U.S. NAVAL RESEARCH LABORATORY

Isocyanate-Free Polysiloxane Topcoats for Aircraft and Ground Support Equipment

Erick Iezzi, Ph.D.
U.S. Naval Research Laboratory
Center for Corrosion Science and Engineering
Washington, DC

ASETSDefense Workshop
December 6-8, 2016

U.S. NAVAL RESEARCH LABORATORY

Aircraft and Ground Support Equipment Topcoats: Current Issues

Topcoats used on DoD aircraft and ground support equipment (GSE) are two-component (2K) polyurethanes that contain hazardous isocyanate-based materials

- Isocyanates are harmful to the environment and can cause severe health issues (e.g., skin irritation, asthma, sensitization) for applicators and those exposed to off-gassing vapors during cure

Spray application of a polyurethane topcoat on a F/A-18 aircraft

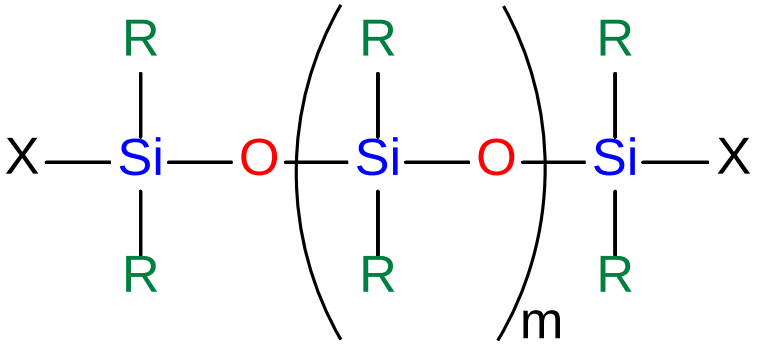
- Navy topcoats are qualified to MIL-PRF-85285E requirements
  - Type I (aircraft), Type II (GSE) and Type IV (aircraft with extended weatherability)
- Air Force topcoats are qualified to MIL-PRF-32239A requirements as a "system"
- Navy's MIL-PRF-81352C touch-up topcoats (e.g., alkyds, acrylics) are non-isocyanate, but they provide limited weatherability, flexibility and fluid resistance

An environmentally friendly technology that offers equivalent or greater performance compared to aircraft and GSE polyurethanes does not currently exist

U.S. NAVAL RESEARCH LABORATORY

Polysiloxanes: Description and Advantages

Polysiloxanes: a class of materials composed of silicon, oxygen and alkanes



X = epoxy, amine, acrylic, isocyanate, alkoxy

R = aromatic, aliphatic, cycloaliphatic

- Polysiloxanes (aka “siloxanes”) have various lengths, composition and functionality
- Si–O bond is stronger (BDE ~110 kcal/mol) than the C–C bond (BDE ~83 kcal/mol) found in all-organic coatings
  - greater resistance to oxidation and degradation from UV-radiation
- Relatively non-toxic, especially when compared to isocyanate-functional materials

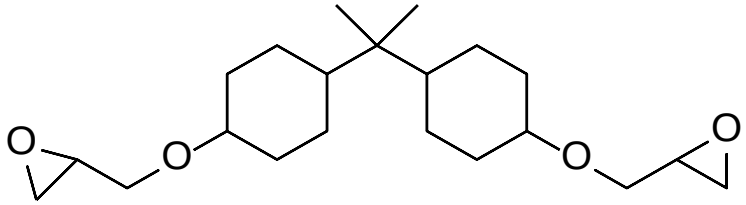
U.S. NAVAL RESEARCH LABORATORY

NRL-Developed 2K Polysiloxane Topcoat

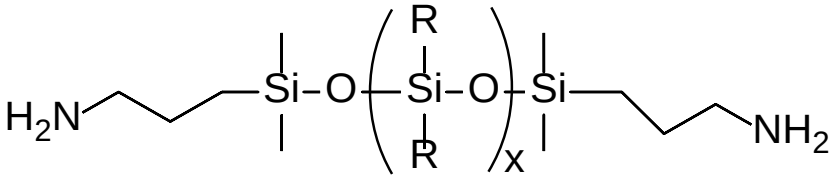
Two-Component (2K) Technology

- Based on polymers/oligomers with amine and epoxy functionality
  - requires mixing of two components to generate a cured coating
- Ambient-curable, solvent borne systems
- Isocyanate-free, HAPs-free and 0 to <340 g/l VOCs

Base (epoxy-functional resin)



Hardener (amino-functional polysiloxane)



R = Methyl, Phenyl and/or Cyclohexyl

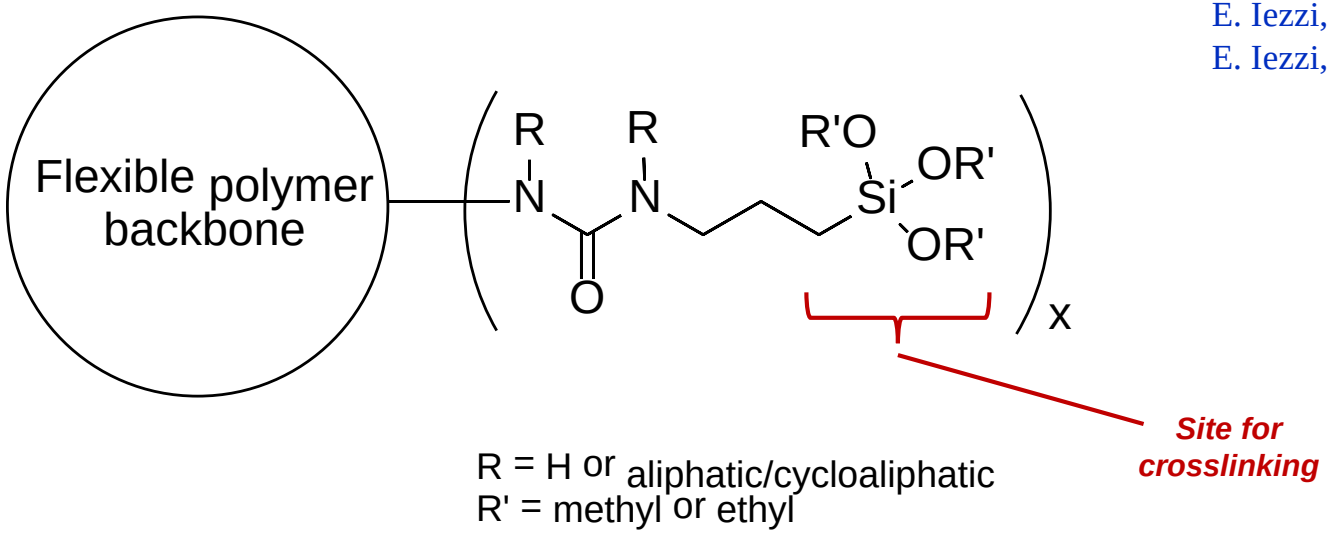
E. Iezzi, U.S. Patent Appl. No. 14/854,407

NRL-Developed 1K Polysiloxane Topcoat

Single-Component (1K) Technology

- Based on novel N-substituted urea polymers with terminal alkoxysilanes
- Moisture-curable, solvent borne system
  - hydrolysis and condensation reactions form the polysiloxane network
- No mixing of components – a “user-friendly” system
- Isocyanate-free, HAPs-free and <340 g/l in VOCs

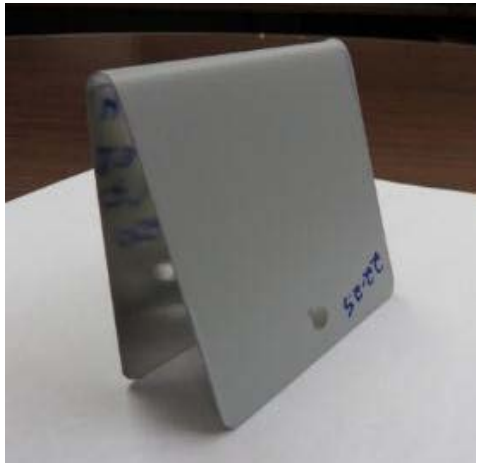
E. Iezzi, U.S. Patent 9,221,942
E. Iezzi, U.S. Patent 9,139,753
E. Iezzi, U.S. Patent 8,133,964



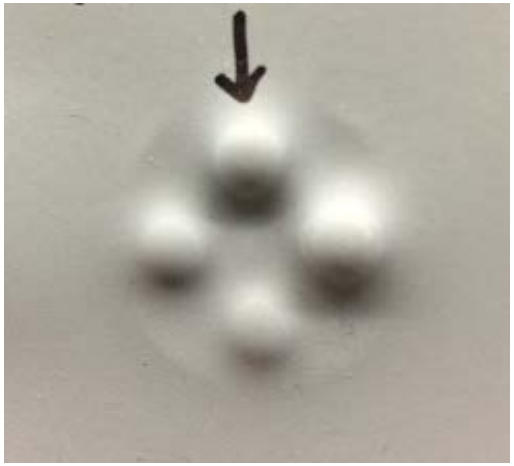
U.S. NAVAL RESEARCH LABORATORY

Polysiloxane Topcoats for Navy Aircraft

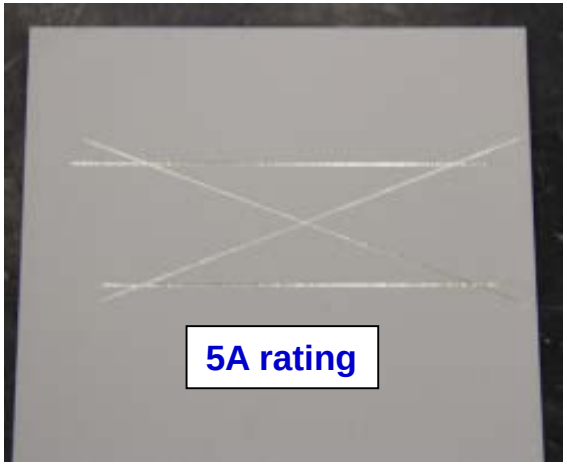
ONR Swampworks Program: Modify polymers used in 1K and 2K ship topcoats and evaluate formulas to aircraft topcoat requirements



1K topcoat after ¼" Mandrel Bend Test – PASS, no cracking



1K topcoat after GE Impact Flexibility Test – PASS @ 40% Elongation



1K topcoat after Wet Tape Adhesion Test – PASS, 5A

NRL-batched topcoats demonstrated the ability to meet the majority of MIL-PRF-85285E, Type IV performance requirements when tested at the Naval Air Warfare Center – Aircraft Division (NAWC-AD)

ESTCP-funded program for Dem/Val of manufacturer-batched technology

U.S. NAVAL RESEARCH LABORATORY

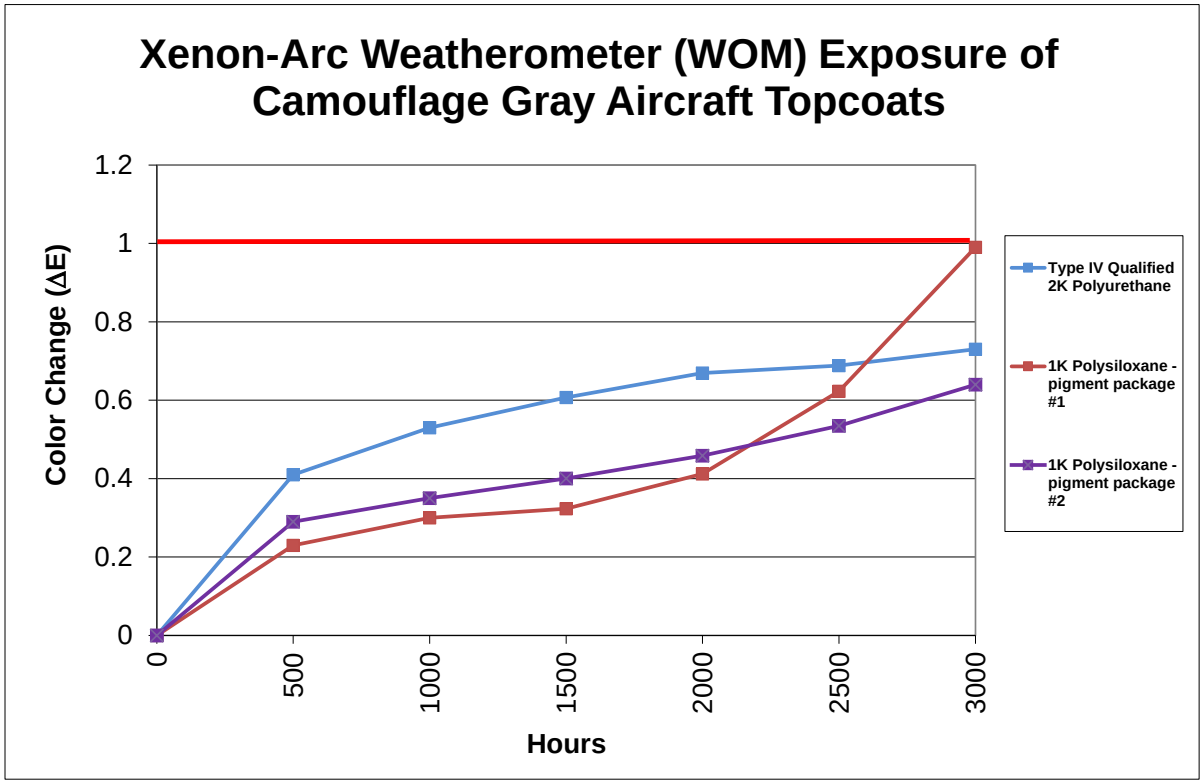
1K Camouflage Gray Polysiloxane Topcoat for Navy Aircraft

Except for flexibility, all tests were performed over a MIL-PRF-85582E, Type II, C1 (chromate) waterborne epoxy primer with a MIL-DTL-81706B chromate pretreatment

MIL-PRF-85285E, Type IV Tests	REQUIREMENTS	1K Camo. Gray Polysiloxane Topcoat	Type IV Qualified 2K Camo. Gray Polyurethane Topcoat
Isocyanates	Permitted	None	Yes
VOCs	≤420 g/l	<340 g/l	420 g/l
Gloss	≤5 GU @ 60°	PASS	PASS
	≤10 GU @ 85°	PASS	PASS
Solvent Resistance	25 MEK Double Rubs	PASS	PASS
Fluid Resistance – Lube Oil	24 hr @ 250 °F	PASS	PASS
Fluid Resistance – Hydraulic Fluid	24 hr @ 150 °F	PASS	PASS
Fluid Resistance – JP-5 Jet Fuel	7 days @ RT	PASS	PASS
Adhesion – Wet Tape	DI H_2O 24 hr @ RT – ≥4A	PASS, 4A	PASS, 4A
GE Impact Flexibility	≥40% Elongation	PASS @ 40%	PASS @ 40%
Low-Temp. Flexibility	–60 °F Over 2” Mandrel - No cracking	PASS	PASS
Room Temp. Flexibility	1” Cylindrical Mandrel - No cracking	PASS	PASS
Humidity Resistance	30 days 120 °F / 100% RH	PASS	PASS
Heat Resistance	250 °F @ 1 hr, ΔE <1.0	PASS, ΔE = 0.10	PASS, ΔE = 0.44
Cleanability	>75% efficiency for camo.	PASS, 92.61%	PASS, 98.58%
Strippability	>90% Method B (unexposed)	Topcoat removed	Topcoat removed

1K Camouflage Gray Polysiloxane Topcoat for Navy Aircraft

MIL-PRF-85285E, Type IV Tests	REQUIREMENTS	1K Camo. Gray Polysiloxane Topcoats	Qualified 2K Camo. Gray Polyurethane Topcoat
Weather Resistance	3000 hrs. Xenon-Arc WOM: color change (ΔE) <1.0, 60° & 85° gloss change <3 GU	ΔE = 0.99 avg. @ 3000h (#1); ΔE = 0.64 avg. @ 3000h (#2)	ΔE = 0.73 avg. @ 3000h
		<3 GU	<3 GU



The 1K polysiloxane topcoat meets the Type IV weatherability requirement and has demonstrated slightly greater color retention than a qualified Type IV polyurethane

U.S. NAVAL RESEARCH LABORATORY

1K Camouflage Gray Polysiloxane Topcoat for Navy Aircraft

Assets for Demonstration of the 1K Polysiloxane Topcoat

MV-22 Osprey

CH-53 Sea Stallion

AV-8B Harrier

U.S. NAVAL RESEARCH LABORATORY

1K & 2K Camouflage Gray Polysiloxane Topcoats for Air Force Aircraft

All tests were performed as a "system" over Akzo Nobel's Aerodur 2100 Mg-Rich epoxy primer with Prekote pretreatment

MIL-PRF-32239A Tests	REQUIREMENTS	1K Camo. Gray Polysiloxane Topcoat	2K Camo. Gray Polysiloxane Topcoat	Qualified 2K Camo. Gray Polyurethane Topcoat
Isocyanates	Permitted	None	None	Yes
VOCs	≤420 g/l	<340 g/l	<340 g/l	420 g/l
Gloss	Camouflage - 60° ≤5 GU, 85° ≤9 GU	PASS	PASS	PASS
Solvent Resistance	25 MEK Double Rubs	PASS	PASS	PASS
Adhesion – Wet Tape	DI H_2O 24 hrs. @ RT – ≥4A	PASS, 5A	PASS, 5A	PASS, 5A
Adhesion – Crosshatch	RT – ≥4B	PASS, 5B	PASS, 5B	PASS, 5B
Fluid Resistance – Jet Fuel (JP-8)	30 days @ RT - no delamination, ≤2 pencil hardness change, color change (ΔE) ≤3.0	PASS; 5B adhesion, <2 pencil hardness change, ΔE = 0.36	FAIL; 5B adhesion, >2 pencil hardness change (increased in hardness), ΔE = 0.38	PASS; 4B adhesion, no change in pencil hardness, ΔE = 0.13
GE Impact Flexibility - before weathering	≥10% Elongation	PASS, 10%	PASS, 10%	PASS, 10%
Low-Temperature Flexibility	–60 °F over 2" Cylindrical Mandrel - No cracking	PASS	PASS	FAIL
Strippability with non-toxic / less-toxic paint stripper	>90% removed within 24h and with <4 applications using a benzyl alcohol / hydrogen peroxide stripper	PASS, 100% of topcoat removed	PASS, 100% of topcoat removed	FAIL, 75% of topcoat removed
Weather Resistance	3000 hrs. Xenon-Arc: color change (ΔE) <1.0	ΔE = 0.73 @ 2500 hours	N/A	ΔE = 0.78 @ 2500 hours

U.S. NAVAL RESEARCH LABORATORY

1K & 2K Camouflage Gray Polysiloxane Topcoats for Air Force Aircraft

Assets and Areas for Demonstration of the Polysiloxane Topcoats

C-130 Hercules

C-130 Troop Door

C-130 Engine Nacelle

C-5 Galaxy

C-5 Horizontal Stabilizer

U.S. NAVAL RESEARCH LABORATORY

2K Gloss White Polysiloxane Topcoat for Navy GSE

Except for flexibility, all tests were performed over a MIL-DTL-53022E, Type IV lead and chromate-free epoxy primer with a MIL-DTL-81706B chromate pretreatment

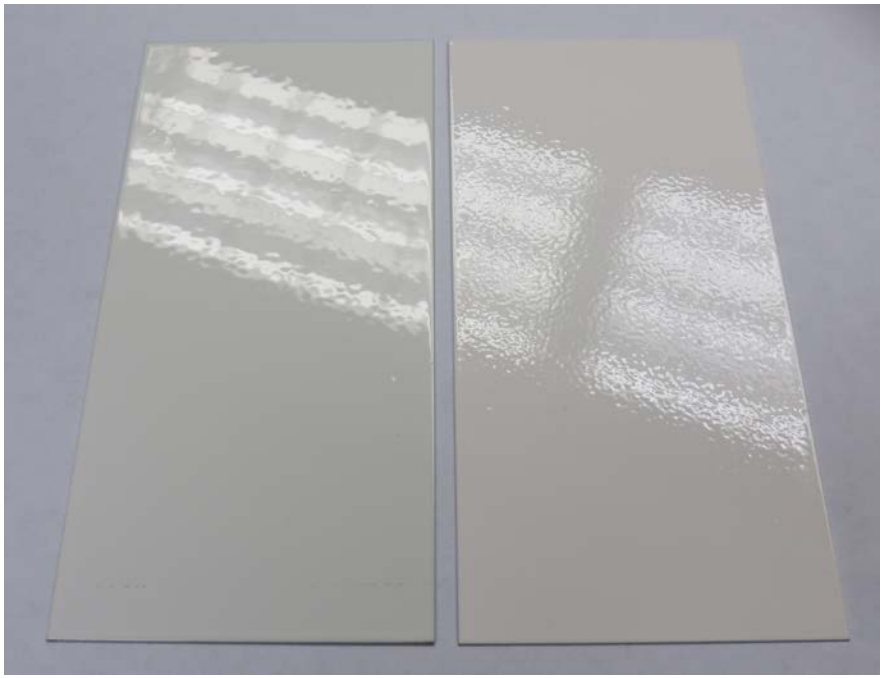
MIL-PRF-85285E, Type II Tests	REQUIREMENTS	2K Gloss White Polysiloxane Topcoat	Type II Qualified 2K Gloss White Polyurethane Topcoat
Isocyanates	Permitted	None	Yes
VOCs	≤340 g/l	65 g/l*	336 g/l
Dry – Set-to-Touch	<6 hours	30 min	1 hour
Dry – Hard	<12 hours	9 hours	9 hours
Gloss	≥90 GU @ 60°	91.3 GU	93.6 GU
Solvent Resistance	25 MEK Double Rubs	PASS	PASS
Fluid Resistance – Lube Oil	24 hr @ 250 °F	PASS	PASS
Fluid Resistance – Hydraulic Fluid	24 hr @ 150 °F	PASS	PASS
Fluid Resistance – JP-5 Jet Fuel	7 days @ RT	PASS	PASS
Adhesion – Wet Tape	DI H_2O 24 hr @ RT – ≥4A	PASS, 4A	PASS, 4A
GE Impact Flexibility	≥5% Elongation	PASS @ 5%	PASS @ 10%
Room Temp. Flexibility	1” Cylindrical Mandrel – No cracking	PASS	PASS
Humidity Resistance	30 days 120 °F / 100% RH	PASS	PASS
Heat Resistance	250 °F @ 1 hr, ΔE <1.0	PASS, ΔE = 0.62	PASS, ΔE = 0.85
Cleanability	≥90% efficiency for gloss	PASS, 94.9%	PASS, 96.8%
Strippability	≥90% Method B (unexposed)	PASS	PASS

*2K polysiloxane can be formulated at 0 VOCs

2K Gloss White Polysiloxane Topcoat for Navy GSE

Testing of gloss topcoats to MIL-PRF-85285E, Type II requirements, cont'd…

MIL-PRF-85285E, Type II Tests	REQUIREMENTS	2K Gloss White Polysiloxane Topcoat	Type II Qualified 2K Gloss White Polyurethane Topcoat
Weather Resistance	500 hrs. Xenon-Arc WOM: color change (ΔE) <1.0, 60° gloss ≥80 GU	Pass, 87.9 GU @ 60°	Pass, 91.4 GU @ 60
		Pass, ΔE = **0.72** after 500 hours	Pass, ΔE = **0.87** after 500 hours



2K Polysiloxane (left) vs. Qualified Type II Polyurethane (right)

U.S. NAVAL RESEARCH LABORATORY

2K Gloss White Polysiloxane Topcoat for Navy GSE

Assets for Demonstration of the 2K Polysiloxane Topcoat

A/S32A-32 Aircraft Towing Tractor

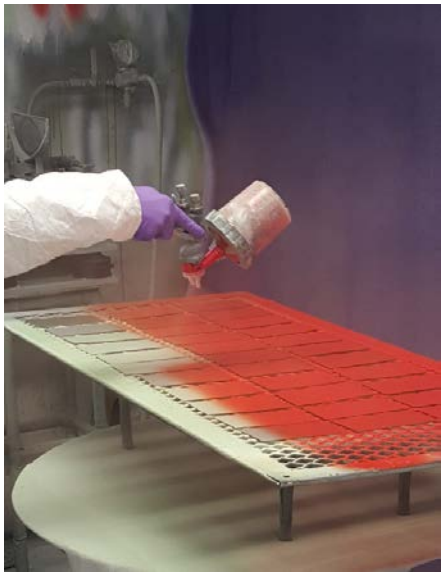
Mid-Range Tow Tractor

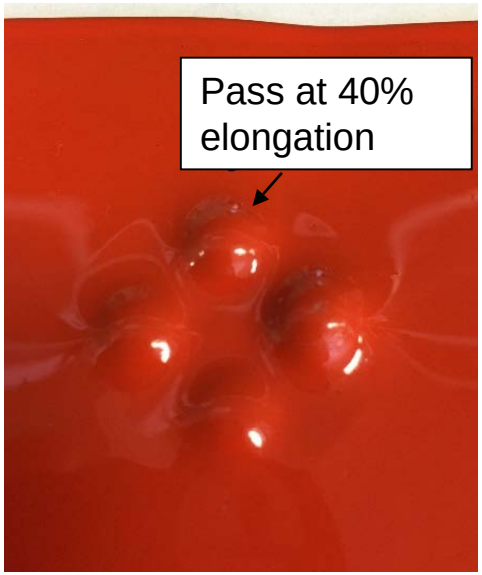
A/S32P-25 Shipboard Fire-Fighting Vehicle

U.S. NAVAL RESEARCH LABORATORY

1K Gloss White and Orange Polysiloxane Topcoats for Navy Trainers

Spray application and testing of NRL's 1K gloss white and orange topcoats for Navy trainers





T-45 Goshawk trainer

U.S. NAVAL RESEARCH LABORATORY

Summary

NRL has developed novel polysiloxane polymers for use in single- (1K) and two-component (2K) topcoats for DoD aircraft and GSE

- 1K topcoat is a “user-friendly” system – no mixing of components before application
- Environmentally friendly – isocyanate-free, HAPs-free, lower in VOCs than qualified polyurethanes, and reduced generation of hazardous waste
- Topcoats demonstrate equivalent to slightly greater laboratory performance compared to qualified polyurethanes
- Demonstration of topcoats on Navy aircraft and GSE are planned for the near future

U.S. NAVAL RESEARCH LABORATORY

Acknowledgements

Environmental Security Technology Certification Program (ESTCP)

Naval Air Warfare Center – Aircraft Division (NAWC-AD)

Air Force Research Laboratory (AFRL), Corrosion Technology Integration Office (CTIO) and University of Dayton Research Institute (UDRI)

NCP Coatings, Inc.