Surfactant-Based Chemical and Biological Agent Decontaminating Solution Development

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**Surfactant-Based Chemical and Biological Agent Decontaminating Solution Development**

Background

- Current Decontaminating (Decon) Solutions (Navy HTH and Army DS-2) Are:
  - Toxic
  - Corrosive to Materials
  - Environmentally Unfriendly

  - Must Be As Effective As Current Decons
  - Effective Against Biological Agents
  - Compatible (Noncorrosive) with Military Materials
  - Environmentally “Green” and Nontoxic to User
Objectives

- Develop a Surfactant-Based Decon Solution That Will Meet JSFDS Requirements
- Most Challenging Requirements
  - Neutralization Time of 15 Minutes for VX, HD, and TGD
  - Pot Life of 12 Hours
  - Disinfect Vegetative and Endospore Forming Bacteria, Fungi, and Viruses in 15 Minutes
  - Noncorrosive to Military Materials
  - Nontoxic and Environmentally “Green”
Decon Formulation Components

- **Surfactants**
  - Use to Replace Organic/Halogenated Solvents to Solubilize Chemical Agents
  - Must Be Stable Against Oxidation and Hydrolysis
  - Utilize to Increase Biocidal Efficacy by Lowering Interfacial Tension Between Spores and Biocide

- **Peroxygen Compound**
  - Utilize as Environmentally Green Reactant for Both Chemical and Biological Agents
  - Some Peracids Available in Neat Form (Peracetic acid) and In-Situ (Commercial Detergent Technology)

- **Catalyst**
  - Promote Oxidation of the Sulfur in V and HD
  - Reported to Promote Hydrolysis at Lower pH (for G Agent Decontamination)
Decon Formulation Components - Surfactants

- Basics of Microemulsion Formulation

![Diagram of Microemulsion Formulation](image)

- Surfactant
- Lipophilic Group
- Hydrophilic Group
- Agent - Nonpolar Molecules (Liquid)
- Oxidizer - Polar Molecules (Liquid)
- Mix these 3 Components

Water-in-Oil Microemulsion

Oxidizer Salt Solution
**Microemulsion Formulation**

- Identify surfactant(s) slightly soluble in the aqueous phase
- Identify surfactant(s) slightly soluble in the oil phase
- Combine oil soluble and water soluble surfactants to reduce interfacial tension between oil and water phase to produce microemulsion
Decon Formulation Components - Surfactants

<table>
<thead>
<tr>
<th>J</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
<th>H</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>control</td>
<td>C₁₆ Diphenyloxide sulfonate</td>
<td>C₁₄-17 sec-Alkyl sulfonate</td>
<td>C₆-₁₆ Cocamidopropylamine oxide</td>
<td>C₁₀ Amine oxide</td>
<td>C₁₂ Amine oxide</td>
<td>C₁₄ Amine oxide</td>
<td>C₁₂-₁₈ Amine oxide</td>
<td>C₁₈ Amine oxide</td>
</tr>
</tbody>
</table>

Oil/Water = 20/80; Surfactant = 3%; Oil = Dibutylsulfide; Water = water + 500-mg Na carbonate
### Decon Formulation Components - Surfactants

#### Surfactant Scan – Amine Oxides

<table>
<thead>
<tr>
<th></th>
<th>J</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1/S2=</td>
<td>100/0</td>
<td>90/10</td>
<td>75/25</td>
<td>50/50</td>
<td>25/75</td>
<td>10/90</td>
<td>0/100</td>
<td></td>
</tr>
</tbody>
</table>

- O/W = 20/80; (S1+S2) = 3%; V(T) = 5-mL; O = Dibutyl sulfide, W = water + 500-mg Na carbonate
- **J**: control (no surfactant),
- **S1**: C\textsubscript{10} Amine oxide
- **S2**: di-C\textsubscript{10} Amine oxide
Decon Formulation Components - Surfactants

- **Current System - Mixed Amine Oxide Surfactant Microemulsion**

- **C<sub>10</sub> Amine oxide.** Dimethyldecylamine oxide

- **Di-C<sub>10</sub> Amine oxide.** Didecylmethylamine oxide
Decon Formulation Components - Surfactants

● Why Microemulsion?
  – Increased Stability
  – Increased Reactivity
    (Surface Area)

Lipophilic (Agent)

Hydrophilic (Oxidizer)

10 nm
Peroxogen Compounds

- **Organic Peroxides (t-Butyl hydroperoxide)**
  - Requires Catalyst to Meet Decon Reactivity Requirement
  - Stable - Does Not Require Special Handling
  - One of Two Organic Peroxides That Meet DOT Shipping Regs for Bulk Shipment

- **Peracids**
  - Strong Oxidizers
  - Broad Spectrum Disinfectants
  - Use Neat or Generate In-Situ (Tide With Bleach)
  - Stability (Handling / Storage) Can Be an Issue
Decon Formulation Components – Catalyst

- **Dimanganese-Based Complex**
  - Developed for Laundry and Detergent Industry
  - Catalyst Activates Stain ($\text{Mn}^{4+} + e^- \rightarrow \text{Mn}^{3+}$)
  - Stain More Susceptible to Bleach (Oxidation)

- **Macrocyclic Tetradeutate Liqand (TAML)**
  - Developed by Carnegie Mellon
  - Complexes the Peroxygen
  - Stable in Presence of Strong Oxidants
  - Defluoro Reported to Promote Hydrolysis and Oxidation at Lower pH
Decon Formulation Components – Catalyst

- Dimanganese-Based Complex
  - 1,4,7-Trimethyl-1,4,7-triazacyclononane ligands (Me3TACN)
Decon Formulation Components – Catalyst

- Macrocylic Tetradeutantate Ligand
  - FeMB: $X_1$ Me $X_2$ H $R_1$ Me
  - FeB: $X_1$ H $X_2$ H $R_1$ Me
  - FeF$_2$B: $X_1$ H $X_2$ H $R_1$ F
  - FeF$_2$DCB: $X_1$ Cl $X_2$ Cl $R_1$ F

![Diagram of Macrocylic Tetradeutantate Ligand]
Decon Formulation Components – Peroxygen Compound and Catalyst

Oxidation of Calmagite Dye by t-Bu Hydroperoxide

TAML FeMB and Dimanganese Catalysts

![Graph showing oxidation of Calmagite Dye by t-Bu Hydroperoxide with different catalyst concentrations.](image-url)
Decon Formulation Components – Peroxygen Compounds and Catalysts

Oxidation of Calmagite Dye by Peracetic Acid

TAML FeMB Catalyst

![Graph showing the oxidation of Calmagite dye by peracetic acid with different TAML concentrations.](image-url)
Decon Formulation Components – Peroxygen Compounds and Catalysts

Agent Decontamination by t-Bu Hydroperoxide in Microemulsion
TAML FeMB Catalyst

% Neutralized vs. Reaction Time, min

FeMB* 0.0006M (320ppm)
Amine Oxide Surfactant System
Buffer, pH 10
t-BHP (0.3M0
Agent (0.1M)
Agent Decontamination by Peracetic Acid
Uncatalyzed

Mixed Surfactant System
Buffer pH 10
Peracetic acid (0.3M)
Agent (0.1M)
Peracetic Acid (PAA) Found to Be an Effective Disinfectant

Reduction in *Bacillus globigii* after 15 minute Exposure to Candidate Solutions

<table>
<thead>
<tr>
<th></th>
<th>BG Initial CFU/mL</th>
<th>Log Reduction, CFU/mL</th>
</tr>
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<tbody>
<tr>
<td>Damox 1010 (1)</td>
<td>$10^6$</td>
<td>0 (30 min exposure)</td>
</tr>
<tr>
<td>Barlox 10S (2)</td>
<td>$10^6$</td>
<td>0 (30 min exposure)</td>
</tr>
<tr>
<td>PAA, 5%</td>
<td>$10^8$</td>
<td>4</td>
</tr>
<tr>
<td>PAA in uEm</td>
<td>$10^8$</td>
<td>8</td>
</tr>
</tbody>
</table>

1. C_{10} Amine oxide
2. di-C_{10} Amine oxide
Summary

- Microemulsions Developed From Oxidation and Hydrolysis Resistance Surfactants

- Peracids (Peracetic) Demonstrated Efficacy Against Chemical Agents (HD, VX, GD)
  - Efficacy Achieved Without Catalyst

- Peracids (Peacetic) Demonstrated Efficacy Against Biological Agent Simulant (BG)