Nano-Engineered Additives for Active Coatings

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.

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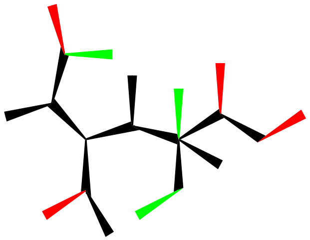
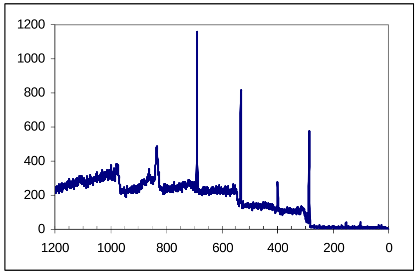


Underlying Concepts

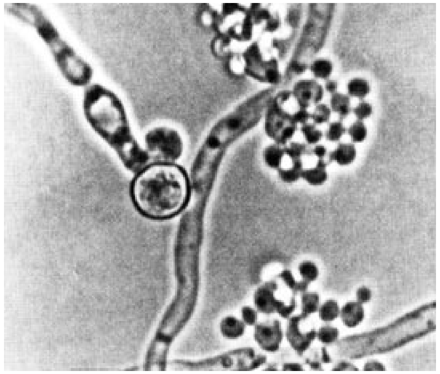


Model Systems

Implementation

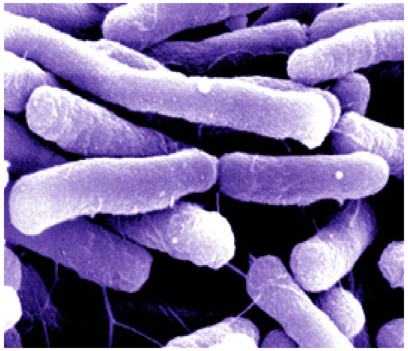
Changing threats dictate new approaches to asset protection

vs.



C. albicans

Staph

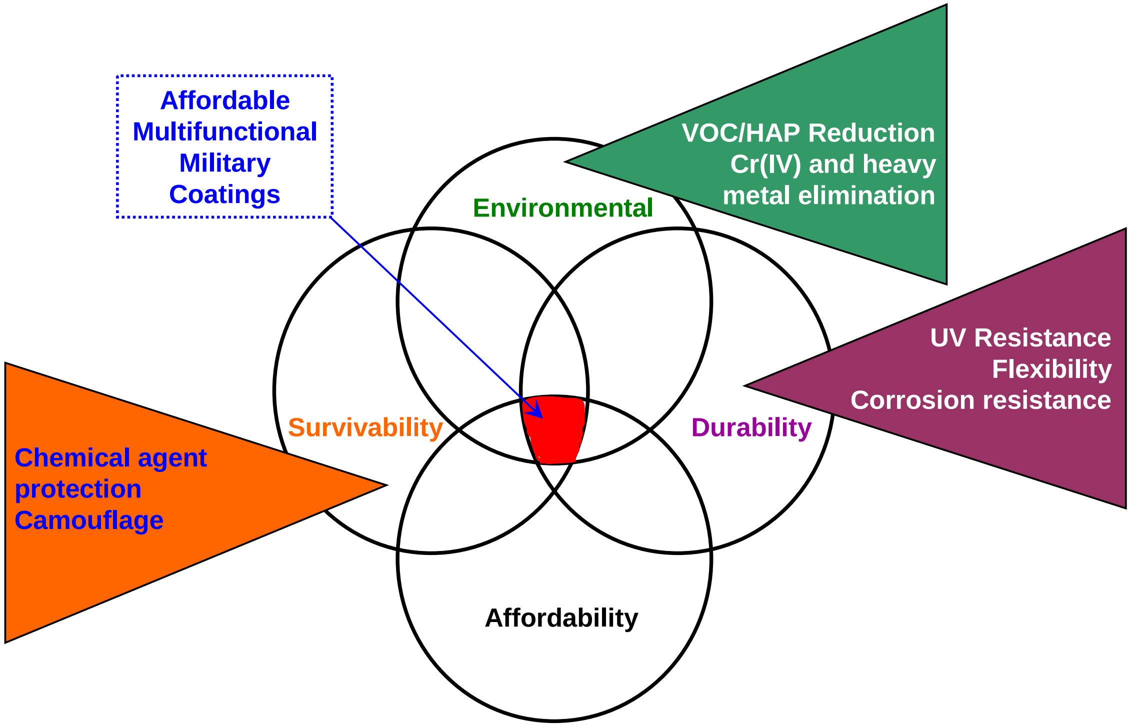


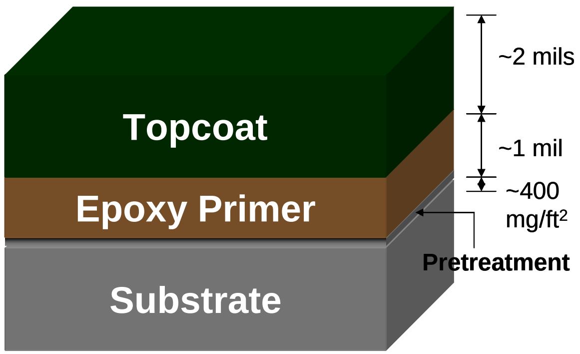
E. coli

Reduce Asset Susceptibility to Non-Conventional Attacks

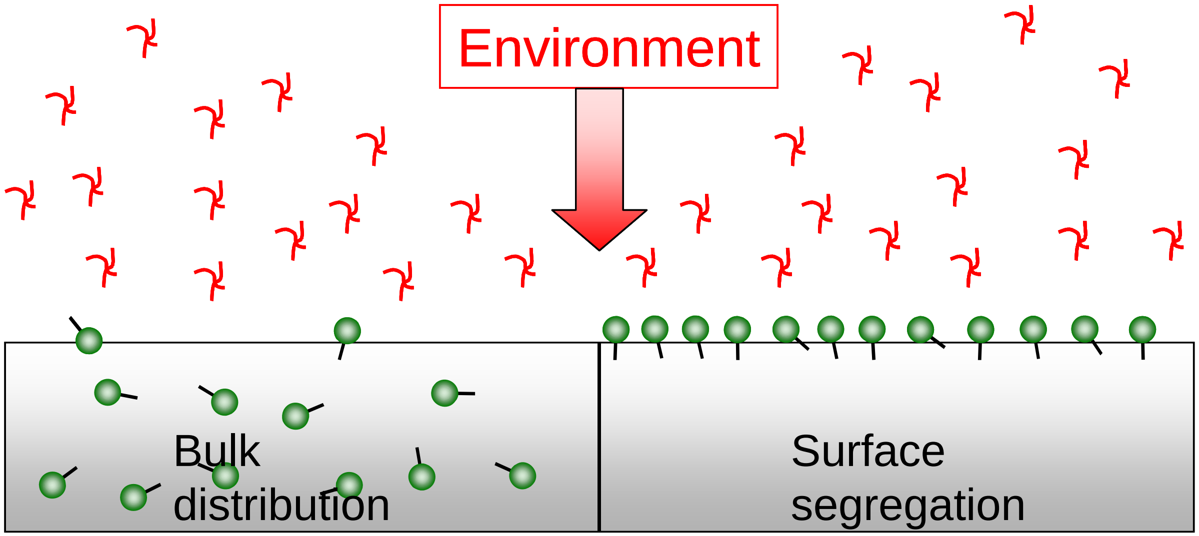
Critical performance characteristics

- Topcoats are complex multirole formulated systems
  - Camouflage
  - Corrosion protection
  - Low sorption
  - Materials limitations
  - Cost effective
- Approaches for surface modification
  - Plasma treatment
  - Self-assembly
  - Additive incorporation





Self-Directing Materials

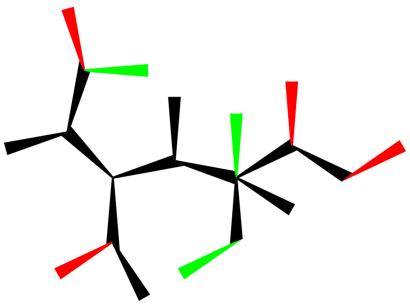


Asymmetric response desired to maximize additive impact

Self-segregating materials address several issues

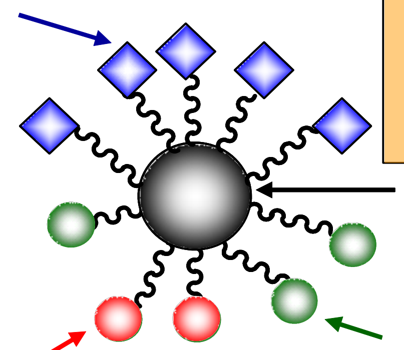
- **Decreased additive requirement**
- **Minimizes mass transport issues**
- **Minimizes diffusion limitations**
- **Minimal impact on base coating**

Hyperbranched polymers provide readily available scaffolds for the preparation of polymer additives



“Buoy” groups
-Fluorinated Chains
-Aliphatic Chains

“Delivered” groups
-Ionic species
-Fluorescent tags
-Bioreactive sites
-Catalysts



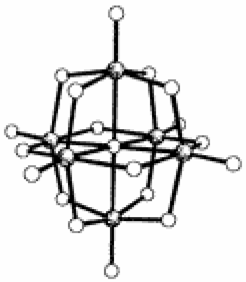
Polymer scaffold
-Copolymers
-Hyperbranched polymers or Dendrimers

“Anchor” groups for adhesion

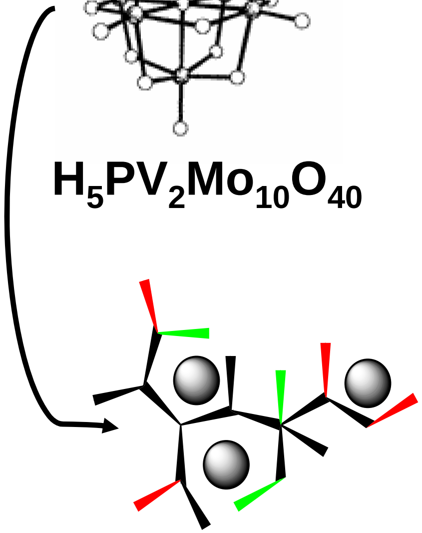
Desired characteristics

- **Low chain entanglements**
- **High solubility**
- **Large number of reactive sites**

Surface transport was demonstrated for polyoxometalates, mild oxidation catalysts



$H_5PV_2Mo_{10}O_{40}$

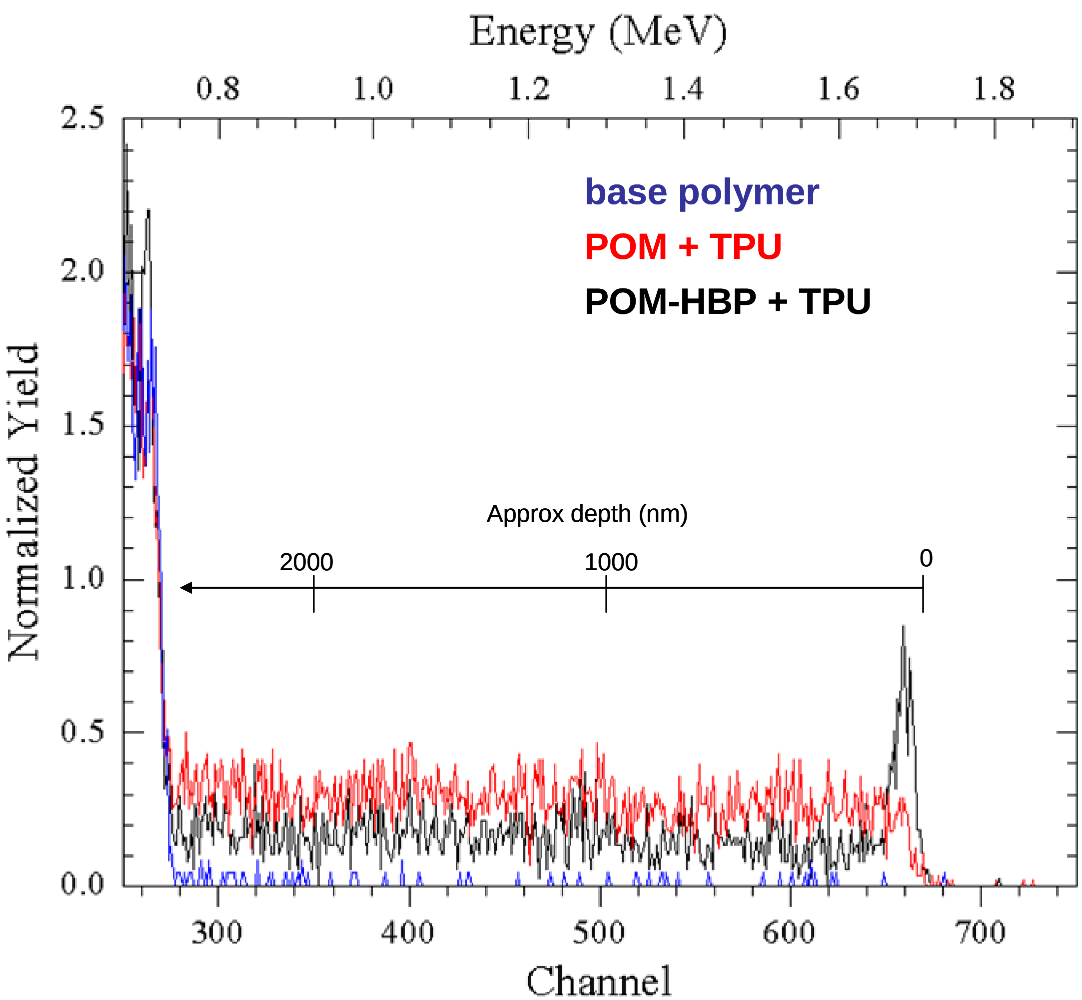


Soluble complex when protonated

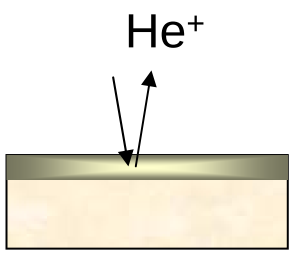
Polymer	90° TOA- Atomic Comp.				30° TOA- Atomic Comp.			
	C	F	Mo	O	C	F	Mo	O
POM + TPU	79.32	-	-	18.09	82.75	-	-	15.62
TPU + HBP 6-H$^+$	64.28	13.52	-	9.59	68.23	12.90	-	7.84
I	61.61	10.31	2.90	24.02	60.54	17.48	2.34	18.33
II	61.65	14.51	2.31	19.11	60.25	22.18	1.99	13.30
III	62.11	16.56	1.73	16.26	60.14	23.56	1.54	11.82
IV	63.33	11.39	2.30	21.70	62.30	17.45	2.14	16.79
V	63.80	12.03	2.65	18.71	63.59	17.80	2.21	13.55
VI	63.61	13.49	2.10	19.09	58.66	24.10	1.94	13.68

- HBP-POM complex demonstrates migration, ~ 10 fold increase in surface concentration

Visualization of depth profile was accomplished with RBS, confirming enhancement



RBS results correlate with XPS results, show ~11 fold increase in surface concentration of metal catalyst sites

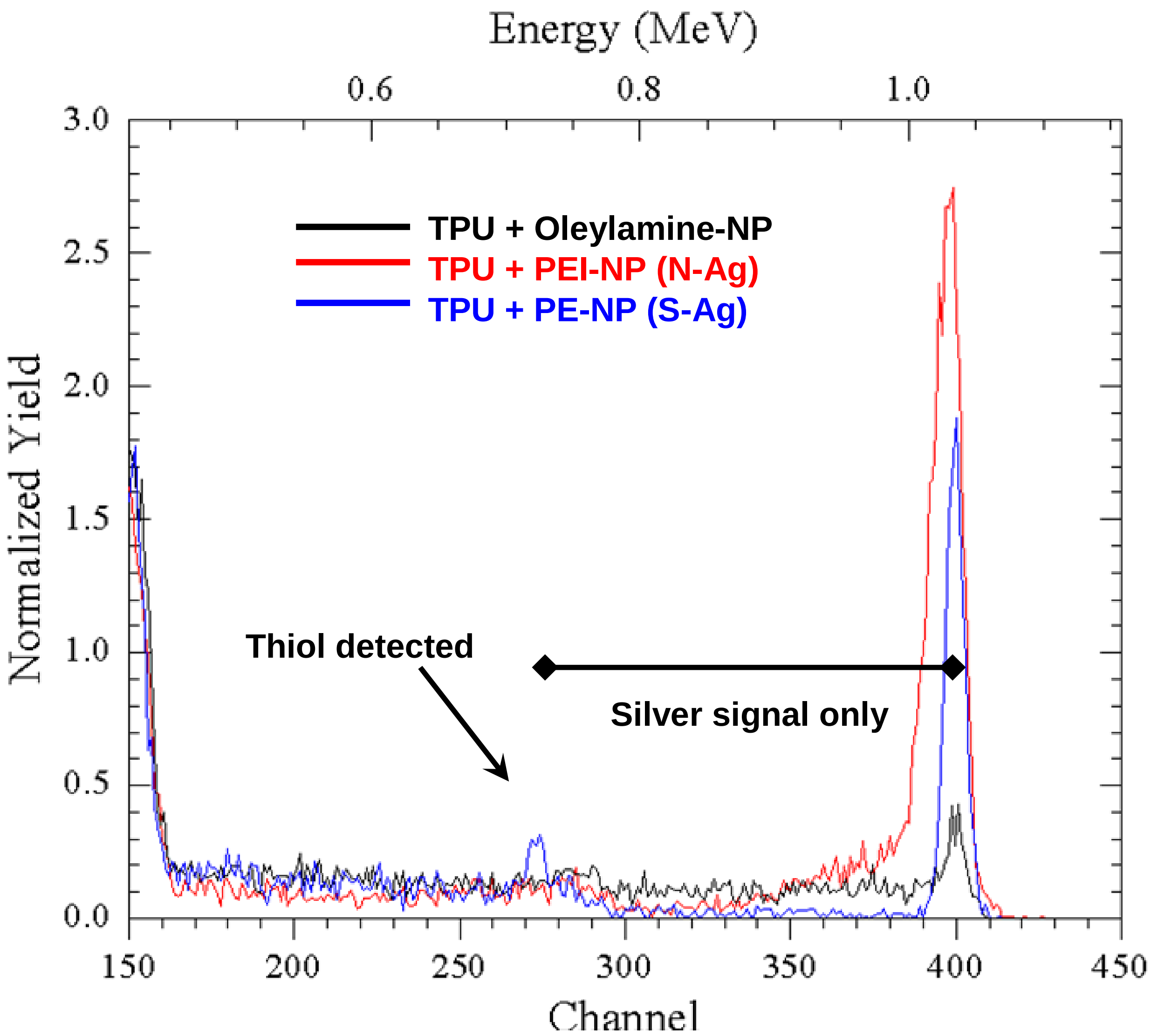


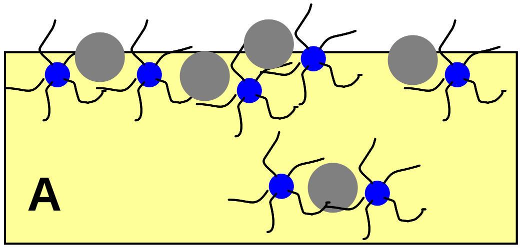
Alternate Surface Materials

- Silver is good candidate
  - Forms bonds readily; S-Ag or N-Ag good covalent, ligand interactions
  - Known antimicrobial activity
  - Available as nanoparticle (NP), ion, or inorganic-supported particles
- Heavy element allows use of XPS or RBS

YahooNews, 08/19/2005

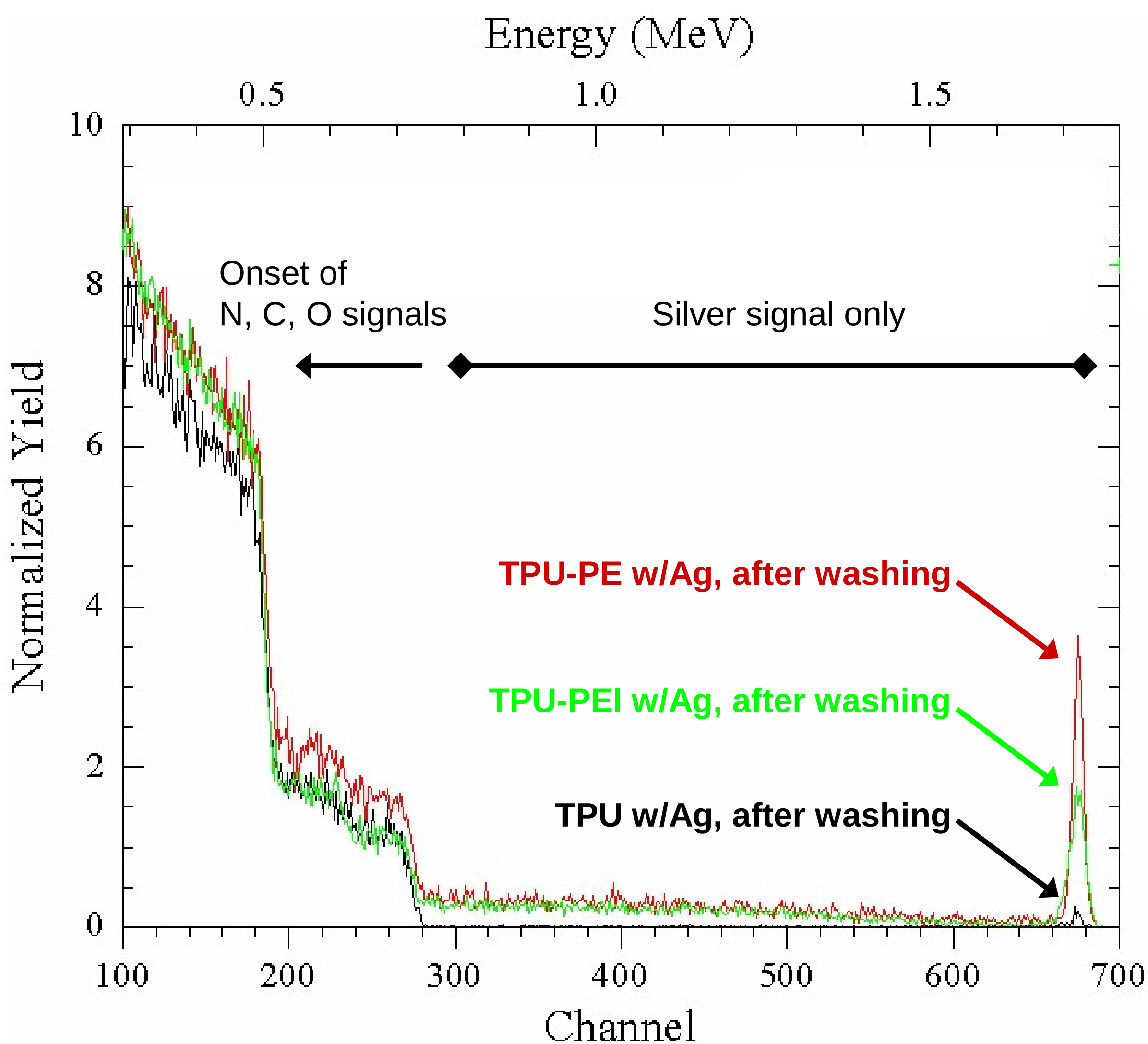
Sharp band of Ag enrichment indicates efficient surface migration

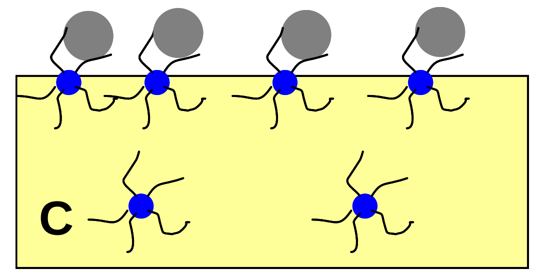




- Limited Oleylamine transport
- PEI-HBP-AgNP yields thick
- layer, tapering conc. profile; ca. 2% Ag by RBS
- PE-HBP-AgNP yields sharp layer, ~ 2nm in depth, large depletion zone, RBS indicates ca 10% Ag in thin slice
- Ag layer thinner than resolution of instrument

Ag uptake at surface scales with strength of Ag-X bond formed, delivery by Ag-protein complex

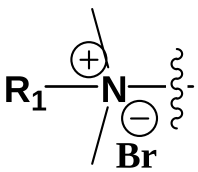


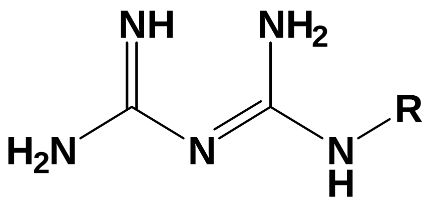


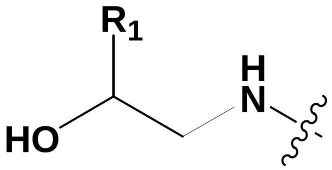
- Rinsing removes 99+% of Ag
- Ag-protein complex delivery
- Note intensity of RBS signal correlates to bond strength: Ag-S >Ag-N > physisorption
- Trend reverses in hexane delivery solvent

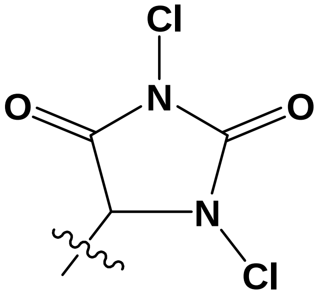
Expanded palette of functional groups/active sites are being investigated, shortfall from commercial sources

- **AgNP are a nice model system, but cost and long-term stability remain question marks**
- **Commercial options for antimicrobials and chemical decon groups are low probability solutions**
  - **Silver zeolites– leaching, sorption**
  - **Small molecule biocides– leaching, porosity**
  - **M_xO_y nanoparticles for chemical decon (Al, Mg, Zn, Cu)– deactivation**
  - **TiO_2 particles– long term coating stability, light driven**
- **ARL developing library of mixed end-group additives with specific functionality**
  - **Quaternary ammonium salts (in conjunction with TSI, Inc.)**
  - **Biguanides (in conjunction with TSI, Inc.)**
  - **Alkanolamines**
  - **N-halamines, hydantoins**









Antimicrobial activity in TPU was assayed using an array of techniques to show efficacy

- **ASTM E2180 test for hydrophobic surfaces challenged with *E. coli*, *S. aureus*, *C. albicans, P. aeruginosa***
- **AATCC Method 100, adapted for hydrophobic surfaces challenged with *S. aureus*, *K. pneumoniae***
- **Kirby-Bauer test for leaching of additives challenged with *E. coli* and *S. aureus***

HBP	% Reduction *C. albicans*	% Reduction *E. coli*	% Reduction *MRSA*	% Reduction *S. aureus*
PEI/Q	**99.9999**	**99.99**	**52.51**	**99.9999**
PE/ Q		**99.54**		**86.05**
PEI/B	**65.99**	**99.93**	**99.9999 (2 wt%)**	**99.9999**
PE		**94.10**		**60.63**
PEI		**21.80**		**No reduction**

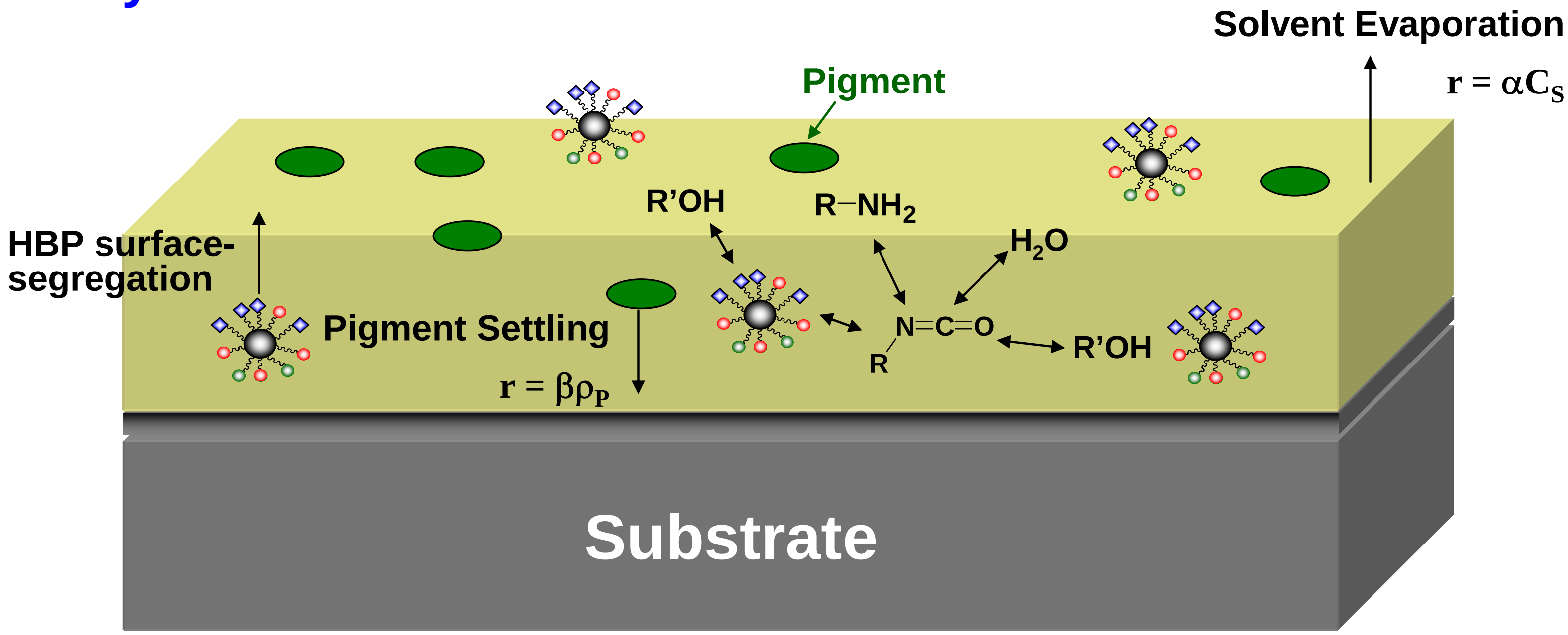
- **Increased efficacy at elevated additive levels**
- **Reasonable activity in TPU proxy system**

- **ASTM E2180 test w/ 1% additive in TPU, 24 h exposure**

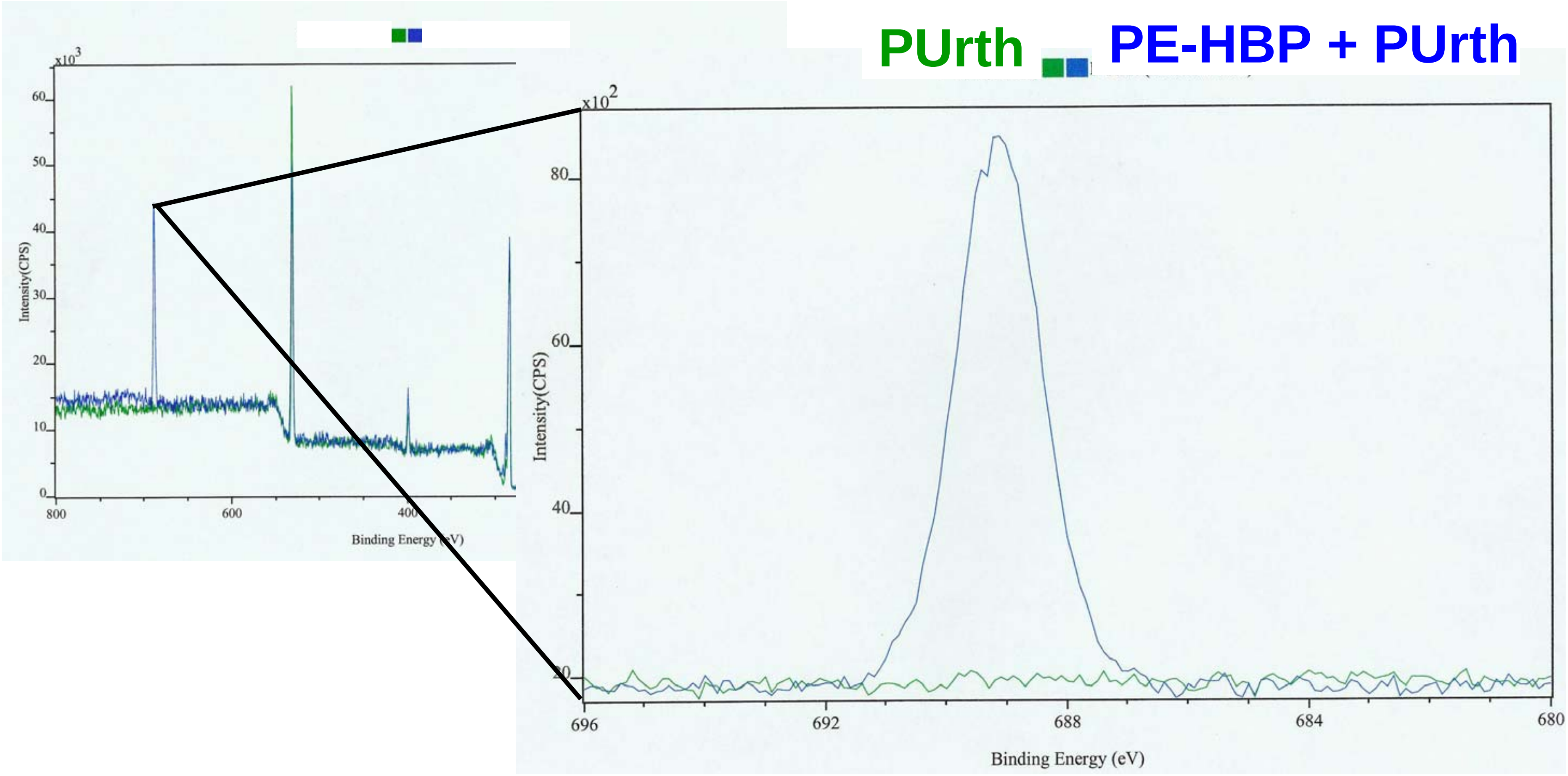
Transitioning technology to coating systems presents new technical barriers, performance characteristics, requirements

Additive reacts during cure, potential for anchoring additive at surface, may also influence cure kinetics and migration efficiency

Surface characteristics of coatings are of paramount importance



XPS provides most direct method to ascertain surface composition of additive, monitoring fluorine



Bulk concentration of fluorine ~0.3 %, observed ca. 7% at surface of coating

Candidate HBP scaffolds evaluated in a range of coating systems demonstrate migration, ca. 20 – 30 fold increase

	Coating	HBP	F 1s	N 1s
Solvent-based primer	Polyurea	None	0.0	5.22
	Polyurea	PEI-F-Alk	2.01	7.36
Water-based primer	Epoxy	None	0.0	3.15
	Epoxy	PE-F-Alk	7.18	3.16
Water-based topcoat	Polyurethane	None	0.0	4.62
	Polyurethane	PE-F-Alk	9.62	5.80
	Polyurethane	PEI-Alk	0.0	5.64
	Polyurethane	PEI-F-Alk	0.62	5.14
	Polyurethane	PEI-F-Alk-Quat	0.32	5.58

- **Most HBP segregated to surface of coatings using PEI and PE-based additives:**
  - **Coating/PE bulk Fluoro conc. = 0.3 mol%**
  - **Coating/PEI bulk Fluoro conc. ~ 0.07 mol%**

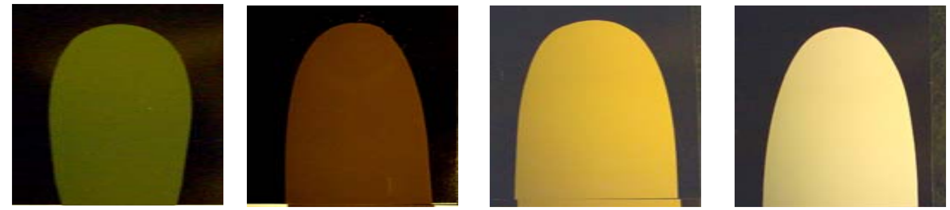
Acceptable performance of topcoat against selected qualifying tests

Test	Polyure-thane	PUrth + PEI-F	PUrth + PEI-aliph.	PUrth + PE-F	PUrth + PEI-Quat.
Color	Pass	Pass	Pass	Pass	Pass
Gloss	1.3/1.1	1.2/1.1	1.2/0.8	1.2/1.0	1.3/1.1
DFT	3.1-3.6	3.1-3.7	2.1-2.9	2.5-2.7	2.7-3.7
MEK Dbl Rub	200+	200+	200+	200+	200+
Impact Resistance, lb-in, direct/reverse	40/20	40/20	40/20	40/20	40/20
Cross-cut adhesion WET/DRY	5B/5B	5B/5B	5B/5B	5B/5B	5B/5B
QUV (cyclic test) 600 h	Pass/no change	Pass/no change	Pass/no change	Pass/no change	Pass/no change
STB	Pass	Pass	Pass	Pass	Pass
Flexibility/DFT	Pass	Pass	Pass	Pass	Pass
Water Resistance	Pass	Pass	Pass	Pass	Pass

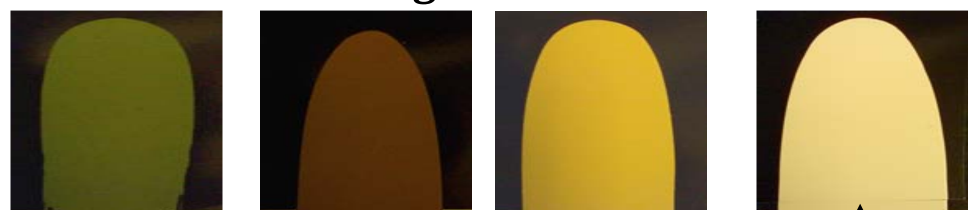
Integration into CARC coatings

- **Negligible difference in appearance of coatings with and w/o HBP**
  - **Draw-down**
  - **Spray coat**

Control



Coatings with HBP



1 Component Polyurea CARC MIL-C-53039

2 Component Polyurethane CARC MIL-DTL-64159

2 Component Epoxy CARC MIL-P-53022

- **Acceptable coating properties**
  - **Gloss**
  - **Color**
  - **Adhesion**

HBPs incorporated into reactive coatings exhibit variable activity, improved at 2% loading

CARC	HBP & Additive	% Reduct. *C. albicans*	% Reduct. *E. Coli*	% Reduct. *S. aureus*	% Reduct. *MRSA*
Epoxy (primer)	PEI C10 C4 Q	X	18.54 (99.99)*	5.41 (100)*	X
Polyurea 1 wt%	PE C10 C4 Q	99.68	98.02 (99.54)*	100 (86.05)*	X
Polyurea 2 wt%	PEI C10 C4 Q	X	100	100	100
Polyurethane	PEI C10 C4 Q	X	18.29 (99.99)*	25.44 (100)*	X
Polyurethane	PE C10 C4 Q	X	NR (99.54)*	5.92 (86.05)*	X
Polyurethane	PEI B	94.26 (65.99)*	25.65 (99.93)*	43.66 (100)*	X
Int. Epoxy 2 wt%	PEI C10 C4 Q	X	90.26	100	X

- Q denotes quaternary ammonium salt (values in (x) from TPU system)
- B denotes biguanide group
- Reduced efficacy relative to TPU system overcome by loading increase

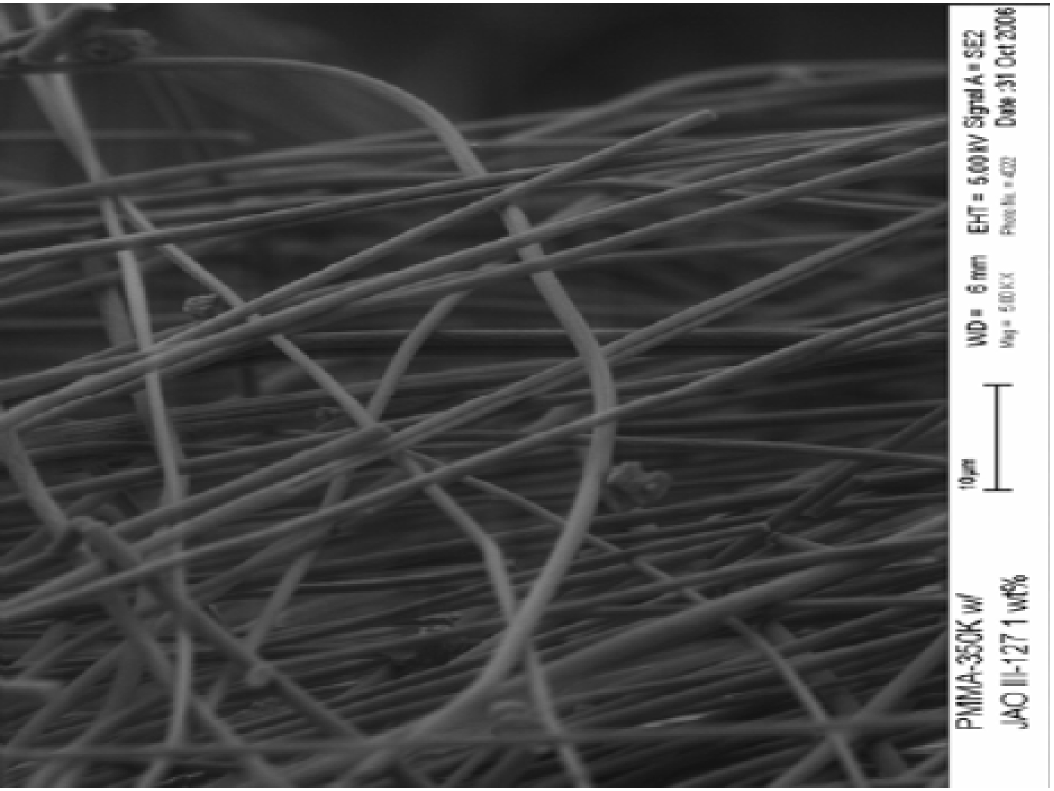
XPS Analysis of HBP in COTS Paints

Sample	Composition - Atomic % C	O	N	F
COTS Polyurethane Baseline 2-22-06*	41.269	23.658	0.166	*ND*
COTS Polyurethane Baseline 4-13-06	74.52	21.32	3.98	*0.19*
COTS Polyurethane PEIquat*	68.541	16.448	3.920	*ND*
COTS Polyurethane PEquat	69.60	25.84	4.52	*0.05*
COTS Oil/Alkyd Baseline 4-13-06	81.570	17.410	0.870	*0.15*
COTS Oil/Alkyd PEquat	81.35	17.12	1.25	*0.28*
COTS Acrylic Latex Baseline 2-15-06*	74.687	23.043	0.888	*ND*
COTS Acrylic Latex Baseline 4-21-06	73.8	24.84	1.09	*0.27*
COTS Acrylic Latex PEIquat*	73.764	18.859	2.949	**2.628**
COTS Acrylic Latex PEquat	77.18	20.84	1.54	*0.44*

- COTS – Commercial off-the-Shelf.
- Good segregation of HBP only in acrylic latex
- HBP caused instant gelation regular latex

Licensing our patented technology to numerous paint and coating companies

E-Spinning permits significant surface migration.



- ➢**E-spinning performed by collaborators at Virginia Tech.**
- ➢**E-spinning accomplished using 120K, 350K PMMA**
- ➢**Fiber sizes unpertrubed by additive inclusion**
- ➢**Initial experiment demonstrating Ag uptake met with some success (3 min exposure)**

XPS RESULTS	C	N	O	F	Ag
350 K PMMA	79.84	0	20.16	0	0
350K PMMA, 1% add.	71.38	5.67	15.5	7.45	0
350K PMMA, 3% add.	53.35	15.56	14.24	16.85	0
350K PMMA, Ag dip	77.42	0	22.05	0	0.53
350K PMMA, 1% add., Ag dip	78.18	2.33	14.83	3.09	1.57
350K PMMA, 3% add., Ag dip	70.24	8.08	11.2	8.44	2.04

•**E-spinning performed by M. Hunley; T.E. Long at Virginia Tech.**

Conclusions

- Demonstrated repeatable >30 X self segregation of active components to the air/polymer interface in coatings
- HBP scaffold universal. Favorable for attachment of a myriad of reactive species through straight forward chemistry.
- Transitioned to low VOC TPU coating systems
- Demonstrates strong activity (99.9999 % kill) towards environmental hazards: *S. aureus, C. albicans, E. Coli, MRSA*
- Preliminary evidence: Compatible with existing coating systems
- Potential in coated fabrics, latex paints, etc

RDECOM

Acknowledgements

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