Low HAP Materials

John La Scala
Army Research Laboratory
RDRL-WMM-C
Aberdeen Proving Ground, MD 21005
jlascala@arl.army.mil
1. REPORT DATE
   SEP 2009

2. REPORT TYPE

3. DATES COVERED
   00-00-2009 to 00-00-2009

4. TITLE AND SUBTITLE
   Low HAP Materials

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

6. AUTHOR(S)

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
   U. S. Army Research Laboratory, RDRL-WMM-C, Aberdeen Proving Ground, MD, 21005

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR’S ACRONYM(S)

11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
   Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES
   ASETSDefense 2009: Sustainable Surface Engineering for Aerospace and Defense Workshop, August 31 - September 3, 2009, Westminster, CO. Sponsored by SERDP/ESTCP

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:

   a. REPORT
      unclassified

   b. ABSTRACT
      unclassified

   c. THIS PAGE
      unclassified

17. LIMITATION OF ABSTRACT
   Same as Report (SAR)

18. NUMBER OF PAGES
   57

19a. NAME OF RESPONSIBLE PERSON

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18
Outline

• Fatty Acid Vinyl Ester Resins/Composites with low hazardous air pollutant contents

• Other low HAP composite resin developments

• Low HAP Adhesives and Sealants
UPE and VE Resins

Unsaturated Polyester

Vinyl Ester

HAP Emissions

Styrene

Initiator + Heat

Thermosetting Polymer
VOC/HAP Emissions

- Liquid resins used in molding large-scale composites are a significant source of Hazardous Air Pollutants (HAP)

- Composites industry consumes 9% of the styrene, but accounts for 79% of styrene emissions

- EPA - Reinforced Plastic Composites National Emissions Standards for Hazardous Air Pollutants (NESHAP)
  - Executed and legally enforceable as of April 28, 2003
  - Regulation imposes a substantial barrier to fielding and development of new composite technologies for military platforms.
Technical Approach

- Use fatty acid monomers to reduce styrene content.
  - Non-volatile
  - Maintain low viscosity

FAVE: Fatty Acid-Based Vinyl Ester Resin

Bimodal blends and other chemically modifications

Reduce styrene content from 40-50 wt% to 10-25 wt%
Demonstration Platforms

- HMMWV ballistic hardtop
- HMMWV transmission container
- M35A3 hood
- T-38 dorsal cover
- MCM composite rudder
- M939 hood

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.
• **Vacuum Assisted Resin Transfer Molding (VARTM)**
  - Cured at room temperature using CoNap and DMA catalysts, 2,4-P inhibitor, and Trigonox initiator
  - Post-cured for 2 hours at 130°C
• Very similar Tg for FAVE composites relative to commercial composites.

• Tg decreases as a result of water ingress
• Water (DI and salt) and Xenon weathering:
  – Tg, strength, and modulus reduced for wet samples.
  – FAVE and commercial resins performed similarly.

• Solvents/fuel immersion:
  – Tg, strength, and modulus reduced for wet samples.
  – FAVE performed similarly or out-performed commercial resins.
Navy Composite Rudders

- Straight rudder (MCM)
- Composite twisted rudder (CTR) – DDG51 and DDG1000
- Easier to fabricate and less cavitation than steel twisted rudders
- Composite rudder on MCM-9 has good success after 6 year fielding trial

Demonstrate/Validate low VOC/HAP formulations for one of these applications
MCM Rudder Fabrication

- 1 hr resin infusion
- Rudder fabrication done by Structural Composites, Inc., overseen by NSWCCD

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.
• Some excess resin pockets (wrinkling)
• One rudder will be demo piece.
• The other rudder was sectioned and is being analyzed by NSWCCD to validate the structure.
Army Tactical Vehicle Replacement Parts

- Corrosion issues with M35A3
- Sheet molding compound (SMC) HMMWV hood has poor performance
- Transmissions damaged in shipment without good packaging
- Test demo parts
  - Flexural, impact, cyclic load, High T, etc.
HMMWV Transmission Container

- Container designed to protect HMMWV transmissions from damage during shipping
- Container must have:
  - desiccant port
  - lifting handles
  - latches – no accidental opening
  - humidity indicator
  - pressure relief valve
  - drainage plug
  - forklift and pallet jack tine pockets
- Container designed by CCM/Sioux Manufacturing Corp. (SMC)
- Container manufactured by SMC
According to SMC, resin infused as well or better than incumbent resins.

Resin required only 30 minutes for infusion.

Infusion
HMMWV Trans. Container: Commercial Prod.

Infused Top

Infused Bottom

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.
HMMWV Trans. Container: Commercial Prod.

Top with hardware

Bottom with external hardware

Bottom with internal hardware
Assembled Container
HMMWV Transmission Container

• Drop tests
  – Rotational Edge Drop Test per ASTM D6179 Method A
  – Rotational Corner Drop Test per ASTM D6179, Test Method B
  – Unsupported free fall drop test per ASTM D6179 Method D
  – Tipover Test per ASTM D6179, Method G
  – Vibration Test per ASTM D999 Test Method B
  – Later Impact Test per ASTM D880, Procedure B, 179, Test Method B

• Leakage test
  – Pressurize to 10 kPa, $\Delta P<0.2$ Pa in 30 minutes
  – Pull a vacuum of 7 Pa, $\Delta P<0.2$ Pa in 30 minutes

• Validation tests are nearly completed at CCM
• Fielding trials are in progress at RRAD
Commercial Production – M35A3 Hood

- M35A3 Truck hood manufactured by SMC

Bagged Hood

After 10 min of infusion

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.
According to SMC, resin infused as well or better than incumbent resins

- Resin required only 51 minutes for infusion
Final Part

- Low HAP hood painted with low VOC/HAP water-dispersible CARC (MIL-DTL-64159)
Top Front Load

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- Test passed.

- Elastic deflection 0.04” at 250 lbs.
- Much less than 0.50” allowed
- Test passed.
M35A3 Hood Validation – Corner Lifts

Driver Corner Lift

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- Test passed.

- Elastic deflection 0.16” at 85 lbs.
- More than 50 lbs required to lift corner 0.375”
- Test passed.
Cyclic Handle Load

• No permanent deformation.
• No separation of reinforcements from the hood.
• No cracks.
• No broken fibers visible on areas where the hood contacts the fixture
• Test passed.

Elastic deflection 0.16” at 85 lbs.
More than 50 lbs required to lift corner 0.375”.
No significant change in stiffness after cyclic loading.
Test passed.
Durability (cyclic loading followed by load deflection)

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- No broken fibers visible on areas where the hood contacts the fixture.
- Test passed.
M35A3 Hood Validation – Impact

Impact on stiffener (near and between stiffener – not shown)

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- Test passed.

Impact between stiffeners

Impact on large radius corner
M35A3 Hood Validation

- FAVE M35A3 passed all validation testing
- FAVE M35A3 performed nearly identically to baseline epoxy M35A3
- Hoods installed on M35A3 trucks at RRAD for field testing
FAVE-O-25S Ballistic Performance

- Performance assessed in all-composite panel form
  - 100oz 3TEX 3WEAVE S2 Glass Construction
  - 4 ply panel for NIJ IIIa (44 magnum) equivalent
  - 12 ply panel for NIJ III (7.62 M80 Ball) equivalent
  - Compared directly to Derakane 8084 VE Resin – slightly different fabric architectures (24oz faces on 8084 panel) and FCS2 Epoxy
- FAVE resin had similar or better performance with 44 mag. and M80 threats relative to both commercial resins
T-38 Dorsal Cover

- 400 planes upgraded to ‘C’ model
- Upgrade caused pre-mature failure
- AFRL developed new VARTM dorsal cover
- Requirements
  - Drop-in replacement
  - Thermal, mechanical, electrical, solar

Demonstrate/Validate low VOC/HAP formulations for one of these applications
Dorsal Cover Demonstration – Initial Failure

- Short-shot infusion of T-38 dorsal cover
- FAVE-L resin viscosity was too high
  - *Used FAVE-L-25S instead and solved processing issue*
- Current resin uses 47% styrene – substantial reduction
Manufactured and validated composite panels
Manufactured T-38 dorsal cover
- Validation of structure will take place in the coming months

AFRL expanded demonstration to F-22 canopy cover
- Protects canopy against overspray during painting operations
- Far easier and quicker than taping a cover in place
- Used FAVE-L-25 resin to manufacture demo part
Infusion of F-22 Canopy Cover
Life Cycle Analysis

• Current estimated MFA price range: $1.23-$2.85/lb
• Cost of fatty acid VE resin is $0-$1.16 higher per pound
  – Depends on resin formulation and scale
• Cost for emissions capture and treatment avoidance is $1.13 per pound of resin
• Cost of carbon footprint is $0.30 per pound of resin.

• FAVE resins are more cost effective
• FAVE resins have a lower environmental impact
• FAVE resins have recently been licensed by Dixie Chemicals
HAP-Free Repair Resin Similar to Bondo

- **Binder**
  - Use MFA to replace styrene
  - Use VE and/or UPE cross-linkers

- **Fillers**
  - Use similar fillers/contents as in BONDO

- **Promoters**
  - Dimethylaniline

- **Curing agents**
  - Use BONDO hardeners
  - Formulate hardeners
HAP-Free Bio-Based Gel Coats

- Gel coats used to provide smooth surface for composites
- Gel coats emit large HAP percentages.

- Use maleinized triglycerides to replace UPE
- Use novel bio-based reactive diluent to replace styrene
Bio-Based Carbon Fibers and Thermosetting Resins

- SERDP proposed new start, FY10
- Microbially breakdown lignin into oligomers that can be melt spun and carbonized
- Modify renewable resources and bio-based chemicals to make bio-based monomers
- Assess, fiber, resin, and composite properties
Background:
RRAD currently uses adhesives for tank treads and road wheels that contain very high HAP contents. The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP is requiring reduced HAP in all DoD coating operations.

Objectives:
• Successfully replace current rubber to metal bonding adhesives with non-HAP alternatives or reduce HAPs through identification of compatible non-HAP thinners.
• Dem/Val best performing candidates at RRAD.

Participants:
U.S. Army Research Laboratory
TARDEC
RRAD
Hayfire, inc.
CTC/NDCEE

Progress to Date:
• Identified non-HAP thinners compatible with existing adhesive systems with similar bench-level performance.
• Identified low HAP alternative adhesives. Bench level testing of these adhesive systems is still in progress.

Benefits:
• Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness.
**Background:**
The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP will require reduced HAP in all DoD coating operations. Rubber to metal contact adhesives under MMM-A-121 are used on various weapons platforms and produce ~1200 lbs/yr HAP emissions.

**Objectives:**
- Successfully replace current contact adhesives with non-HAP alternatives.

**Participants:**
SPOTA  
U.S. Army Research Laboratory,  
AMCOM G-4  
Fort Rucker  
Hayfire, inc., CTC/NDCEE

**Progress to Date:**
- Identified 3M Scotchweld 847 as a zero HAP, zero VOC alternative  
- Laboratory testing showed similar performance relative to baseline  
- Dem/val ongoing at Fort Rucker on blackhawk nose door seal and aviation helmet

**Benefits:**
- Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness  
- Improved performance.
Background:
The Defense Land Systems and Miscellaneous Equipment (DLSME) NESHAP will require reduced HAP in all DoD coating operations. Inspection lacquers, such as F-900 Torque Seal, contain 20 wt% methanol HAP.

Objectives:
• Successfully replace current inspection lacquer with a non-HAP alternative.

Participants:
SPOTA
U.S. Army Research Laboratory,
AMCOM G-4, Fort Rucker
Hayfire, inc., CTC/NDCEE

Progress to Date:
• Manufactured zero HAP Torque Seal
• Laboratory tested
• Successful dem/val of zero HAP Torque Seal on UH-1 rotor.
• HAP-free product is now listed on the GSA.

Benefits:
• Reduced HAP will comply with future EPA regulations, improve worker health, and improve mission readiness.
• Improved performance.
Summary

• Environmentally friendly VE and UPE resins using fatty acid monomers and tailored VE molecular structure
  – Effectively reduce HAP emissions
  – Comparable resin and composite performance

• Variety of other uses for plant oils in composites
  – Bio-rubber toughening agent increases toughness dramatically while maintaining $T_g$ and viscosity.
  – HAP-free repair resin performs similar to Bondo™ similar

• Low HAP adhesives and sealants.

• “Army Green” does not only refer to Army colors!
Acknowledgements

- Army Research Laboratory

- Drexel University – Palmese research group

- CCM, University of Delaware
  - S. Anderson, David Fudge, N. Shevchenko, K. Brand
  - Jack Gillespie, Prof. Wool Research Group

- NSWC, Carderock Division – R. Crane, M. Foley

- Advanced Composite Office, Hill AFB and Air Force Research Lab
  - Larry Coulter, Ken Patterson, Lt. Dane Morgan, Frank

- Resin Suppliers: Applied Poleramics, Inc., Ashland, Hexion, Corezyn

- ESTCP WP-0617, SERDP PP-1271, EQBRD, SPOTA for funding
Low VOC Resin Technology
Low Cost and High-Impact Environmental Solutions for Composite Structures

Need for Low VOC Resins

Liquid resins used in molding large-scale composites are a significant source of Volatile Organic Compound (VOC) emissions. In fact, the composites industry only consumes 9% of the styrene, but produces 79% of the emissions. For this reason, the EPA has enacted the Reinforced Plastic Composites NESHAP, which mandates the maximum HAP content in liquid molding resins.

Applications

Applicable to all uses of unsaturated polyesters and vinyl esters, including all methods of manufacture.

- Military vehicles and structure
- Automobile parts
- Boats
- Gel coats

Solutions

- Fatty acid monomers as styrene replacements
- Tailor molecular structure of vinyl ester monomers

Resin Processing
- Low viscosity
- VARTM, SCRIMP, SMC capabilities

Polymer Properties
- High $T_g$, strength, toughness
- Comparable to commercial resins

Facilities

Army Research Laboratory
Rodman Materials Building
APG, MD

Drexel University
Philadelphia, PA

To discuss licensing this technology, contact: Professor Giuseppe R. Palmese, Drexel University, Department of Chemical Engineering, Philadelphia, PA 19104, 215-895-5814, palmese@cbis.ece.drexel.edu
Low HAP Fatty Acid Vinyl Ester Resins (FAVE)

- Use fatty acid monomers to reduce styrene content
  - Non-volatile and inexpensive
  - Copolymerizes with styrene and vinyl ester
  - Soluble in VE and UPE
  - Increases renewable content in polymers
  - Reduces VOC/HAP emissions by 55-78%

Commercial Resins
Low VOC ~ 33 wt% Sty
Standard ~ 40-50 wt% Sty

Styrene
10-25 wt%

MFA – methacrylated fatty acid

FAVE: Fatty Acid-Based Vinyl Ester Resin
<table>
<thead>
<tr>
<th>Application</th>
<th>Fabric</th>
<th>Resin</th>
<th>Resin Replacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amtech Helmet Hardtop</td>
<td>3-Tex 100 oz S2-glass and 24 oz S2-glass</td>
<td>Derakane 8084</td>
<td>FAVE-O-25S</td>
</tr>
<tr>
<td>HMMWV Hood</td>
<td>3D E-glass</td>
<td>Hetron 980-35</td>
<td>FAVE-L-HT/O-HT</td>
</tr>
<tr>
<td>M35A3 and M939 Hood</td>
<td>3-Tex 96 oz E-glass</td>
<td>Hetron 980-35 (VE) or Huntsman 8605 (Epoxy)</td>
<td>FAVE-L-HT/O-HT</td>
</tr>
<tr>
<td>Transmission Container</td>
<td>3-Tex 54 oz E-glass</td>
<td>Derakane 8084</td>
<td>FAVE-L-25S/O-25S</td>
</tr>
<tr>
<td>T-38 Dorsal Cover and F22 Canopy Cover</td>
<td>Fibre Glast Developments Corp. 120 3 oz E-glass and Style 7781 E-glass 9 oz</td>
<td>Hexion 781-2140</td>
<td>FAVE-L-25S/O-25S</td>
</tr>
<tr>
<td>Rudders</td>
<td>Fiber Glass Ind. 18 oz E-glass</td>
<td>Corezyn Corve 8100 and Derakane 510A-40</td>
<td>FAVE-L-25S</td>
</tr>
</tbody>
</table>

- Derakane 8084: ~40 wt% styrene
- Hexion 781-2140: 47 wt% styrene
- Corve 8100: 50 wt% styrene
- Hetron 980/35: <35% styrene
- Derakane 441-400: 33 wt% styrene (low HAP resin)
- FAVE-L/FAVE-O-25S: 25 wt% styrene, L – methacrylated Lauric acid O – methacrylated Octanoic acid
- FAVE-O-HT: 25 wt% styrene, Novolac VE
Both FAVE-L and FAVE-L-25S are similar or exceed performance of commercial resins.

Toughness alone decreased, but this was likely due to incomplete cure.
FAVE-O-25S and FAVE-L-25S Performance

<table>
<thead>
<tr>
<th>Property</th>
<th>Strength (ksi)</th>
<th>Requirement (ksi)</th>
<th>Modulus (msi)</th>
<th>Requirement (msi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FAVE-O-25S 4 pt bend Room Temp</td>
<td>62.0</td>
<td>55.0</td>
<td>3.70</td>
<td>3.70</td>
</tr>
<tr>
<td>FAVE-O-25S Short beam shear Room Temp</td>
<td>4.80</td>
<td>4.50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FAVE-L-25S 4 pt bend Room Temp</td>
<td>70.0</td>
<td>55.0</td>
<td>3.85</td>
<td>3.70</td>
</tr>
<tr>
<td>FAVE-L-25S Short beam shear Room Temp</td>
<td>5.10</td>
<td>4.50</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- FAVE-O-25S and FAVE-L-25S meet specs for Army transmission containers and HMMWV hardtop
### FAVE-O-HT Performance

<table>
<thead>
<tr>
<th></th>
<th>Batch 2 Strength (ksi)</th>
<th>Batch 1 Strength (ksi)</th>
<th>Requirement (ksi)</th>
<th>Batch 2 Modulus (msi)</th>
<th>Batch 1 Modulus (msi)</th>
<th>Requirement (msi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 pt bend Room Temp</td>
<td>62.0</td>
<td>56.6</td>
<td>55.0</td>
<td>3.76</td>
<td>3.67</td>
<td>3.70</td>
</tr>
<tr>
<td>4 pt bend 250 F</td>
<td>36.2</td>
<td>29.3</td>
<td>30</td>
<td>2.9</td>
<td>2.69</td>
<td>3.0</td>
</tr>
<tr>
<td>Short beam shear Room Temp</td>
<td>4.08</td>
<td>3.70</td>
<td>4.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Short beam shear 250 F</td>
<td>3.20</td>
<td>2.90</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

- Reformulated (Batch 2) FAVE-O-HT meets specs for Army hoods.
M35A3 Hood Validation

Impact 4 – large radius corner

Impact 5, 6 – Small radius corner

- No permanent deformation.
- No separation of reinforcements from the hood.
- No cracks.
- Test passed.
MCM Rudder Fabrication

Composite Hub

Foam with Composite Hub and Cut outs for installation of Vertical Shear Ties

Installation of Vertical Shear Ties

After Infusion of Vertical Shear Ties

DRIVEN. WARFIGHTER FOCUSED.
MCM Rudder Fabrication

During infusion of first packet (5 layers)

After infusion of first packet

TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.
Container Testing

Andersen/Gillespie
M35A3 Hood

- The major steps in hood production are:
  - cut 3Tex 96 oz main ply
  - stiffeners consisting of a foam core and wrapping ply are purchased pre-cut
  - lay-up plies and stiffeners. Place additional reinforcement plies over the stiffeners and along the perimeter of the hood
  - bag part
  - mix resin, CoNap, and MEKP and infuse with FAVE-L vinyl ester resin or vantico 8605 epoxy resin
  - post-cure part
  - trim hood in router
  - drill holes for hardware
  - bond safety latch and handles
Bimodal Vinyl Ester Resins (BM-VE)

Low Molecular Weight VE

- Low VE molecular weight
  - Low viscosity
  - Low fracture properties

High Molecular Weight VE

- High VE molecular weight
  - High viscosity
  - High fracture properties

Reduces Styrene content to 28-38 wt.%

**Commercial Resins**

Low VOC ~ 33 wt% Sty
Standard ~ 40-50 wt% Sty


**VE molecular weight affects resin and polymer properties**

**GPC**

- VE 828
- VE 828/1004F 42/58
- VE 828/1009F 54/46
Bimodal resins have superior fracture properties.
Bio-based Rubber (BR) Toughening Agents

- Designed plant oil-based toughening agents
- Uses phase separation to capture MFA reactive diluent
- Increases toughness while decreasing styrene content and maintaining viscosity

![Graphs showing the relationship between weight fraction of toughener and G1c (J/m²), Tg (°C), and viscosity (cP)]

![Diagram illustrating phase separation of MFA and styrene]