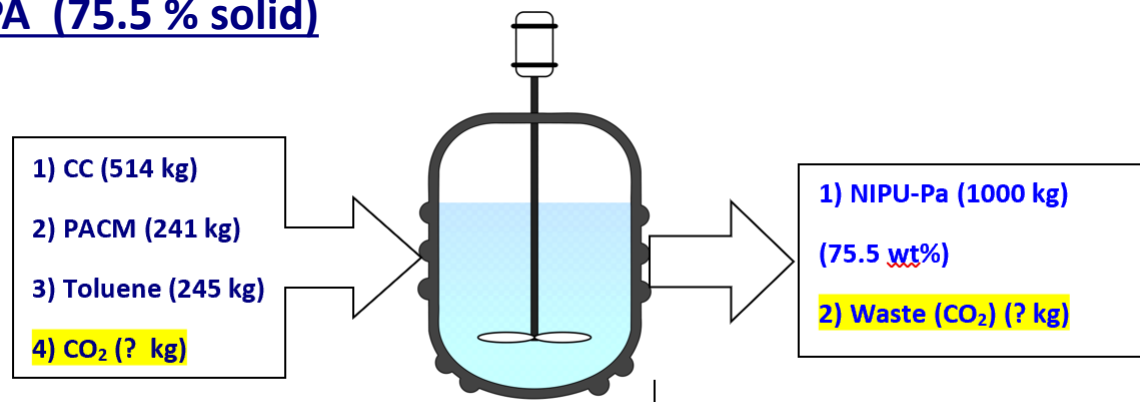
Basis: 1000 kg of NIPU-PA (75.5 % solid)

STEP 1: Cyclic carbonation (multi-functional cyclic carbonate, CC)



First Step: 1000 kg Cyclic Carbonated product

STEP 2: NIPU-PA (75.5 % solid)



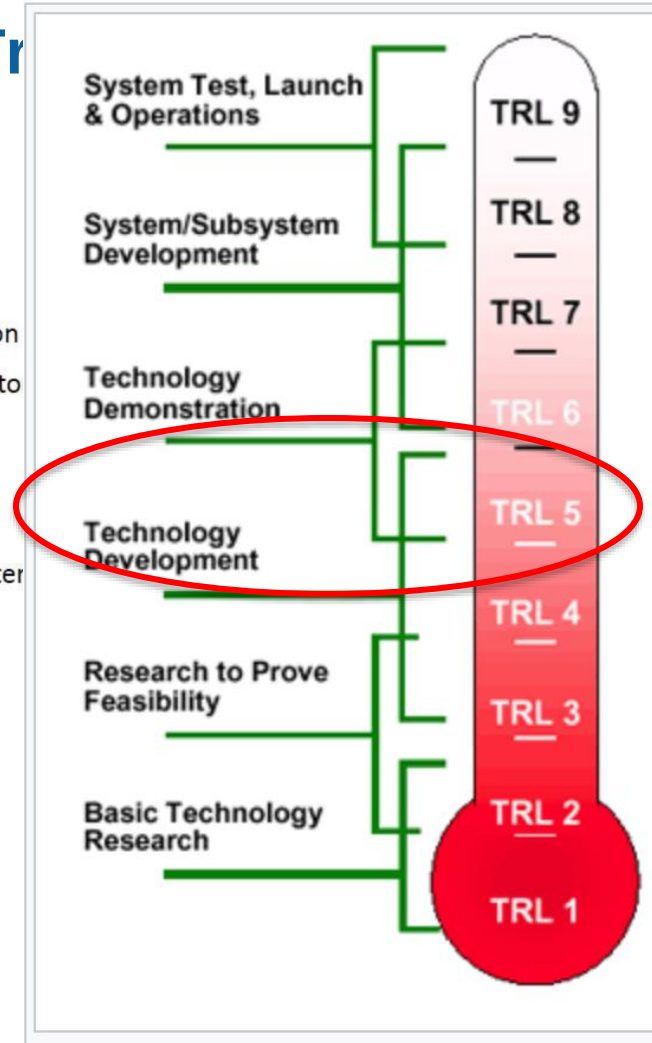
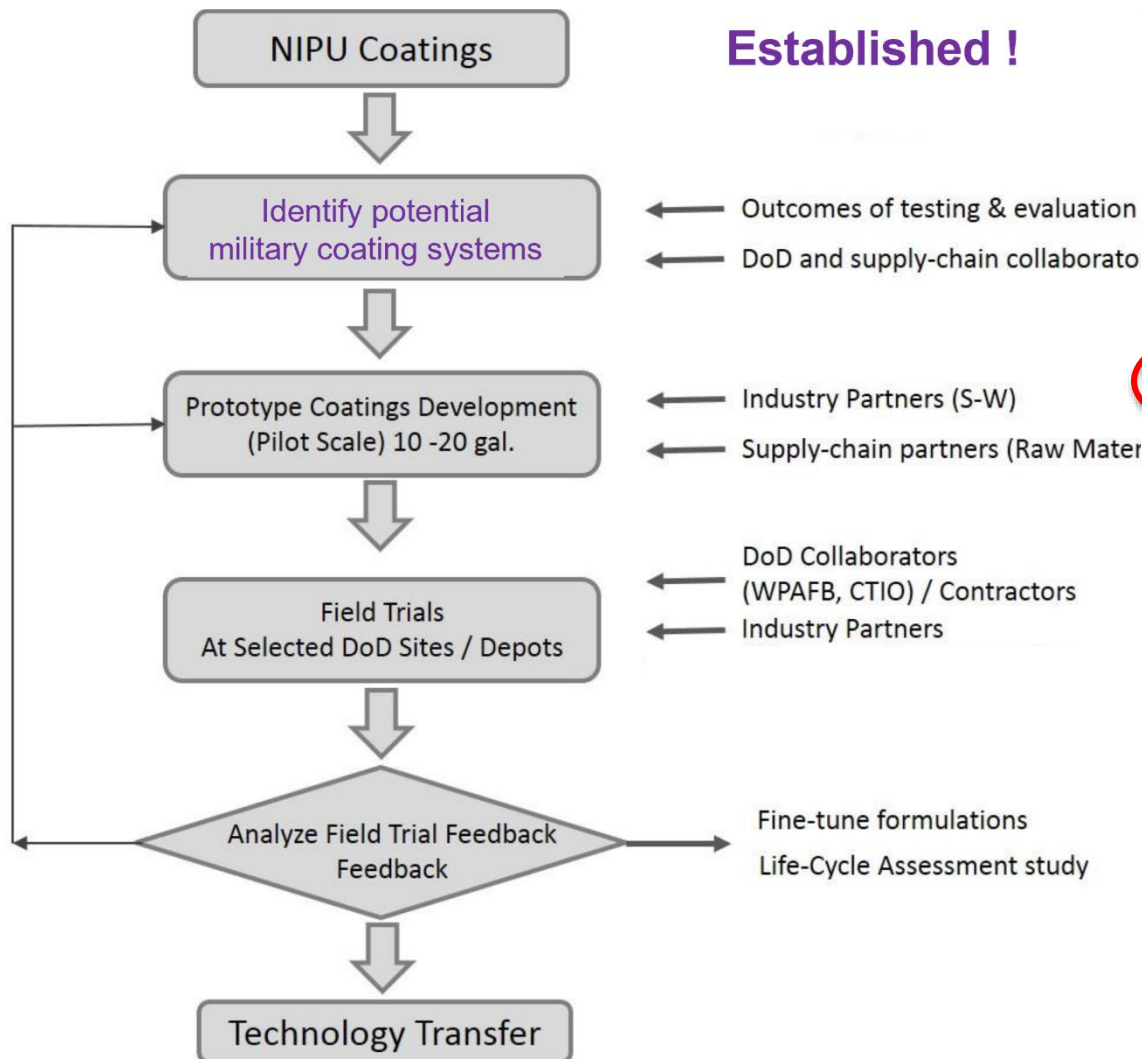
Second Step: 1000 kg NIPUPa product

Environmental Profile –NIPU-PA

- No Isocyanates or other toxic compounds used in manufacturing of NIPU-PA
- No by-product formed in making NIPU-PA. Reaction can be carried out in a single vessel under mild conditions
- VOC contents of final NIPU coating = 1.16-1.50 lb/Gallon
Conventional Military protective coatings = 6.67 lb/Gallon
- HAPS – NIPU Coatings = 0.8 – 1.00 lb/Gallon
- Total energy input for 1000 kg of NIPU-PA = 763×10^3 KJ
(Energy balance calculations)

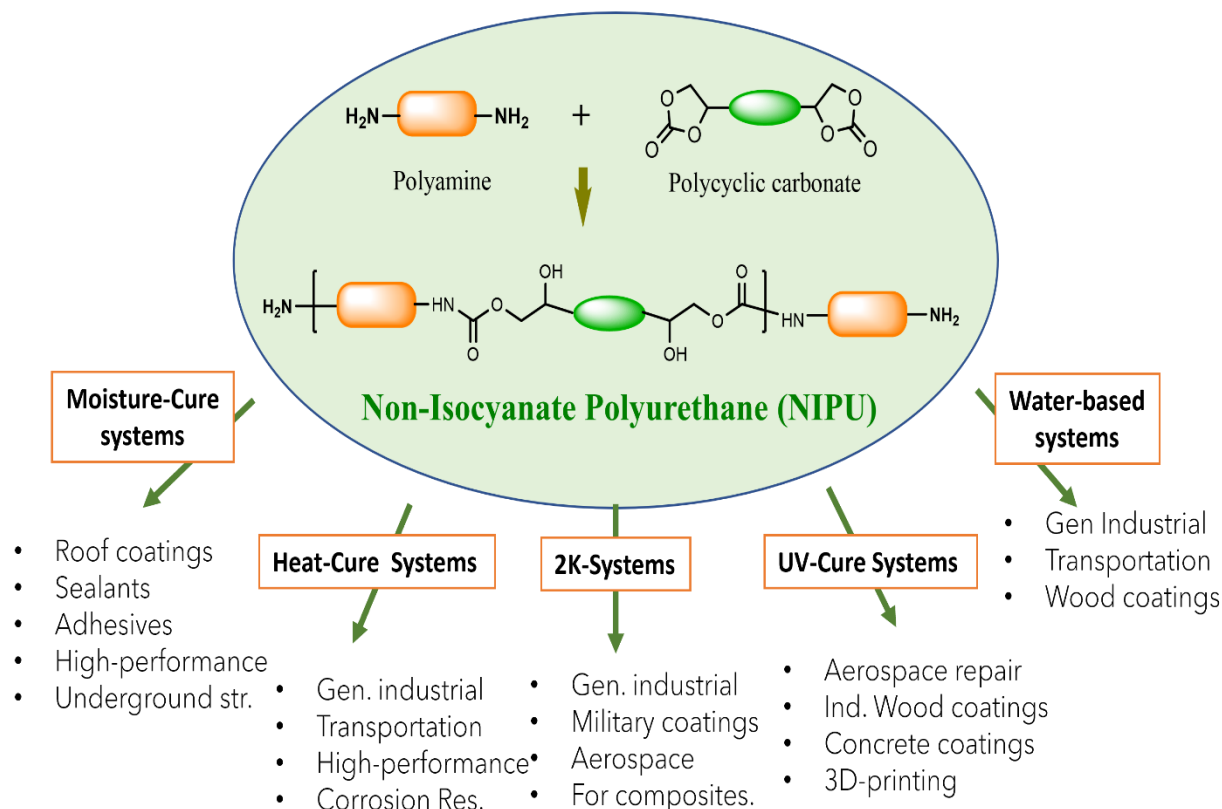
Technology Transfer

NIPU Coating Platform: Technology. Tr



Technology Transfer

Non-Isocyanate Polyurethane Platform for Coatings



Key Attributes

- ☐ No Isocyanates, HAPs, VOCs
- ☐ Single-step low energy process using conventional manufacturing facilities
- ☐ NIPU-platform can be utilized to suit contemporary and emerging coating and 3D-printing technologies.
- ☐ Product performance comparable to conventional PU.
- ☐ Cost-competitive
- ☐ Readiness level – TRL-5-7

Key Points

- NIPU Coating platform has tremendous potential for military and industrial coatings BUT IS NOT FOUND SUITABLE FOR RAIN EROSION COATINGS.

◆ Rain erosion coating specifications are very unique and do not represent general military coatings.

- Very high elongation (500+ %)
- High tensile strength and modulus (6.5 mPa)
- Flexibility at low T (-56 deg C , 1/8")
- Very low VOC and HAPs

Derived from CAPCO specs

Requires thermoplastic binders not suitable on NIPU platform.

CAPCO uses very high VOC and isocyanates.

- **Most military coatings or industrial coatings do not have these stringent requirements. So NIPU Coatings for many other military coatings or Industrial / protective coatings are possible and should be pursued on this platform to realize potential of NIPU technology.**

Key Takeaway Points

- A platform of building blocks that allows formulation of polyurethane coatings without use of any toxic isocyanates is available. (NIPU Technology)
- The NIPU building blocks (coating materials /intermediates) can be manufactured using environmentally safe and energy efficient process in conventional resin manufacturing facilities without additional capital investment.
- Sustainable and high-performance NIPU coatings based on advanced technologies such as high-solids, UV-cure, Moisture-cure, thermal-cure are possible and have been demonstrated. It is possible to develop water-based NIPU on this platform.
- Heat-curable industrial coatings and moisture-curable (ambient T) coatings technologies for a variety of industrial /military end-use applications are available at readiness level -TLV of ~ 6-7.
- This technology is not suitable for coatings requiring very high % elongation (>300%), high tensile strength (>3.5 mPa).. Such as for Rain Erosion Resistant coating specification.

NIPU Coatings

BACKUP SLIDES

Publications

- **List of Journal Paper Publications:**

1. Hamid Asemani and Vijay Mannari, Dual-curable coatings obtained from multi-functional non-isocyanate polyurethane oligomers, *Journal of Coatings Technology and Research*, 2022 (Accepted)
2. Hamidreza Asemani, and Vijay Mannari, Ambient temperature and UV-cured hybrid coatings from acetoacetylated non-isocyanate polyurethanes, *Journal of Coatings Technology Research*, 2021.
3. F. Zareanshahrakia, H.R. Asemania, J. Skuzab, V. Mannari, synthesis of non-isocyanate polyurethanes and their application in radiation-curable aerospace coatings, *Progress in Organic Coatings*, 138, 2020, 105394
4. *H.R.Asemani, V.Mannari, Synthesis and evaluation of non-isocyanate polyurethane polyols for heat-cured thermoset coatings*, *Progress in Organic Coatings*, 131, 247-258, 2019.
5. Asemani Hamidreza, Forough Zareanshahraki, and Vijay Mannari, *Design of hybrid non-isocyanate polyurethane coatings for advanced ambient temperature curing applications*, *J. Appl. Polym. Sci.* 2018, DOI: 10.1002/APP.47266.

Oral Presentations

Conference Presentations and Conferences and Symposia

1. American Coatings Conference, April 2018,
Advances in Non-Isocyanate Polyurethane Coatings platform
Vijay Mannari, Forough Zareanshahraki, Hamidreza Asemani
2. Coatings Trends and Technologies Conference, September 2018.
Non-Isocyanate Polyurethane Technology For Sustainable and High-Performance Coatings
Vijay Mannari, Forough Zareanshahraki, Hamidreza Asemani

Poster Presentations

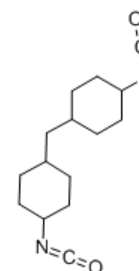
List of Presentations to conferences and Symposiums

1. American Coatings Conference, April 2018.
Radiation-Curable Non-Isocyanate Polyurethane Green Coatings: Synthesis, Characterization, and properties
Forough Zareanshahraki, Hamidreza Asemani, and Vijay Mannari.
2. American Coatings Conference, April 2018.
Novel Two-Component Non-Isocyanate Polyurethanes for Sustainable Coatings
Hamidreza Asemani, Forough Zarean, and Vijay Mannari
3. SERDP Symposium 2018
Non-isocyanate Polyurethanes: A Green and Sustainable Approach towards Two-Component High Performance Coatings
Hamidreza Asemani, Forough Zareanshahraki, and Vijay Mannari
4. SERDP Symposium 2017
Non-isocyanate Polyurethanes: A Green and Sustainable Approach towards Two-Component High Performance Coatings
Hamidreza Asemani, Forough Zareanshahraki, and Vijay Mannari

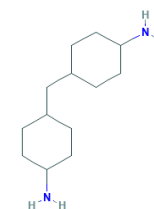
Benchmark Product

- We identified with the help of ARL, a benchmark product CAAPCO Cw-4, and evaluated. 2K-PU system

Part A	NCO functional polyester
Solvents	MIBK (12-14%) Xylenes (36-42%) Ethylbenzene (7-12%)
Solid content	45.75%
Free Isocyanate	Bis(4cyclohexylisocyanate) 0.5%
NCO% (total mixture)	1.27
Pigment wt.% (TGA)	17.9% of solids 8.1 % total
Pigment wt.% (Muffle furnace)	16.2% of solids 7.4% total
Approx. PVC	6%
Total NCO eq. wt.	3308
Resin solid NCO eq. wt. (resin=37.41% of total)	1237
Part B	Curing agent Aliphatic amine
Solvent	MIBK (45-90%)
Solid content	54→40→10 (Amine seems to be volatile)
Amine Value (total mixture)	338
Amine eq. Weight	165
Mixing ratio (A/B)	100/4.5
NCO/Amine eq. ratio	1.12
Amine value (amine solid)	??

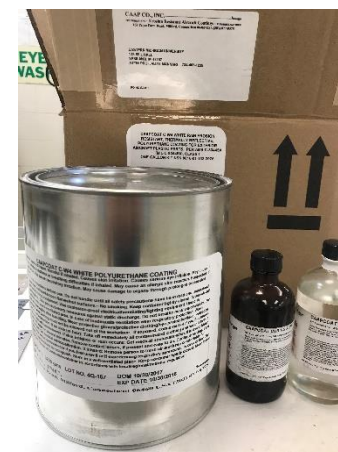


Iso-crosslinker



Present in Base

As per, product datasheet

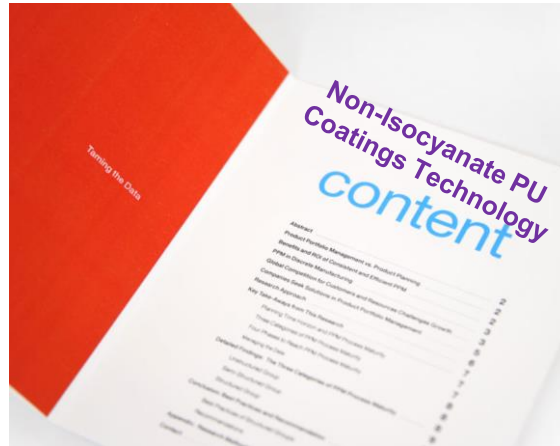


Benchmark analysis

CAAPCO Cw-4 : Film Properties

Pot-life	4 h
Curing time (tack-free)	2-3 h
Solid content	45 wt. %
MEK Double Rubs	165±5
Flexibility (1/8" at -56 °C)	Pass
Adhesion	5B
Water resistance	Pass
Pencil Hardness	7H
Impact Resistance	Direct: >160 (lb. in) Indirect: >160 (lb. in)
T _g	-23 °C
T _d (50%)	401 °C
Elongation at Break	548%
Tensile Strength	9.42 MPa
Young's modulus	1.35 MPa

Technology Transfer modes /tools



- Training workshops, live or via webinar
- Presentations at key conferences
- Journal Articles, posters at symposiums and conferences
- Web-based tools <http://t2.serdp-estcp.org/>
- White Papers / Tech. fact sheets circulation in DoD community

WP-2602: Non-Isocyanate Polyurethane Platform for Sustainable and Advanced Rain-Erosion Resistant Coatings

Performers: Prof. Vijay Mannari & co-performers, Eastern Michigan University

Technology Focus

- *Development of Isocyanate-free PU coating platform based on Cyclo-carbonate + Amine chemistry by customizing building blocks for high-solids and UV-cure systems with significantly reduced environmental impact for military coatings..*



Research Objectives

- *Development of Non-isocyanate PU coatings that complies with or exceeds the requirements of performance and environmental benefits for rain erosion-resistant military coatings.*

Project Progress and Results

- *A platform for non-isocyanate PU coating building block has been established. This can be leveraged to develop NIPU coatings based on various technologies (HS, UV-cure, moisture-cure, heat-cure). While specific rain-erosion coatings were not successful, NIPU coatings based on this technology can meet many military coating specifications such as transportation coatings for ground vehicles, ground installations, and for protecting composite substrates while keeping low environmental impact.*

Technology Transition

- *Technology transition will require development of prototype coatings for specific end-use applications prepared at the pilot scale and their field trials. A gate-to-gate Life-Cycle Assessment is required to demonstrate environmental benefits of these new generation coatings. Various DoD divisions needs to be contacted to harness the potential of this technology.*