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DEVELOPMENT OF MULTIFUNCTIONAL PERFLUORINATED POLYMER BLENDS AS AN ACTIVE BARRIER CREAM AGAINST CHEMICAL WARFARE AGENTS

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Introduction

Chemical warfare agents (CWA's) represent a real and growing threat both to U.S. Armed Forces as well as to civilians. Within the last three decades, chemical weapons have been used by the Soviets in Cambodia (yellow rain, tricothecene mycotoxins),[1] by Iraq against Iran (HD and tabun),[2] and by Iraq against its own dissident Kurdish population at Halabja (HD, $HCN_{(g)}$).[3] In the United States' experience in World War I, almost one-third of hospitalized casualties were a result of CWA's.[4] Furthermore, the 1000 casualties and 12 deaths[5] resulting from the 1995 terrorist use of sarin (GB) in Tokyo show that civilians have also become targets.

In this paper we focus on protection against two classes of CWA's: nerve agents (soman, GD) and blister agents (sulfur mustard, HD).[6] Protection against these agents in the United States Army consists of a chemically resistant outer layer of clothing (BDO) and protective mask (M40).[7] This scheme of protection allows operation in a chemically contaminated area but results in decreased performance and increased heat retention. We have investigated a material that serves as a physical barrier to CWA's *and* contains an active moiety to neutralize hazardous chemicals. This Active Topical Skin Protectant (aTSP) would be used in conjunction with other protective procedures. Herein we report the preparation, characterization, and evaluation of aTSP's.

Experimental

Suppliers for base cream materials (Polymist F® and Fomblin®) and active moieties have been previously described.[8] NMR spectra were recorded on a Varian Unity INOVA NMR at the appropriate frequency (^{1}H: 600 MHz, ^{13}C: 150 MHz, ^{31}P 242 MHz). FTIR spectra were acquired on a Nicolet 360 Avatar FTIR system. Experimental details of the *in vitro* and *in vivo* analyses of aTSP's have been reported previously.[8, 9]

Formulation of aTSP's paralleled the technique developed in the production of a *non*-active topical skin protectant (SERPACWA) barrier cream.[10] The active moiety is suspended in either Fomblin® or Polymist F® by mechanical or manual stirring. The other polymer is slowly added with vigorous mechanical stirring.

Results and Discussion

Selection of Active Components

Two criteria constrain our selection of active components. First, the barrier properties of the base cream must not be degraded by the incorporation of the compound(s). Second, the moiety must neutralize CWA's in the environment of the base cream. We have investigated over 100 active compounds organized into 4 broad classes (Table 1).

Table 1. Classes of Active Moieties.

Class of Active	Examples
Organic	S-330, Iodobenzenediacetate
Inorganic	Polymer/metal alloys (TiFeMn), Metal oxides (MgO, CaO), Polyoxometallates(POM's)
Polymers	Dendrimers, Bridged Polysilsesquioxanes, XE-555 resin
Enzymes	Organophosphorous Acid Anhydride Hydrolase (OPAA) Crosslinked Enzyme Crystals (CLEC's)

These compounds have been formulated into over 250 aTSP's and have been evaluated according to a Decision Tree Network.[9] Two organic compounds, S-330 and IBDA, have shown particular efficacy against sulfur mustard (HD) (Figure 1).

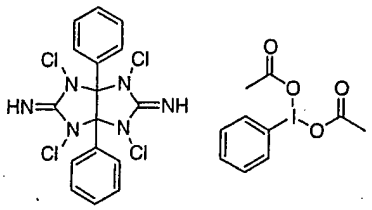

Figure 1. Structures of S-330 (1,3,4,6-tetrachloro-7, 8-diimino glycouril) and iodobenzene diacetate (IBDA).

Other constituents showing efficacy against HD include inorganic compounds, polysilsesquioxanes, dendrimers, and XE-555 resin. The best moieties against GD include inorganic oxides, metal precipitates, and dendrimers.

Characterization and Evaluation of Materials

The aTSP's are opaque white or off-white creams. Light microscopy of effective aTSP's indicates a fine dispersion of polytetrafluoroethylene particles and active moieties in the oil matrix. FTIR analysis shows peaks in the region of C-O-C (1116 cm^{-1}), CF_2 (1198 cm^{-1}), and CF_3 (1259, 978 cm^{-1}) bands.[11] The ^{13}C NMR spectrum of the perfluorinated oil itself tends to be without detail due to C-F coupling.

Using a penetration cell system[8] attached to a continuous air monitor (MINICAMS®),[12] the quantity of either GD or HD that penetrates the material was periodically monitored for 20 hours. From these data we obtain the cumulative amount of CWA that penetrates through the aTSP (Figure 2).

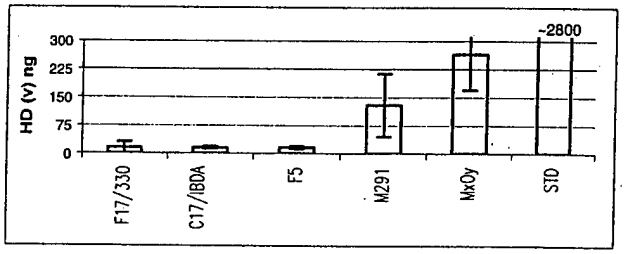

Figure 2. Cumulative amount of HD vapor through aTSP after 20 hours.

Both the dendrimer (F5) and combinations of S-330 or IBDA with dendrimers (F17, C12) are among the best reactive components, reducing the amount of HD vapor by 99.4% relative to the TSP alone. In addition, materials containing the M-291 resin or porous metal oxides (MxOy) also reduced the amount of HD by ~90%. S-330 reacts with HD to produce a variety of reaction products.[8,13,14] IBDA presumably oxidizes HD to give the non-toxic sulfoxide and the sulfone (Figure 3).

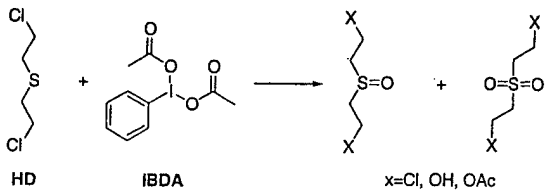

Figure 3. Proposed products from the oxidation of HD by IBDA.

In a similar fashion we evaluated the increased protection offered by various materials against GD vapor (Figure 4).

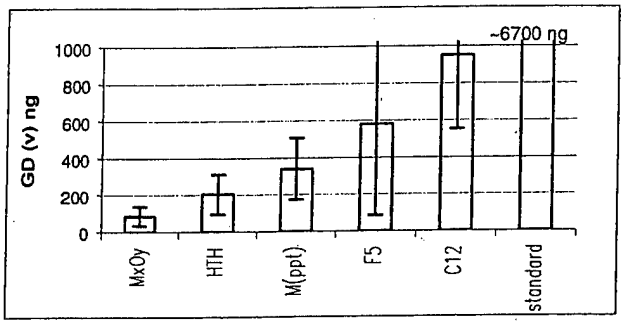

Figure 4. Cumulative amount of GD vapor through aTSP after 20 hours.

Against GD vapor, the most effective reactive components were metal oxides (up to 99% reduction) followed by metal precipitates (~95% reduction), dendrimers (F5) (91% reduction), and other dendrimers (C12) (86% reduction). As a comparison, high-test hypochlorite (HTH) resulted in a 95% reduction in total amount of GD vapor.

We have used two assays to determine the extent of neutralization with these materials: one- and two-dimensional NMR; and headspace gas chromatography mass spectroscopy (HS-GC/MS). Using the HS-GC/MS, we determined the concentration of HD, GD, or VX using a solid phase microextraction (SPME) technique (Table 2).[15]

Table 2. SPME-HS-GC/MS Results

CWA	HD	GD	VX
% Reduction	99 %	10%	31%
Active Component	S-330	F17 dendrimer	C12 dendrimer

We theorize that the disparity of the results between HD and GD is due to the limited solubility of GD in the matrix. Thus, the material is acting as a *barrier* to the GD and therefore the percentage of GD in the headspace remains high. In contrast, the HD reacts *with* the S-330 in the barrier matrix.

Because of the high viscosity of the complete material, we evaluated these materials in the perfluorinated oil with the reactive component. Thus far, we have used simulants for HD (CEES) and GD (DFP). For example, we were able to monitor the hydrolysis of DFP by the dendrimer catalyst in the perfluorinated oil by monitoring the disappearance of the ^{31}P signal for the DFP (-13.5, -9.5 ppm) to the corresponding phosphonic acid (-2.5 ppm). Using HMQC, we have detected both CEES (40, 32, 24, 11 ppm) and its hydrolysis product (58, 32, 24, 12 ppm) in the perfluorinated oil.

Conclusions

We have reported the preparation and evaluation of a composite material to act as an active barrier against CWA's. Thus far, the optimum formulations display excellent resistance against GD (99% reduction of break-through after 20 hr) and HD (99% reduction in vapor break-through after 20 hr). We determined the extent of neutralization in the materials by one and two-dimensional NMR. These materials continue to move towards advanced development with the ultimate goal of complete protection for U.S. military and civilians against CWA's.

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