Water-Based Ensemble Coating

Phase II Final Report

by:

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12345 W. 52nd Avenue
Wheat Ridge, CO 80033-1917

For:
Naval Air Warfare Center – Aircraft Division
Contract No. N68335-00-C-0326

Christopher Zech, TPOC

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13. ABSTRACT (Maximum 200 words)

In this project, TDA successfully developed and demonstrated a safe and effective prophylactic coating to achieve very effective decontamination of porous substrates with a water wash. The coating is particularly effective against G-agents (virtually complete protection), and is also very effective against sulfur mustard, agent HD, reducing heavy ($10\ g/m^2$) HD contamination by over 99.5% when rinsed with water. The coating does require considerable water to rinse and therefore may not be applicable for forward-deployed forces, but may be useful to maintain operations in, for example, a contaminated air base. The formulation is inexpensive, uses commercially available ingredients, and can be efficiently applied by a hand-operated trigger sprayer. It is non-corrosive by DOT standards, and is a minimal-to-mild ocular irritant and a borderline dermal non-irritant/irritant. It is non-flammable and self-extinguishing. Once applied, the coating remains effective indefinitely, with no degradation in performance upon storage of coated items for at least five months. The present formulation does have some limitations. While it is colorless, it is not optically clear and therefore cannot be applied to visors, night vision goggles, etc. The coating would need to be reapplied after rinsing and may be somewhat tacky and less durable in very humid environments.

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Table of Contents

1. Executive Summary 1
  1.1 Technical Approach 2
  1.2 Coating Features 3
  1.3 Coating Performance 5
  1.4 Coating Limitations 7
  1.5 Conclusions 8
2. Background and Research Objectives 9
  2.1 Technical Approach 9
3. Analysis of Efficacy Against Chemical Contamination 12
  3.1 Application of Simulant 13
  3.2 Rinsing of simulant from samples 15
  3.3 Analysis 16
4. Formulation Development 17
  4.1 Poly(Ethylene Imine) 18
  4.2 Fluorinated Surfactants 22
  4.3 Additives to Prevent Stickiness in High Humidity Environments 23
  4.4 Coating Permeability 34
  4.5 Indicators for Coating Application and Removal 40
  4.6 Fire Retardant Additives 43
  4.7 Final Coating Formulation 53
  4.8 Testing of Soiled Substrates 53
  4.9 Freeze-Thaw Testing 53
  4.10 Shelf Stability of Coating Performance 54
5. Large Scale Decontamination Testing 54
6. Live Agent Testing 60
7. Corrosiveness and Dermal/Ocular Irritation Testing 64
8. Packaging 65
9. Conclusions 66
10. References 66

Table of Figures

Figure 1. Hypothetical structure of the proposed coating around a substrate fiber. The fluorocarbon surfactant (not to scale) allows the coating to wet all substrates while protecting it from penetration by CWAs. 2
Figure 2. Common reactions of sulfur mustard. The only particularly toxic product is the fully oxidized sulfone, which is a vesicant like HD. 2
Figure 3. Hydrolytic detoxification of sarin, agent GB. 2
Figure 4. Reaction of VX with hydroxide ion gives several products, one of which (EA-2192, ~15% of total products) is only about 1/10 as toxic as VX itself. 3
Figure 5. Foam generated by rinsing Precon™ with water. 4
Figure 6. Aerosol application of Precon™. 4
Figure 7. Water vapor permeability of Nomex cloth as a function of coating application density. A typical coating density is 4-5 mg/cm^2. Apparent permeation rate decreases with time since the relative humidity in the test chamber decereases during the experiment. 4
Figure 8. Fraction of CEES remaining after rinsing for coated and uncoated Nomex samples both treated and untreated with Sandia foam. 5
Figure 9. Percent of sulfur mustard (agent HD) remaining after rinsing. 6

Figure 10. Percent of agent VX remaining after rinsing. 7
Figure 11. Percent of agent GB remaining after rinsing 7
Figure 12. Hypothetical structure of the proposed coating around a substrate fiber. The fluorocarbon surfactant (not to scale) allows the coating to wet all substrates while protecting it from penetration by CWAs 11
Figure 13. Steps in testing coating formulations for their protection against the CWA simulant: a) apply coating; b) apply a metered aerosol of simulant; c) water wash; d) extract residual simulant and analyze by GC. Between steps b) and c), the contaminated coupons were stored for one hour in small glass bottles or pitri dishes with very little headspace to prevent the contamination from evaporating. 13
Figure 14. Basic scheme of device for reproducible dosing of simulant aerosol onto samples. 13
Figure 15. Photograph of automatic contamination device used at TDA. 14
Figure 16. Diagram of Chemical Warfare Agent Simulant Spray Device. 14
Figure 17. Schematic of 2-Position Injection Valve 15
Figure 18. Automated sample washing apparatus 15
Figure 19. Photograph of automated washing apparatus. 16
Figure 20. Viscosities of Basocoll 8125, Basocoll 8139, Lupasol P as a function of polymer concentration. 30
Figure 21. Test apparatus for parallel measurement of CEES permeation rates through coatings. 35
Figure 22. The permeation data for blank, uncoated coupons to the data from coupons coated with 20% Lupasol P, 0.5% Zonyl FSA. Data was obtained by adsorbing CEES onto carbon for a specified amount of time and calculating the average permeation rate over that time period. Each data set is the average of three trials with CEES loading averaging 0.297 mg/cm^2 for the blanks and 0.283 mg/cm^2 for the coating. The average coating density was 4.965 mg/cm^2 ± 5.4%, corresponding to an average thickness of about 50 um assuming the density of the coating is 1 g/cm^3. Note both axes have logarithmic scales. .36
Figure 23: This figure compares permeation data of blank coupons to those coated with the 20%PEI, 0,5% FSA, average loading of 4.97mg/cm^2 ± 5%, and coupons coated with Coating #48 which contains 4%PEI, 20%Glass, 2.5% Flexbond, 4% Polacryl, 0.2%FSA, average loading 17.9mg/cm^2 ± 12%. 37
Figure 24: This figure shows the permeation results from silicone coupons coated with the 20% PEI, 0.5% FSA coating. The average loading for "20% PEI, 0.5% FSA" was 4.97 mg/cm^2 ± 5%. The average loading for "20% PEI, 0.5% FSA 3x Loading" was 16.88 mg/cm^2 ± 1%. 38
Figure 25: This figure shows the permeation data from the Poly(allyl)amine coating (5% PAA M.W. 60,000, 0.1%FSA) where the permeation cell sweep gas was either dry N_2, or N_2 bubbled through water. 39
Figure 26. Water Vapor Permeability of Nomex Cloth. Permeability appears to decrease as a function of time presumably because the moisture absorption from the atmosphere is more rapid than replenishment from the stock solution, lowering the relative humidity in the chamber and thereby decreasing the apparent permeation rate during the course of the experiment. 40
Figure 27. Aluminum frame for flammability testing 44
Figure 28. Digital Image of Large-Scale Contamination/Rinsing Apparatus. 55
Figure 29. Schemiatic of Large-Scale Contamination Apparatus 56
Figure 30. Agent GB remaining on coupons after rinsing gently with 150 ml water. 61
Figure 31. Agent HD remaining on rinsed Nomex coupons. 62
Figure 32. Agent VX remaining on rinsed Nomex coupons. 62
Figure 33. CEES remaining on rinsed Nomex coupons. 64

Figure 34. A Schematic Diagram Depicting the Biobarrier and Chemical Detection System of the Corrositex® Test Method. 64

Table of Tables

Table 1. Final formulation prepared in pilot batch. 3
Table 2. Characteristics of Various Poly(ethylene imine) (PEI) products tested. 18
Table 3. Efficacy of Various Poly(ethylene imine) Samples Against CEES Contamination. 19
Table 4. Physical Performance of Waterfree and P Poly(ethylene imine)s in Varying Humidities. 20
Table 5. Tensile strength of coated and uncoated Nomex fibers. 21
Table 6. Viscosity and surface tension of PEI solutions. 23
Table 7. Chemical contamination performance of coatings containing Zonyl FSA and Fluorolink 7004. 23
Table 8. Rinse test results of percentage of coating removed rinsing with 600 mL @ 20 psi. 27
Table 9. Rinse protocol adjustment with coating containing 28
Table 10. Rinse Test: Coatings with PAA or Lupasol P. 29
Table 11. Analysis of residual CEES after rinsing coatings from formulations containing 9/1/0.5 neutralized, dialyzed Catiofast PR8106/Lupasol P/Zonyl FSA and 10/0.5 PAA (65K MW) /Zonyl FSA. 31
Table 12. Analysis of Residual CEES from formulations containing Lupasol P, and either PAA (65K MW) or dialyzed Basocol 8139. 32
Table 13. Analysis of Residual CEES for coatings containg Catiofast 8106 and Basocoll 8139. 33
Table 14. Results for Rinse Analysis of Coatings Containing Poly (Vinyl Alcohol). 34
Table 15. Surfactant Testing of Coatings Containing a Single Surfactant at Two Concentrations. 41
Table 16. Surfactant Testing in Coatings Containing both Arlasolve 200 and Zonyl FSA. 42
Table 17. Coating Formulations Containing Ethoxylated Nonyl Phenol. 42
Table 18. Coating Formulation Containing Dodecyl Sulfate. 42
Table 19. Coating Formulations Containing Ethoxylated Nonyl Phenol. 43
Table 20. Coating Formulation Containing Dodecyl Sulfate. 43
Table 21. Flammability testing results for coatings with flame retardant additives. 45
Table 22. Residual CEES analysis results of coaitings containing Flame Retard and $(NH_4)H_2PO_4$. 45
Table 23. Flammability testing results for coatings containing Antiblaze products. 46
Table 24. Flammabilty testing for coatings containing mixtures of retardants or H_3PO_4. 46
Table 25. Fire Tesistance Testing for Uncoated Nomex. 47
Table 26. Fire Resistance Testing for containing 15 wt% based on total solids Phosphoric Acid. 47
Table 27. Fire Resistance Testing for containing 20 wt% based on total solids Phosphoric Acid. 48
Table 28. Fire Resistance Testing for containing 25 wt% based on total solids Phosphoric Acid. 48
Table 29. Fire Resistance Testing for containing 5 wt% based on total solids Octoguard Mix. 49
Table 30. Fire Resistance Testing for containing 10 wt% based on total solids Octoguard Mix. 49
Table 31. Fire Resistance Testing for containing 15 wt% Phosphoric Acid and 5 wt% based on total solids. 49
Table 32. Fire Resistance Testing for containing 4.6 wt% Decabromodiphenyl oxide and 0.4 wt% Phosphoric Acid based on total solids. 50
Table 33. Fire Resistance Testing for containing 9.2 wt% Decabromodiphenyl oxide and 0.8 wt% Phosphoric Acid based on total solids. 50

Table 34. Flame Resistance Test for Coatings containing 10% total DBDPO & H_3PO_4(70/30). 51
Table 35. Flame Resistance Test for Coatings containing 10% Total DBDPO & H_3PO_4(85/15). 51
Table 36. Flame Resistance Testing for Coating with 10% total DBDPO & H_3PO_4. (85/15) Variable Coating Density. 52
Table 37. Residual CEES Analysis for Coatings B(0.02) & B(0.1). 52
Table 38. Final formulation prepared in pilot batch. 53
Table 39. Residual CEES Analysis for Coated Soiled Samples. 53
Table 40. Residual CEES Analysis Final Coating Formulation. 54
Table 41. Residual CEES Analysis, Applied Coating Shelf Life. 54
Table 42. Quantification of CEES on Mannequin Without Water Rinse. 57
Table 43. Mannequin in Coated Jumpsuit, Pressure Vest, and Utility Vest. 57
Table 44. Mannequin in Coated Jumpsuit and Utility Vest. 58
Table 45. Mannequin in Poncho**. 58
Table 46. Mannequin, No dress**. 58
Table 47. Residual CEES Analysis Equipment Samples. 59
Table 48. Rinse Test of Flight Equipment Swatch Samples. 59
Table 49. Preliminary Results Live Agent Testing Batch #2. 61
Table 50. Residual CEES Analysis for Varied Foam Application & Soak Time. 63

1. Executive Summary

The U.S. military has a foreseeable need to restore and continue operations in a chemically contaminated battlespace. One potential limitation for these continuing operations is a supply of clean, non-contaminated materiel for the fighting personnel to use and wear. Of particular concern to our sponsors in the Naval Air Warfare Center was the logistics burden associated with replacing the aircrew ensemble and associated equipment for every airman after every sortie in a contaminated battlespace. We therefore sought to develop a coating that would allow rapid, safe decontamination and reuse of equipment exposed to chemical contamination.

Such a coating would be applied at least hours before a mission in a contaminated area. After returning to an airbase or carrier, the air-crews would remove their contaminated items and these would be thoroughly rinsed to decontaminate them. The rinsed items would be dried, tested for safety (residual contamination), and recoated/reused if safe. During development, we assumed that water was available at pressures and flow rates typical of a standard garden hose (several gallons per minute at 40 psig). As a target, we assumed that removing 99.9% of chemical contamination would be a minimum for a successful product/system. Although it represents an exceptionally high contamination loading, we typically challenged our developing coating formulations with the standard 10 g/m^2 of contaminant, be it a simulant in our laboratory or a live agent at an appropriate surety facility.

A prophylactic product would have to compete with a variety of currently available options to address chemical contamination after the fact. Chief among these is simply disposing of the contaminated items and replacing them with new supplies from stockpile. Unfortunately, this can become moderately expensive and inconvenient, since several replacement items would need to be stockpiled to prepare for the contingency of continuing operations in a contaminated environment and the shipping and storage of these replacement items would present a large logistics burden. Contaminated items might also be subject to decontamination with one of a variety of current decontaminant solutions.

Decontamination solutions are unlikely to be acceptable, however. The old decontamination solution, DS2, could effectively decontaminate the surfaces of many items, but is known for its severe corrosive interactions and decontaminated materials would likely suffer significant mechanical damage. More modern decontaminants, like the hypochlorites High-test Hypochlorite (HTH) and Supertropical Bleach (STB) and the peroxide-based decontaminants "Sandia foam" and Decon Green may all serve to decontaminate the surface of materials with minimal risk of collateral damage, but none of these decontaminants is likely to be able to decontaminate the interior of plastics or porous materials where the agents may be absorbed, wicked in, or otherwise physically separated from the decontaminants.

To compete with these options, we designed a water-based coating that inhibits chemical agents from diffusing into coated equipment and allows decontamination by simply rinsing with water. We sought to make it very inexpensive, optically clear, thin, flexible, and safe to use. To our knowledge, this sort of prophylactic approach toward decontamination had not been previously attempted. Our minimum goal was to remove at least 99.9% (3X) of heavy contamination (10 g/m^2) with a water rinse, with a target of 99.999% removal (5X) of agents HD, VX, and the fluorophosponate nerve agents as represented by agent GB. Below, we summarize the development of Precon™, the decontamination-aid coating developed at TDA Research, Inc.

1.1 Technical Approach

The general idea was to develop a reactive barrier that would wet all surfaces and surround cloth fibers without filling the pores in a cloth weave. The outer layer of the coating comprises a fluorinated surfactant to aid wetting and to provide a lipophobic barrier to agent permeation. The bulk of the coating comprises soluble polyamines that react with chemical agents to detoxify them before they can permeate to and diffuse into the substrate. Figure 1 shows the technical concept.

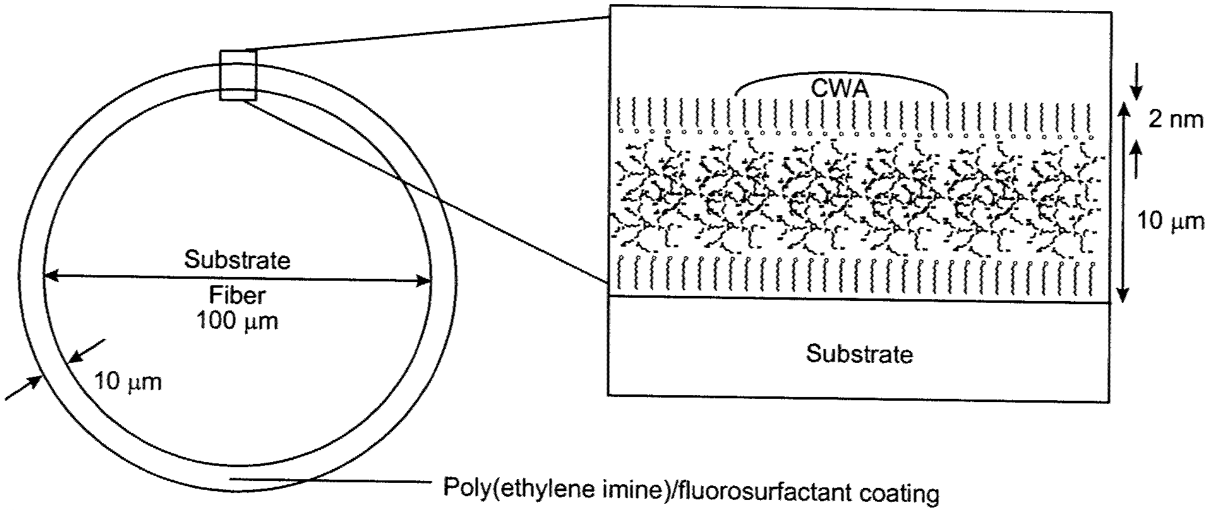


Figure 1. Hypothetical structure of the proposed coating around a substrate fiber. The fluorocarbon surfactant (not to scale) allows the coating to wet all substrates while protecting it from penetration by CWAs.

Polyamines react with the three primary classes of chemical agents: mustards, G-type nerve agents, and agent VX. For mustards, the polyamines can serve as sacrificial nucleophiles for the alkylation reaction shown in Figure 1, or they may serve as general bases to catalyze the hydrolysis of mustards to the corresponding glycols. Both of these reactions produce strong acids which are neutralized by the amine groups.

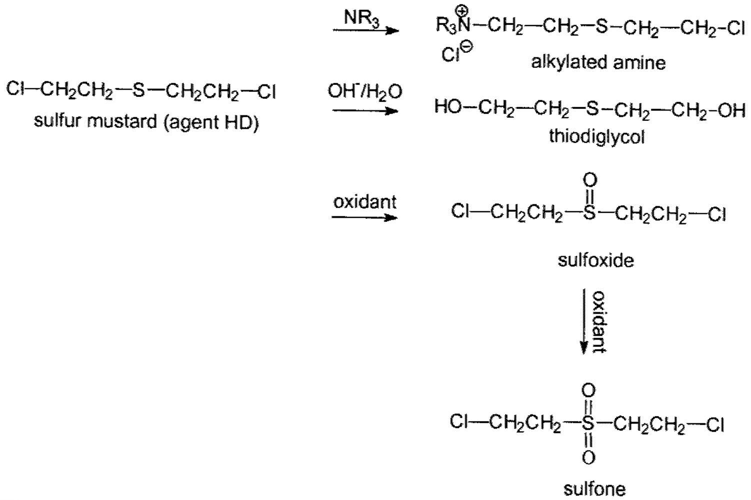


Figure 2. Common reactions of sulfur mustard. The only particularly toxic product is the fully oxidized sulfone, which is a vesicant like HD.

The fluorophosphonate G-agents are readily susceptible to detoxification by hydrolysis of the P-F bond (Figure 3). As with hydrolysis of HD, the hydrolysis of G-agents produces strong acids (in this case both hydrofluoric acid and the phosphorous-based acid).

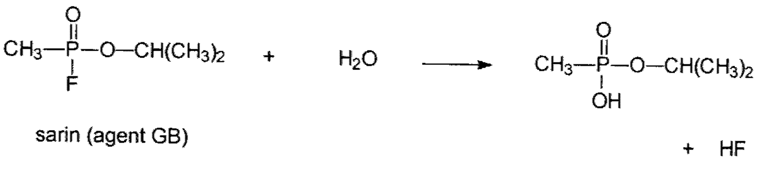
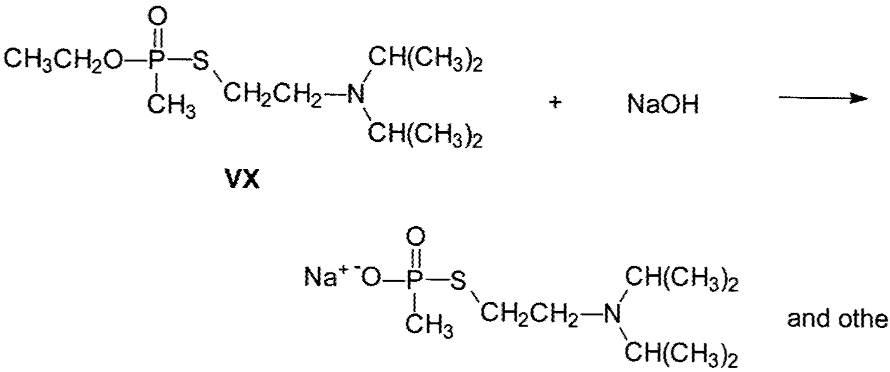


Figure 3. Hydrolytic detoxification of sarin, agent GB.

While G-agents have been decontaminated by a variety of oxidant solutions and solid powders (see e.g. Wartell 1999, Table 5-3), all of these systems have had aqueous or basic sites capable of hydrolytic detoxification, and there is no evidence of exclusively oxidative decontamination reactions for any of the G-agents. Polyamines will both catalyze the hydrolytic detoxification of G-agents and neutralize the toxic and acidic reaction products.

The nerve agent VX presents a particular problem in decontamination. It reacts rather slowly with aqueous bases including polyamines, and one of the hydrolysis products is still very toxic and not readily susceptible to further hydrolysis (Figure 4). Full detoxification of VX requires selective cleavage of the P-S bond, which can be accomplished by hydrolysis, especially with a moderately basic nucleophile like phosphonate or hydroperoxide anions (Yang et al. 1995 and 1997). Organophosphorous hydrolases have recently been modified to have broader catalytic activity against a wide variety of organophosphate esters, including the V- and G- nerve agents (Di Sioudi et al. 1999a, 1999b). These and similar catalysts can selectively cleave the critical P-S bond in phosphorothioates and might eventually be used in conjunction with polyamines, where the polyamines would provide a secondary role of neutralizing the acid produced, preventing product inhibition from slowing the catalytic reaction rates.



VX

and other products

(EA-2192, still very toxic)

Figure 4. Reaction of VX with hydroxide ion gives several products, one of which (EA-2192, ~15% of total products) is only about 1/10 as toxic as VX itself.

1.2 Coating Features

Table 1. Final formulation prepared in pilot batch.

Component	**Wt % solids**
Lupasol P, Poly(ethylene imine)	12.0 %
Celvol 24-203, Poly(vinyl alcohol)	4.0 %
Zonyl FSA	0.32 %
Arlasolve 200	0.32 %
Sodium Dodecyl Sulfate	0.032 %
Carboxy Methyl Cellulose	0.006 %
Decabromodiphenyl Oxide	1.57 %
Phosphoric Acid	0.27 %
Water	81.482 %

We formulated Precon™ with commercially available ingredients, making it inexpensive to produce. Table 1 shows our final formulation. We have successfully packaged the coating both in a single component aerosol and in a simple hand operated spray bottle. We prefer the hand operated trigger sprayers, because the aerosol packaging severely limits

Figure 5. Aerosol application of Precon™.

Figure 6. Foam generated by rinsing Precon™ with water.

the deliverable quantity of liquid. To apply the coating, it is simply sprayed onto the substrate from a distance of about 2-3 feet, as shown in Figure 5, until the substrate looks wet but is not yet saturated with the liquid coating formulation. The coating then dries on the substrate and dries to a loading of about 0.05 kg/m^2.

To make it easy to use, we formulated Precon™ with surfactants that produce foam when the coating is rinsed (see Figure 6), removing both contamination and coating from the substrate. In practice, the substrate will be rinsed until the foam production diminishes, which indicates that the coating and the contamination have been removed. In practice, for a full aircrew ensemble, removing the coating and contamination will require several minutes of rinsing.

Precon™ is safe to use. In the ASTM test for flammability of fabrics (ASTM F1358), coated Nomex cloth is no more flammable than uncoated Nomex. Based *in vitro* eye and skin irritation tests conducted by InVitro International (Irritection assay, Irvine, CA), the formulation is classified as a borderline mild irritant/non-irritant to the skin and eyes. Precon™ also should not contribute significantly to heat stress, since coated cloth items retain their water vapor permeability as shown in Figure 7.

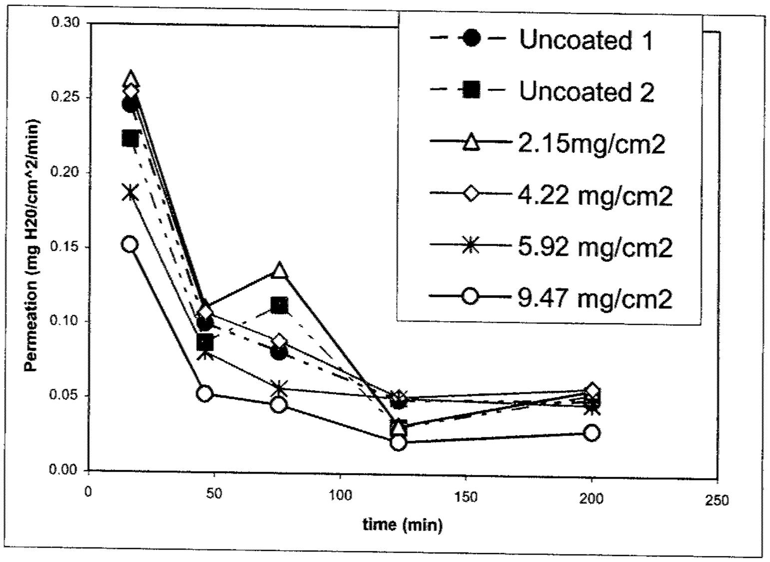


Figure 7. Water vapor permeability of Nomex cloth as a function of coating application density. A typical coating density is 4-5 mg/cm^2. Apparent permeation rate decreases with time since the relative humidity in the test chamber decereases during the experiment.

1.3 Coating Performance

Testing the coating performance against chemical agents and simulants consisted of contaminating the 4 cm diameter Nomex coupons with an aerosol of the agent (ca. 10 g/m^2), storing each of the contaminated coupons in a small glass vial or petri dish for 1 hour, rinsing each with a controlled amount of water, then extracting the remaining agent from the coupons and quantifying the amount of agent left in/on the sample by gas chromatography. Both the aerosol agent delivery device and the rinsing apparatus were mechanized to remove operator bias in contamination and rinsing procedures. Contaminant loading, measured gravimetrically, was typically reproducible to within 10%.

We tested the coating in our laboratories, using a chemical agent simulant, chloroethyl ethyl sulfide (CEES), as a surrogate for live agents. Figure 8 shows the fraction of a chemical agent simulant, chloroethyl ethyl sulfide (CEES), remaining on coated and uncoated (blank) Nomex coupons for samples tested the day after the coating was applied. The coating formulation for these tests (and the tests with agents HD and VX) was slightly different from the final formulation noted above in that it lacked fire retardants, but was generally very similar. Samples were stored for 1 hour between contamination and rinsing. Both the second and fourth sample sets in the figure were treated for five minutes immediately before rinsing with twice the manufacturer's recommended dose of oxidizing Sandia foam (Modec, Inc.) to determine both the relative efficacy of the developing coating and the compatibility of the coating with a peroxide-based decontaminant. These results with CEES suggest that the developing coating is at least as effective as the Sandia foam product and can advantageously be used in conjunction with the Sandia foam.

With similar testing, we have determined that after the coating dries, it is effective indefinitely. For coated items stored since they were coated, we have demonstrated that efficacy does not diminish in five months. We do not have data, however, on the expected lifetime of the coating on a substrate in daily use.

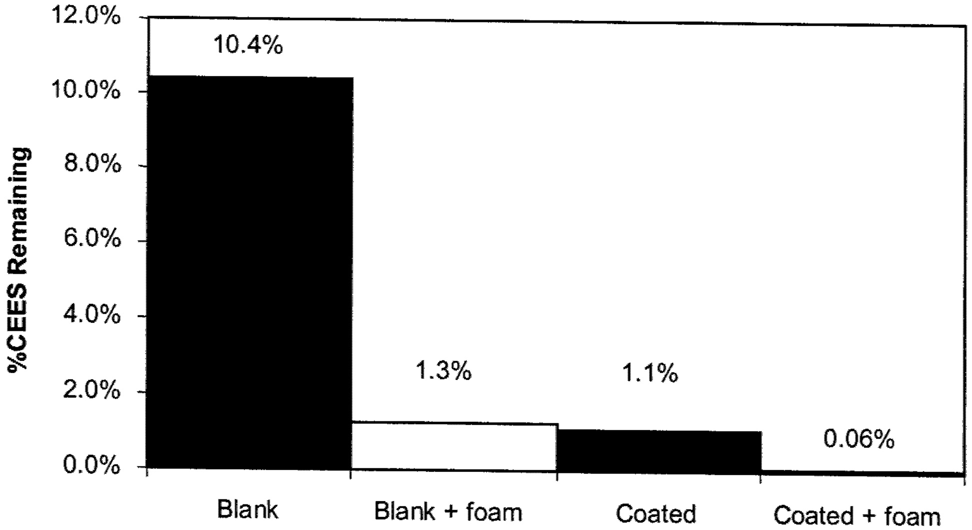


Figure 8. Fraction of CEES remaining after rinsing for coated and uncoated Nomex samples both treated and untreated with Sandia foam.

When the coating formulation was approaching completion (formulation: 7.5% Lupasol P solids, 2.5% PVOH solids, 0.1% Zonyl FSA, and 0.1% Arlasolve 200), we sent coated and blank Nomex samples to the Calspan/University of Buffalo Research Center (CUBRC) for live agent testing. Figure 9 shows the results with sulfur mustard, agent HD. Clearly, agent HD is much less water soluble than CEES and does not rinse off of uncoated coupons. The Sandia foam is not particularly effective at reducing the level of mustard contamination, reducing the percentage of recovered agent from 69% (untreated) to only about 40% of the nominal 10 g/m^2 contamination. In contrast, the precoated samples retained less than 1% of the applied HD aerosol after rinsing (approaching our 3X goal), and the cleanliness of the coupons was not significantly improved by the application of oxidizing foam before rinsing. For several samples, the staff at CUBRC collected the rinse water and extracted it to determine the effectiveness of the foam and the foam/coating combination in detoxifying the chemical agent. For each sample type, a 1 liter rinse volume was split into two 500 mL portions. One was extracted immediately following the rinse step, and the other was extracted 1 hour later. Results indicate that against HD, the amount of agent present in the rinse portion after 1 hour decreases on average by 97%, with coating/foam combinations having lower agent concentrations.

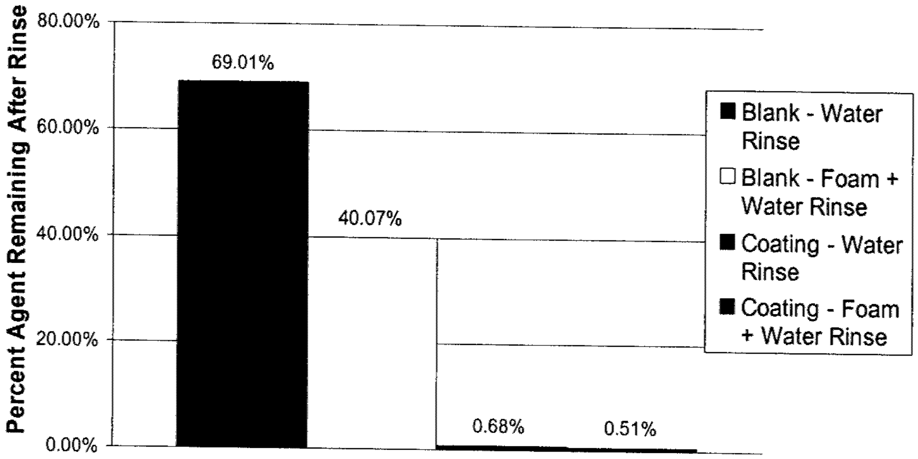


Figure 9. Percent of sulfur mustard (agent HD) remaining after rinsing.

Figure 10 shows the results from testing this same formulation against agent VX. VX is moderately water soluble, and a simple water rinse removes almost 99% of the agent from even untreated Nomex. The Sandia foam treatment (5 minutes at twice the manufacturer's recommended dose) significantly reduces the residual VX contamination, whether or not the samples were pretreated with the coating. This data clearly shows that Precon™ is not particularly effective against agent VX, and that it does not inhibit the detoxifying effects of oxidizing decontaminants. VX is also not rapidly detoxified in the rinse water, where the concentration of the agent decreases by an average of only 14% in one hour.

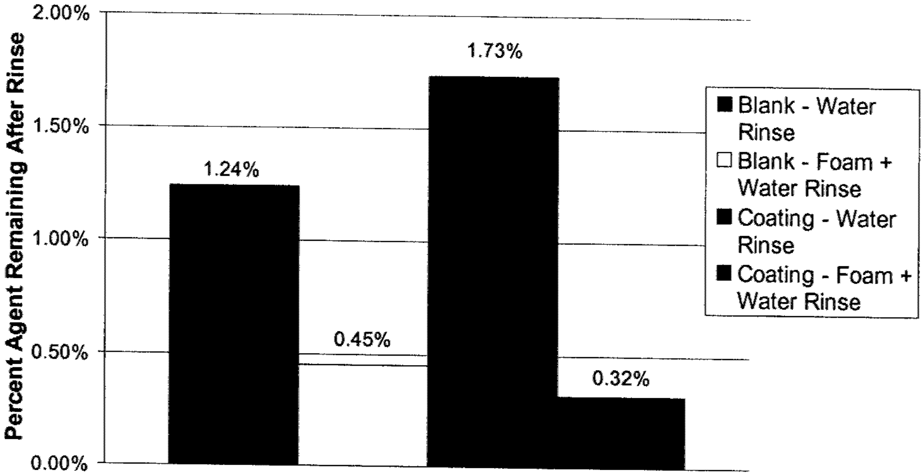


Figure 10. Percent of agent VX remaining after rinsing.

The G-agents are readily detoxified by water and are somewhat water soluble, so the removal of better than 99.9% of the applied agent GB (sarin) with a water rinse is not surprising (Figure 11). Application of a polyamine coating (an early formulation containing 40% of the low molecular weight polyamine Lupasol G20 and 1% of the fluorinated surfactant Zonyl FSA) allows contamination removal nearly to the 5X level (99.999%). In all samples tested, there was never any residual agent GB in the rinse water. We did not test Precon™ in conjunction with the Sandia foam against GB.

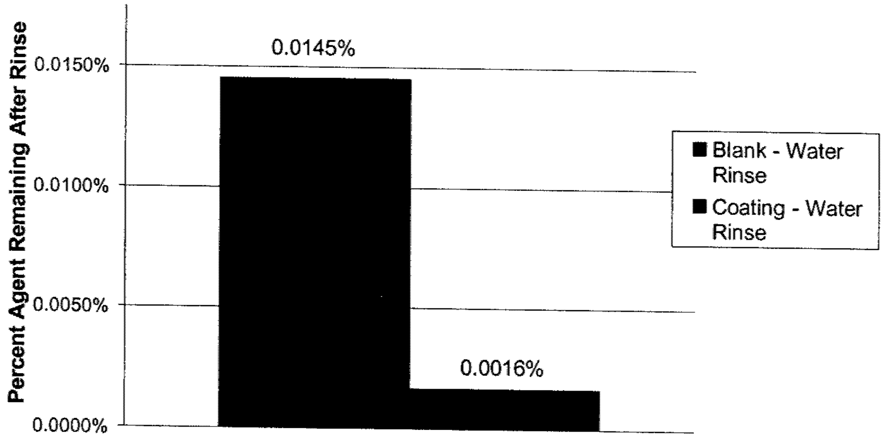


Figure 11. Percent of agent GB remaining after rinsing

1.4 Coating Limitations

During our formulation efforts, we noticed that the coating formulation has several limitations which may be important for particular applications. While colorless, the coating does not dry optically clear and is therefore not suitable for application onto optical surfaces such as visors or night vision goggles. Since the coating is designed to rinse off with the chemical contamination, the coating must be reapplied after rinsing or laundering. Proper rinsing of a substrate will require a considerable amount of water, making Precon™ unsuitable for far-forward use on the battlefield but potentially supportable at most air bases. Finally, in very humid environments (e.g. r.h.>90%), the coating can feel slightly tacky on non-porous substrates, and it may not therefore be well suited to jungle environments.

A large portion of our technical effort in this Phase II project was directed at mitigating the hygroscopic nature of the reactive polyamine ingredients. We investigated a variety of polyamines, only to discover that the most hygroscopic happened to be the most effective against chemical contamination. We also attempted to add solid particulates to improve the feel of the coating, but these efforts led largely to formulations that dried to ineffective sticky pastes. Ultimately, we found that the coating tackiness can be reduced at the expense of slightly decreased efficacy against chemical agents by adding a small portion of poly(vinyl alcohol) to the poly(ethylene imine)-based formulation. There is an unusual reaction between the two polymers that does not appear in the scientific literature: the two polymers appear to form robust gels when mixed at sufficiently high concentrations, presumably through multiple hydrogen bonds. A dilute coating formulation sets to a very slightly hygroscopic, flexible solid as the solvent (water) evaporates

1.5 Conclusions

In a SBIR research and development project, TDA has formulated an inexpensive water-based coating that provides protection of coated equipment from contamination by chemical warfare agents. Should the coated materials be exposed to chemical agents, the agents and the coating can be rinsed off with a water wash. More than 99% of agent HD is removed from the coated substrate when rinsed with water, compared to less than 50% rinsing off of a similarly treated uncoated control. Against agent HD, it is much more effective than a commercially available peroxide-based decontaminant we tested. The coating is also particularly effective against G-agents, and does not hinder the oxidative detoxification of agent VX. The coating has been successfully packaged in both aerosol cans and unpressurized trigger sprayers.

2. Background and Research Objectives

Chemical and biological warfare are among the most serious threats facing the U.S. today. The U.S. government and its contractors have developed and deployed a variety of defenses against chemical and biological weapons, from carbon-cloth adsorbent suits to filtration masks and decontamination solutions. Like many personnel, aircrews are protected by air supply masks and carbon-cloth suits. These aircrews are also required to wear a considerable amount of specialized gear over their protective layer. This ensemble includes the flight helmet and visor, the survival vest and air supply apparatus. Currently there is no suitable technique for decontaminating these expensive items and replacement equipment is scarce at the battlefront. Thus, even low levels of comtamination decrease the efficiency and safety of combat personnel. In Phase I of this SBIR project, TDA Research, Inc. (TDA) demonstrated an inexpensive spray-on coating that prevents chemical warfare agents (CWAs) from soaking into the gear and allows the ensembles to be decontaminated with a simple water wash.

This clear, water-based coating was further developed in Phase II and would facilitate the decontamination and reuse of the equipment to which it is applied, thus minimizing the logistics burden of maintaining a large supply of replacement gear. The flight crew will be protected from CWAs by a layer of adsorbent carbon cloth while the coating (probable trade name: Precon™) protects their external survival vest and life support equipment. Precon™ should also provide some added protection to the flight crew upon exposure to CWAs. This coating may have applications in other Services as well, where expensive equipment that is difficult to decontaminate could be protected from contamination. Also, Precon™ may have application in civilian markets where it could be adopted by the agrochemical industry for protection from pesticides, and by hazardous materials response teams and emergency medical personnel responding to potential hazardous materials threats.

2.1 Technical Approach

Our general approach was to develop a clear coating that would not allow the penetration of CWAs through to the substrate. This would leave the CWAs present on the surface where they could be easily removed from the substrate. Specifically, the coatings proposed and developed at TDA consist primarily of a polyamine and a fluorinated surfactant in a water matrix; other additives include flame retardants, poly(vinyl alcohol) to minimize tackiness at high humidity, and foaming surfactants to indicate rinsing effectiveness. The exceptional surface tension reductions afforded by fluorinated surfactants allow their aqueous solutions (which contain the amine decontamination agents) to wet and spread completely over even the most hydrophobic surfaces; without the surfactants, the polyamine solution would bead-up on the surface and the CWAs could soak into the equipment in the unprotected spaces between the drops. Furthermore, because lipophilic molecules like CWAs do not dissolve well in perfluoroalkyl chains, the fluorinated surfactant was also expected to hinder permeation of the CWAs. Since amines are known decontamination agents, the polyamine component was expected to scavenge the small amounts of CWA that penetrated the top fluorinated surface.

The essential feature of any effective chemical-protective coating is its ability to prevent penetration of the CWA aerosols into the ensemble materials (e.g. nylon, fiberglass, butyl rubber, polycarbonate). Preventing penetration of CWA aerosols into the ensemble materials is critical because, once the CWA has penetrated the surface, superficial cleaning will not remove the CWA from the material and it will slowly diffuse out, posing a serious residual risk. Even if such latent contamination is not a direct health threat, it may set off chemical contamination alarms, resulting in decreased fighting efficiency for nearby troops.

A suitable coating must be clear so as not to affect camouflage, chemically compatible with all the substrate materials, and should be water-based. The aerosol coating must wet the ensemble materials and not bead up even on low surface energy materials. Wetting the ensemble surfaces is necessary so that there are no gaps in the coating to allow the CWAs through. In order to make a water based coating completely cover the hydrophobic ensemble materials, we incorporated surfactants to lower the surface tension of the solution and allow it to wet the surfaces. TDA has identified and employed several fluorocarbon surfactants that provide excellent protection because they are extremely effective at lowering surface tension and because they are lipophobic. That is, unlike hydrocarbon and silicone surfactants, fluorocarbon surfactants will hinder the penetration of lipophilic CWAs.

However, an aqueous solution of fluorocarbon surfactant alone will not provide sufficient protection; a small amount of CWAs will penetrate a monolayer of any organic material. In addition to the surfactant, then, we included a material to scavenge the residual CWA that penetrates the surfactant layer. Specifically, TDA incorporated a hyperbranched polyamine, poly(ethylene imine) (PEI, Lupasol P from BASF), into this coating formulation to deactivate any CWA that leaks through the surfactant layer. Amines have been widely used in decontamination solutions and will react with or catalyze the hydrolysis of most CWAs. Polyamines are more nucleophilic than monomeric amines and should therefore be more active decontaminants (Koper et al. 1997), both for direct alkylation reactions by HD (Brown 1995) and for hydrolysis of V- and G-agents (Schwarzenbach et al. 1993). By minimizing polymer entanglements, hyperbranched polymers exhibit significantly lower viscosities than chemically similar linear polymers (Newkome et al. 1996), and a low viscosity is advantageous because it facilitates atomization of the liquid into an aerosol spray and improves the wetting of the coating droplets on the substrate materials.

Figure 12 depicts a hypothetical cross section of Precon™ coating covering the surface of a fiber. We assume that the coating self-assembles into a PEI layer sandwiched between two thin sheets of fluorocarbon surfactant, since this would be the lowest surface energy structure. The fluorinated layer at the air interface prevents the CWA aerosol from wetting the substrate while the PEI layer decontaminates the CWA that manages to penetrate the top surface layer. Throughout this project, we have noted that coatings that have been allowed to dry overnight still contained on the order of 10% water by weight, which bodes well for their activity, by hydrolysis, against V- and G- series agents. For example, pesticide relatives of V- and G-agents would be expected to hydrolyze from 100 to 10,000 times faster in the presence of both water and our polyamine decontaminant than in the presence of water alone (Schwarzenbach et al 1993). Instead of having a half-life on the order of 50 days, a typical organophosphate ester might be all but neutralized after one hour. In practice, these polyamines were found to be very reactive with G-agents, but not particularly reactive with agent VX.

While all the components of the coating are soluble or dispersible in water, the coating was formulated to be solid enough to not wash off in a simple rain, but the impingement of a water stream from a hose would be sufficient to remove both the coating and the CWA that remains on the coating surface. The wash water contains the polyamine decontaminant and may therefore deactivate the agents with no further decontaminant addition; live agent testing suggested good activity against G-agents and moderate neutralizing activity against agent HD.

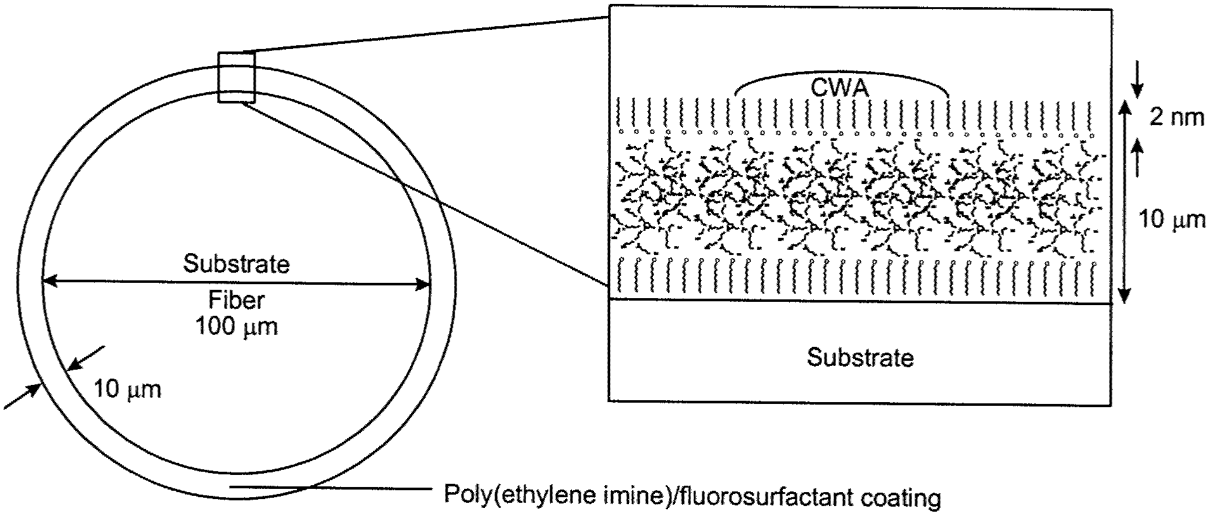


Figure 12. Hypothetical structure of the proposed coating around a substrate fiber. The fluorocarbon surfactant (not to scale) allows the coating to wet all substrates while protecting it from penetration by CWAs.

Other approaches to preventing CWA penetration are also possible, but not so attractive. For example, one could imagine a barrier coating that seals the ensemble from all exposure to the atmosphere, similar to a shrink-wrap. Such a coating would need to be flexible, allowing for ease of movement, but it would also have to be rather thick to be an effective barrier (since flexible coatings tend to be quite permeable), making for a much heavier coating. Unlike commercial shrink-wraps, this barrier coating would have to be chemically lipophobic to minimize the solubility of the chemical agents; flexible lipophilic silicones would not suffice. Perhaps some hydrophilic derivative of a fluorinated silicone polymer would begin to incorporate these properties, but these materials would be very expensive (~$50/lb.), would require considerable synthetic effort, and would likely be difficult to apply due to their low solubility in water. In contrast, Precon™ should cost only about $10/lb when dry, uses commercially available materials, and can be sprayed as an aqueous aerosol.

Alternatively, one might consider an adsorbent coating that would detain the chemical agents and hinder diffusion to the substrate interface. Consideration of the size scales of the coatings shows why this approach is not viable: a typical aerosol droplet of CWA might be 5 μm in diameter and contain 20 μm^3 CWA; an adsorbent coating, with an approximate capacity of 10 mg CWA per gram of coating, would need to be roughly 100 μm thick to adsorb the CWA. Unfortunately, it is not possible to coat the threads of a woven material with a 100 μm thick film because a typical fiber thickness is on the order of 50 μm, with the space between fibers being considerably less. So an ensemble coating designed to simply adsorb CWAs would begin to look like the solid, flexible, barrier coatings described in the previous paragraph and would have many of the same limitations, including chemical synthesis of new materials.

The overall goal of this project was to provide the military with an effective, inexpensive, easily applied coating that will prevent contamination of various substrates when they are exposed to chemical warfare agents. Specifically, the objectives were to:

1. Optimize the coating formulation, paying special attention to the formulation performance against live agents;

2. Investigate possible uses of the coating throughout the military to ensure the widest possible utility; and
3. Prepare and field test a pilot batch of the finished coating.

As described below, with the exception of field testing the pilot batch, these goals were met in this Phase II project.

3. Analysis of Efficacy Against Chemical Contamination

In this section we describe the test procedure we used to evaluate the efficacy of the coating formulations against chemical contamination. Many factors are discussed including choice of substrate, methods for contamination and decontamination, and analytic procedures to quantify the effectiveness of decontamination.

For our testing we selected Nomex, the nylon cloth that makes up the flight suit, as a representative substrate that is difficult to decontaminate since it has porosity and provides plenty of opportunity for agent to hide. The Naval Air Warfare Center supplied us with a cloth sample to get started in our testing. Once we depleted our supply of Nomex provided by the Navy, we obtained a new supply from Noah Lamport Inc. In continuing our evaluation of the coating formulation, it was discovered that the blanks cut from the new supply of Nomex were performing different than our previous supply. We suspected that this nylon was chemically treated by the manufacturer and had additional resistance to chemical contamination. Upon further inquiry we found Nomex from Flight Suits Inc. that more closely matched our original supply from NAWC; we used this Nomex source for the bulk of our testing.

The general procedure we used for analysis of coating performance against chemical contamination is shown in Figure 13. For this test procedure, Nomex samples were cut in circles with an area of 12.6 cm^2. The coating formulation to be tested was applied to the Nomex coupon to yield a coating density in the range of 5 - 6 mg dried coating solids per square centimeter of fabric. A simulant for HD, 2-chloroethyl ethyl sulfide (CEES), was applied coated Nomex coupon in an aerosol using an automated contamination device that allowed for a reproducible dosing of simulant. The samples were then stored in a small vial or bottle with very little headspace for one hour. The contaminated coupon was then rinsed using an automated apparatus which delivered a metered amount of water at a set pressure and flow rate. After rinsing, the Nomex coupon was extracted with acetone and the quantity of CEES remaining on the coupon after rinsing was determined by gas chromatographic analysis of that extract. Uncoated Nomex coupons were analyzed with the same procedure to compare residual CEES and determine the efficacy of the coating. Better coatings resulted in lower amounts of residual simulant after rinsing.

The next section describes the details of the automated devices for chemical aerosol delivery and reproducible rinsing. We built two of each device, one in Phase I for in-house use and another in Phase II for shipment to a surety facility where they were used to conduct similar tests with live chemical warfare agents.

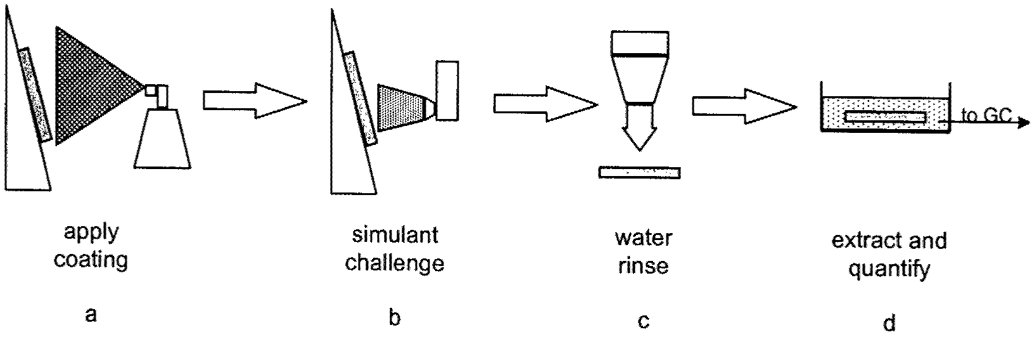


Figure 13. Steps in testing coating formulations for their protection against the CWA simulant: a) apply coating; b) apply a metered aerosol of simulant; c) water wash; d) extract residual simulant and analyze by GC. Between steps b) and c), the contaminated coupons were stored for one hour in small glass bottles or pitri dishes with very little headspace to prevent the contamination from evaporating.

3.1 Application of Simulant

In order to test the resistance of TDA's coatings to warfare agent simulants, TDA constructed in Phase I a metered aerosol delivery device to reproducibly contaminate the sample surfaces with a fixed amount of a chemical warfare agent simulant, CEES. In Phase II, and identical apparatus was constructed and shipped to the Calspan/University of Buffalo Research Center (CUBRC) for live agent testing. To reproducibly deliver a metered aerosol of a liquid chemical, we integrated a Valco, 2-position, 6-port C-22 Cheminert sample injection valve with a 10 ml Kontes brand reagent sprayer, purchased from Fisher Scientific. The basic scheme of this device is shown in Figure 14. The amount of simulant delivered is easily changed by replacing the sample loop with another calibrated for the desired volume; TDA worked typically with a 100 µl Teflon injection loop. Figure 15 is a digital image of the actual device used at TDA and Figure 16 shows a schematic diagram of the device.

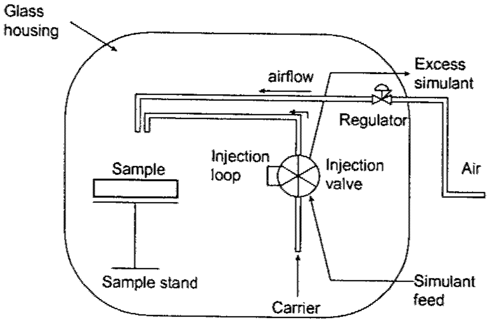


Figure 14. Basic scheme of device for reproducible dosing of simulant aerosol onto samples.

In operation, house air at 100 psig is fed to a regulator at the beginning of the system where the pressure is reduced to approximately 6 psig. The air stream is split at this point to supply the aspirator with air for atomizing and entraining the warfare agent simulant, which airflow can be stopped by means of a ball valve (V-1, in Figure 16), and to supply a three way valve (3WV-1) where the air is either used to pressurize the sample reservoir containing the warfare agent simulant or directed as carrier gas to the sampling valve (SV-1). When the sample reservoir is pressurized, the flowrate of simulant can be controlled using the Teflon needle valve (NV-1) between the reservoir and the sampling valve. Once the simulant enters the sampling valve, it either fills the sample loop, or goes directly to the waste reservoir, depending on the position of the injection valve (Figure 17).

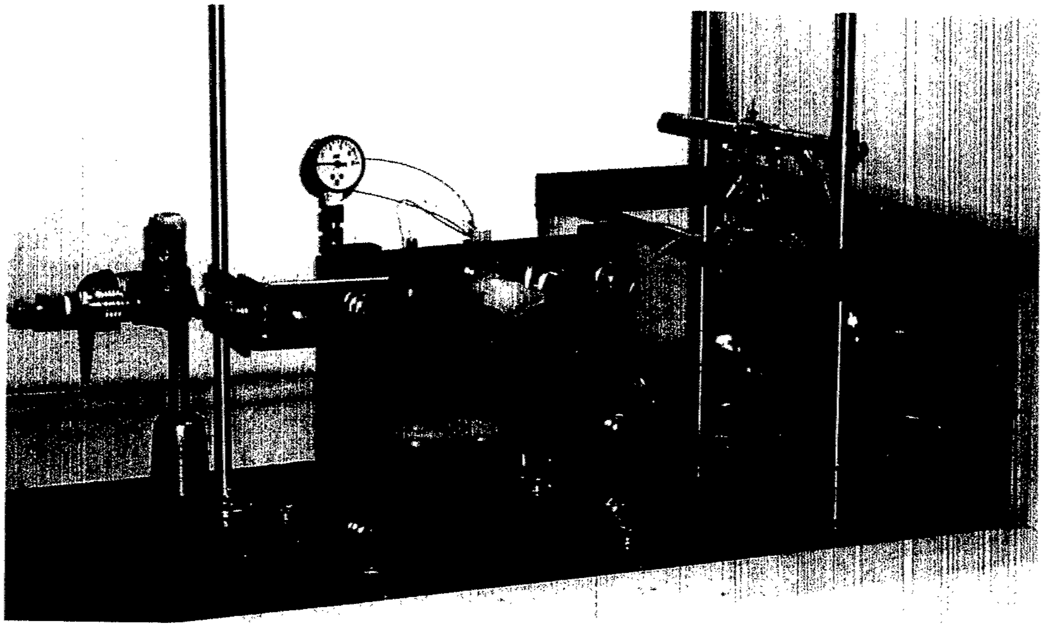


Figure 15. Photograph of automatic contamination device used at TDA.

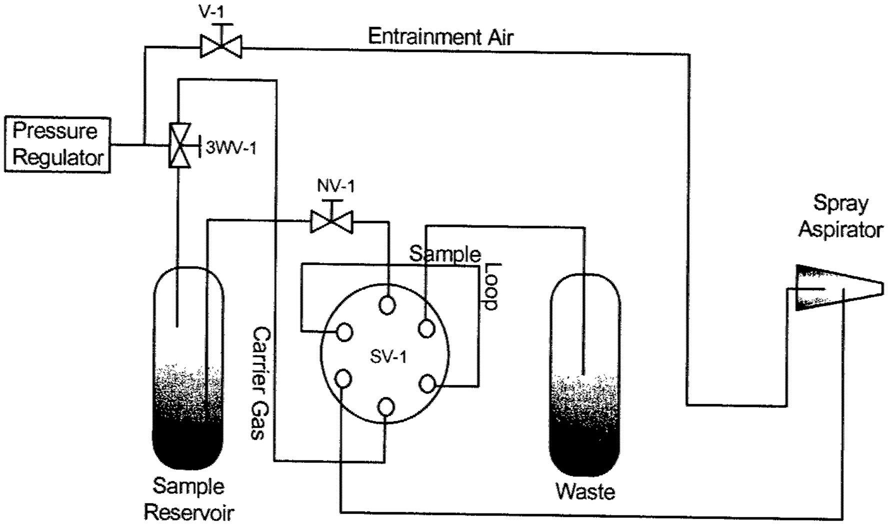


Figure 16. Diagram of Chemical Warfare Agent Simulant Spray Device.

During typical operation, once the sample loop has filled, the needle valve is closed to prevent excessive use of the warfare agent simulant. The operator then actuates ball valve V-1, initiating the flow of entrainment air through the aspirator, and then subsequently actuates the three way valve, 3WV-1, redirecting air through the sample valve as carrier gas. By actuating the sampling valve, SV-1, the air sweeps simulant out of the sample loop to the spray aspirator where it is atomized into a mist and deposited on the substrate placed in the target area. To prevent excessive evaporation of the deposited simulant, the operator then immediately shuts off the entrainment air by returning V-1 to its original position and closing 3WV-1.

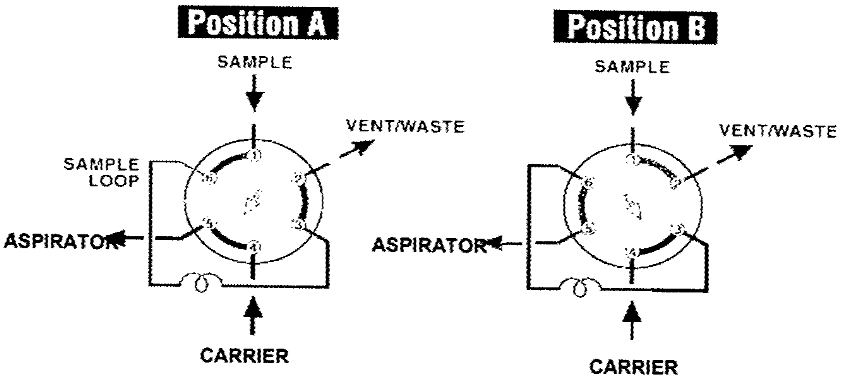


Figure 17. Schematic of 2-Position Injection Valve.

This device reproducibly delivers a fixed amount of aerosol to the sample surface. Applying CEES to paper samples and extracting these samples with toluene for GC analysis (ECLD detector) revealed an average contamination of 34.31 mg CEES ± 2.4% standard error. Preliminary tests with water suggested excellent reproducibility, with an average of 106.6 mg ± 0.4 mg atomized from the nozzle. Not all of the atomized liquid arrived on the sample surface, however, since only 84.0 mg ± .9 mg (by mass, 1.1% standard error) arrived at an absorbent sample surface. Compared to water, considerably less CEES arrives at the sample surface, presumably because CEES has much lower surface tension and therefore tends to atomize into smaller droplets which have less inertia and are readily carried away from the sample by air currents. Nonetheless, the reproducibility of CEES contamination was sufficient. In standard analyses of simulant application and removal, the amount of CEES aerosol applied to each sample was measured with an analytical balance with 0.01 mg resolution. In the initial stages of Phase I, we used a CEES contamination ranging from 38.4 to 44.1 mg per coupon or 30.6 to 34.5 g/m^2. In Phase II, we chose to reduce the simulant challenge to approximately 10g/m^2, the NATO standard corresponding to heavy contamination, believing this contamination quantity to be a more reasonable representation of possible field conditions. This was accomplished by adjusting the distance between the reagent sprayer and the sample.

3.2 Rinsing of simulant from samples

Since, ideally, the aircrew ensemble is to be decontaminated by washing with a hose, TDA designed and assembled an apparatus to simulate this washing procedure in a controlled environment. To test coating effectiveness, automated reproducible washing is critical to avoid unintentional or unconscious operator bias. In fact, in Phase I, reproducible sample washing was the biggest single source of uncertainty in the entire analytical procedure to determine the relative effectiveness of various coating formulations. This device, first constructed in Phase I, was duplicated in Phase II.

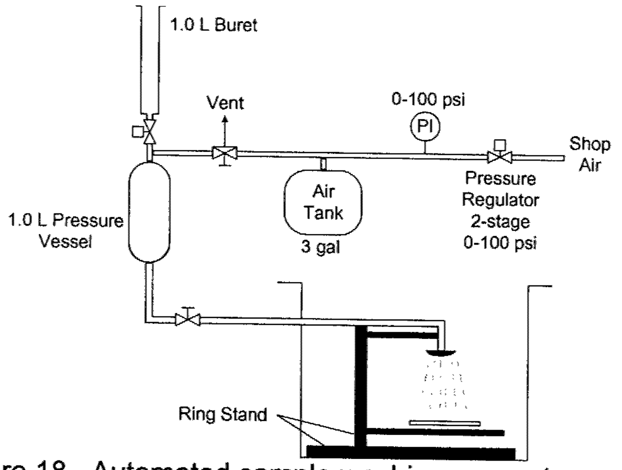


Figure 18. Automated sample washing apparatus.

The washing apparatus, pictured schematically in Figure 18, allowed for a fixed volume of water to be sprayed onto the sample material at a fixed pressure (or rate). The wash volume was metered into a pressure vessel from a graduated 1 L buret. (Later, water was measured by graduated cylinder and added by a funnel in place of the buret.) The pressure vessel was then pressurized with house air to 2-40 psig. Finally, the water in the pressure vessel was sprayed onto the sample material through a small nozzle. During spraying, the water pressure is maintained by means of an air ballast tank. The rinse water, containing the coating solution and some residual CEES was drained from the apparatus and collected for proper chemical disposal. Figure 19 shows a photograph of the actual rinsing device used at TDA.

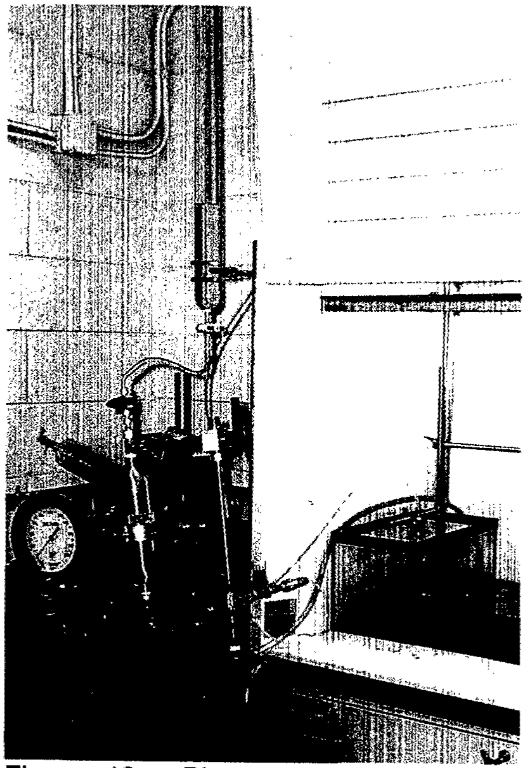


Figure 19. Photograph of automated washing apparatus.

The rinse protocol had to be changed a few times over the course of the project. Initially we were using 300 mL of water delivered continuously at 5 psi. This procedure was sufficient to remove approximately 85% of the coating from a Nomex sample with the initial coating formulation containing a poly(ethylene imine) and a fluorinated surfactant. As the project progressed we found the need to add other components to the formulation to combat the tacky feel the coating had in humid environments. These additives made it more difficult to rinse the coating from Nomex with 300 mL of water at 5 psi. We first changed the rinse protocol to deliver 600 mL of water continuously at 20 psi, which gave adequate coating removal when we were investigating powdered additives. As we moved toward polymer additives, such as poly (vinyl amine) and poly (vinyl alcohol), it was necessary to change the rinse protocol to deliver 1 L of water at 40 psi in four equal portions separated by 1 minute soaking periods. This particular rinse procedure was shown to remove greater than 75% of even the most water-resistant coatings from Nomex cloth. These soaking periods allowed the coating to soften and dissolve the very firm, non-hygroscopic coating formulations. This particular procedure was chosen for convenience in laboratory testing; in use, one could likely use much less water and more and longer soaking times to achieve similar results.

3.3 Analysis

To analyze the sample extracts we used a SRI 8610C Gas Chromatograph with a Flame Ionization Detector (FID). In series with the FID is a Dry Electrolytic Conductivity Detector (DELCD). The DELCD detects halogenated compounds, such as the chemical agent analog 2-chloroethyl ethylsulfide (CEES), in the vapor stream coming from the FID. Hydrogen and compressed air were used for the FID combustion. Helium was the carrier gas for the system. All gases were of high purity grade. The column was a Restek RTX-5, a capillary column with a crossbonded 5% diphenyl / 95% dimethyl siloxane phase, 1.0 μm in thickness. The internal column diameter was 0.53 millimeters and the column length was 15 meters. Based on experimentation and the boiling points of our analytes, we developed a temperature program for the GC that held an initial temperature of 50 °C for 0.25 min then to ramps to 105 °C at 10 °C/min, 5.75 min total analysis time.

A quadratic calibration curve was fit to the DELCD response for CEES standards with a concentration range of 0.0125 mg/mL to 0.250 mg/mL. For analysis, a 10 μL aliquot of a 0.1 mg/mL solution of chloroheptane (CHT) was added as an internal standard to 1.0 mL of extract sample. Initially, 1 μL of sample was injected directly onto the capillary column by hand. We began using an autosampler midway through the project, which proved to be more efficient and precise. It was determined analytically that the DELCD detector can effectively quantify 0.0025 mg/mL for CEES. So for 4.0 mL of extraction solvent, this gives a detection limit of 0.01 mg, or approximately 0.08% of the challenge mass, for each Nomex sample. Prior to analysis, a calibration verification standard, usually 0.5 mg CEES/mL, was analyzed in order to validate the current calibration curve. A new calibration curve was generated periodically or when the detector response was off by more than 20 percent after injecting the middle standard of the calibration curve. Additionally, all samples were analyzed twice.

In order to determine a window of time that our extracted contamination samples could sit before analysis, we reanalyzed several Nomex samples extracts over the course of many weeks. This analysis indicated that our extracts could sit in a freezer for a week with negligible effect on the analytes. However the longer the samples sat, beyond thirty days for example, the more the reanalysis results varied from the original. This was especially the case with the samples containing high concentrations of contaminant. Based on these results, we did not allow samples to sit for more than a week before analysis.

4. Formulation Development

The essential feature of any effective ensemble coating is its ability to prevent penetration of the CWA aerosols into the ensemble materials (e.g. nylon, fiberglass, butyl rubber, polycarbonate). Preventing penetration of CWA aerosols into the ensemble materials is critical because, once the CWA has penetrated the surface, superficial cleaning will not remove the CWA from the material and it will slowly diffuse out, posing a serious residual risk.

The spray-on coating must be clear, chemically compatible with all the ensemble materials, should be water based, and must completely coat the surfaces of all ensemble items. The coating should be clear and water based, so that it can be applied immediately before a mission without fear of solvent vapors. Furthermore, the coating should have a dry feel in all climates, humid or dry, without feeling stiff, sticky or otherwise unwearable.

Polyamines were the preferred CWA neutralizer because of their projected activity against a broad range of CWAs. Decontaminant solutions containing the monomeric amines ethanolamine and isopropanolamine have shown good activity for deactivating V- and G-series agents, and will also react with sulfur mustard, HD, although more slowly (Day 1996). For the V- and G-series agents, the amines can catalyze the hydrolysis of the P-O and P-F bonds and may also react directly with the phosphorous core (Compton 1988). Because they are potent nucleophiles, amines, particularly primary amines, react directly with mustard agents, neutralizing the threat (Brown 1995). We used the HD-simulant CEES (chloroethyl ethyl sulfide, half mustard) to assess the utility of these coatings in the laboratory.

A study of protonation mechanisms in model polyamines suggests that the amine functional groups in a polymer can act with synergism to increase the nucleophilicity of the polymer over that of its component amines (Koper 1997). We therefore believed it likely that polyamines would be even more effective decontaminating agents than the monomeric amines tested previously.

Figure 12 depicts the proposed cross-section of the coating developed at TDA covering the surface of a fiber. We suspect that the coating self-assembles into a PEI layer sandwiched between two thin sheets of fluorocarbon surfactant. The fluorinated layer at the air interface prevents the CWA aerosol from wetting the substrate while the PEI layer decontaminates the CWA that manages to penetrate the top surface layer. While all the components of the coating are soluble or dispersible in water, the coating should not wash off in a simple rain, but the impingement of a water stream from a hose is sufficient to remove both the coating and the CWA which remains on the coating surface.

4.1 Poly(Ethylene Imine)

Of the several polyamines available, hyperbranched poly(ethylene imine) (PEI) seemed to offer the best combination of high functional group density, low viscosity and low cost. Experiments conducted in Phase II confirmed that PEIs are particularly effective and offer better combinations of properties than the few other commercially available polyamines. Being hyperbranched, the PEIs have lower viscosities than corresponding linear polymers (Newkome 1996) and this aids aerosol atomization and flow and leveling of the applied coating. BASF offers a variety of Lupasol™ products which are a series of hyperbranched PEI with differing average molecular weights. Table 2 shows characteristics of the three products from this series that we tested: Lupasols G20, P, and Waterfree.

Table 2. Characteristics of Various Poly(ethylene imine) (PEI) products tested.

Product	Solids %	Viscosity (cps)	Average Molecular Weight (light scattering)	Number Average Molecular Weight
Lupasol™ G20	98	3,000-20,000	1,300	1,200
Lupasol™ Waterfree	99	100,000-250,000	25,000	10,000
Lupasol™ P	50	18,000-40,000	750,000	60,000

We focused on two primary criteria when selecting a poly(ethylene imine), chemical effectiveness against CWA's and the physical characteristics, including look and feel of the dried coating. A series of coatings were made containing each of the PEI products combined with the fluorinated surfactant, Zonyl FSA. These coatings were tested for efficacy against chemical contamination with CEES to compare the performance of the various PEI's. Each of the coatings was sprayed onto three replicate Nomex cloth discs. The samples were allowed to dry overnight and weighed the next day to determine the dried coating density. The samples were then contaminated with CEES at a target level of 30 g/m^2 and allowed to sit in a closed container for 1 hour. Next, the samples were rinsed using 300 mL of H_2O @ 5 psi delivered continuously, and extracted overnight in acetone prior to analysis of residual CEES by GC. Table 3 contains the results of the analysis. Under certain conditions, each of the PEI samples was effective against contamination, but Lupasol™ G20 was only useful at higher coating densities. Additionally, at densities greater than 8 mg/cm^2 the Lupasol™ G20 coating caused the Nomex cloth to feel tacky, even in an arid environment.

We understood that these polyamines were hydrophilic and possibly hygroscopic, so we went on to evaluate how hygroscopic the coatings were in environments of different humidity levels. For these experiments, each of the coatings was sprayed onto Nomex cloth discs. The samples were allowed to dry overnight and weighed the next day to determine the dried coating density. We then placed the Nomex samples in sealed chambers containing various saturated inorganic salts designed to create environments with particular relative humidities. The mass of water each sampled gained in a 24 hour and 72 hour period was recorded and the percentage of the dried coating mass gained in water was calculated. Table 4 shows that Lupasol™ P performed the best, absorbing a somewhat smaller percentage of the coating's dry weight in water at the higher humidities. In addition to weighing the samples we made physical observations. In 97% relative humidity (r.h.) all samples felt sticky to the touch. The degree of stickiness decreased with increasing molecular weight, G20, Waterfree, P (see Table 2). At 79% (r.h.) the coatings were less sticky overall, but with a similar trend to that observed at 97% r.h. Only the Lupasol G20 sample was sticky at 56% r.h.; the others felt dry. All formulations were dry and non-sticky at the lower relative humidities. To improve the look and feel of the coating we explored adding an assortment of compounds to decrease the stickiness at higher humidity without interfering with the chemical performance. Section 4.3 discusses our various approaches to counteracting the tacky feel of the coating in humid environments.

Table 3. Efficacy of Various Poly(ethylene imine) Samples Against CEES Contamination.

Samples	Formulation	Coating Density (mg/cm^2)	Mass CEES (g)	CEES Remaining %
W1, W2	20%Waterfree+1%FSA	6.79 ± 0.17	0.0389 ± 0.0033	0.24 ± 0.01
P1. P2	20% P + 1% FSA	5.79 ± 0.35	0.0401 ± 0.0003	0.30 ± 0.06
1017-13,14,15	20% P + 0.5% FSA	5.66 ± 0.03	0.0417 ± 0.0003	0.15 ± 0.09
G1, G2	40% G20 + 1% FSA	8.62 ± 0.41	0.0303 ± 0.0033	0.15 ± 0.02
1017-7,8,9	40% G20+1% FSA	5.72 ± 0.07	0.0338 ± 0.0024	15.75 ± 4.72
1017-10,11,12	20% G20 + 0.5% FSA	5.36 ± 0.08	0.0403 ± 0.0011	4.48 ± 1.29
Average-B, 1017	Blank	-	0.0365 ± 0.0063	60.92 ± 6.37

Table 4. Physical Performance of Waterfree and P Poly(ethylene imine)s in Varying Humidities.

Sample	Coating Formulation	Relative Humidity %	Dried Coating Density (mg/cm2)	Percent of Dried Coating Mass Gained in Water 24 hrs	Percent of Dried Coating Mass Gained in Water 72 hrs
GA1	40%G20+1%FSA	97	6.7	130.0%	134.6%
GA2	40%G20+1%FSA	85	6.7	54.4%	60.6%
GA3	40%G20+1%FSA	66	6.2	33.3%	33.5%
GA4	40%G20+1%FSA	56	7.0	23.4%	25.9%
GA5	40%G20+1%FSA	44	6.5	15.5%	19.2%
WA1	20%Waterfree+1%FSA	97	5.7	129.5%	135.0%
WA2	20%Waterfree+1%FSA	85	6.3	51.2%	59.9%
WA3	20%Waterfree+1%FSA	66	5.8	32.4%	31.6%
WA4	20%Waterfree+1%FSA	56	5.3	22.0%	24.3%
WA5	20%Waterfree+1%FSA	44	5.7	13.1%	12.4%
PA1	20%P+1%FSA	97	5.7	114.8%	126.9%
PA2	20%P+1%FSA	85	5.8	47.9%	55.9%
PA3	20%P+1%FSA	66	5.8	31.4%	30.4%
PA4	20%P+1%FSA	56	5.9	20.9%	22.0%
PA5	20%P+1%FSA	44	5.9	13.0%	14.0%

4.1.1 Material Strength Testing

One of the concerns about our coating formulation is the effect on the substrates themselves. That is, would the coating weaken the material it was meant to protect? To obtain these answers we performed some simple strength tests of uncoated Nomex and Nomex coated with a mixture of 20% Lupasol P and 1% Zonyl FSA, the polyamide bonds being theoretically susceptible to hydrolysis in the presence of a polyamine. The tests were performed according to ASTM Method D 3822, Standard Test Method for Tensile Properties of Single Textile Fibers. This method gives the criteria for taking a single thread of textile (Nomex in our case) and determining the amount of force necessary to cause it to break when pulled from each end. In addition to this force, we could also obtain how much the thread actually stretched before breaking. As indicated by the method, we used a Constant Rate of Extension Type Tensile Testing Machine to perform the test. Our instrument, Instron Model 4201, was connected to a PC that recorded and processed the pertinent data.

Each sample was clamped into the instrument so that there were five inches of thread between the clamps. The sample was stretched at three inches per minute. Table 5 shows the data obtained by running eight replicate samples under each of four conditions. The average results under each condition indicate that the presence of the coating had no effect on the tensile strength of the Nomex. This is not surprising, since the rate of any possible transamidation reaction is expected to be exceptionally slow (Swartzenbach et al. 1995). Changing the conditions from dry to wet had no effect on the thread strength as well. Therefore coating a flight suit with the final formulation would not be expected to cause any failure in the structure of the suit itself.

Table 5. Tensile strength of coated and uncoated Nomex fibers.

4.1.2 Uncoated Samples

Sample	Breaking Point (lbs.)	Extension @ Breaking Point (in.)
1	1.629	1.383
2	1.661	1.392
3	1.528	1.241
4	1.620	1.382
5	1.588	1.348
6	1.808	1.421
7	1.828	1.526
8	1.744	1.497
Avg.	**1.676**	**1.399**
Std. Dev.	0.107	0.088

Coated Samples Dried For 40 Days

Sample	Breaking Point (lbs.)	Extension @ Breaking Point (in.)
1	1.821	1.354
2	1.806	1.457
3	1.754	1.316
4	1.662	1.428
5	1.596	1.365
6	1.673	1.408
7	1.524	1.318
8	1.624	1.399
Avg.	**1.683**	**1.381**
Std. Dev.	0.104	0.051

Coated Samples Dried For 10 Days

Sample	Breaking Point (lbs.)	Extension @ Breaking Point (in.)
1	1.725	1.254
2	1.661	1.332
3	1.598	1.415
4	1.625	1.298
5	1.674	1.335
6	1.628	1.439
7	1.722	1.502
8	1.733	1.396
Avg.	**1.671**	**1.371**
Std Dev.	0.052	0.081

Sample	Breaking Point (lbs.)	Extension @ Breaking Point (in.)
1	1.537	1.442
2	1.825	1.358
3	1.528	1.415
4	1.547	1.385
5	1.662	1.327
6	1.827	1.391
7	1.756	1.401
8	1.689	1.302
Avg.	**1.671**	**1.378**
Std. Dev.	0.125	0.046

4.2 Fluorinated Surfactants

The choice of which surfactant for use in the final coating formulation was based on two factors: ability to lower the coating's surface tension (allowing it to thoroughly wet all surfaces) and effect on chemical resistance. The fluorinated surfactants have offer good surface tension reduction and do not appreciably increase the solution viscosity. Some of the cationic surfactants caused PEI-water solutions to phase separate, so we focused on anionic and non-ionic fluorinated surfactants. We measured the effects various fluorinated surfactants had on the surface tension and viscosity of different PEI samples. The top performing surfactants from these tests were then challenged for chemical agent resistance in order to select the best surfactant for this application.

4.2.1 Viscosity and Surface Tension Measurements

All solutions for viscosity and surface tension measurements were prepared by mixing 8.0 g of poly(ethylene imine) (Lupasol™ SKA, Lupasol™ Waterfree, or Lupasol™ P) with 0.20g, or 1%, of fluorinated surfactant (FC-120 (3M), Fluorolink 7004 (Aussimont), or Zonyl FSA (Dupont)) and 11.8 g of water. The PEI concentrations in the final solutions are different. The Lupasol products did not all have the same solids percentage, but the viscosity and surface tension results are comparable within a single Lupasol series.

The viscosity of each solution was measured by DV-E Viscometer (Brookfield) at room temperature (~23 °C). Seven milliliters of solution was added into a sample adapter of the viscometer using spindle 18. Table 6 shows the results of the measurements.

To measure the surface tension of the various solutions the drop weight method was used. The detachment of a drop from an orifice at which it is formed depends both on the limit of stability of the pendant drop and on the kinetic process involved in its elongation and rupture, sometimes forming a small secondary droplet and always leaving some of the liquid attached to the dropping tip. Thus, the simple relationship for the weight (W) of a drop, with surface tension γ, detaching itself from an orifice of radius r, known as Tate's Law

$$W = 2\pi r\gamma$$

approaches correctness only for very small values of r and may be in error by as much as 40%. Theoretical studies led to the conclusion that the fraction of the drop that detached was a function of $(r/V^{1/3})$, where V is the volume of the drop, and a table was prepared of values of F for a wide range of values of $(r/V^{1/3})$ for use in the equation

$$\gamma = F(W/r)$$

We used a 2-ml pipette as the dropping tip. The measured radius of the dropping tip was 0.155 cm. The drops of PEI solutions were pushed slowly by a syringe pump at 0.10 ml/min, which causes less error than the speed of 0.49 ml/min. Estimated uncertainty of the reported surface tensions is about 4% relative error. The drops of a PEI solution were counted and the weight of the drops was measured. The density of each PEI solution was measured, from which the volume and weight of a drop were calculated. This data was used to calculate the surface tension of the PEI solutions in Table 6.

Table 6. Viscosity and surface tension of PEI solutions.

Solution	Appearance	Viscosity (cp)	Surface tension γ (dyne/cm)
Water	-	-	69
8% Lupasol SKA	clear	50	58
8% Lupasol SKA &1% FC120	cloudy	60	40
8% Lupasol SKA &1% FSA	cloudy	70	23
8% Lupasol SKA &1% Fluorolink	cloudy	100	24
40% Lupasol Waterfree	clear	560	65
40% Lupasol Waterfree &1% FC120	clear	520	29
40% Lupasol Waterfree &1% FSA	clear	610	26
40% Lupasol Waterfree &1% Fluorolink	clear	610	26
20% Lupasol P	clear	90	70
20% Lupasol P &1% FC120	slightly cloudy	90	24
20% Lupasol P &1% FSA	slightly cloudy	90	19
20% Lupasol P &1% Fluorolink	slightly cloudy	100	22

4.2.2 Chemical Contamination Performance of Fluorinated Surfactants

Based on surface tension and viscosity measurements we chose to test Fluorolink 7004 (Aussimont) and Zonly FSA (Dupont) against chemical contamination. These surfactants were better at lowering the surface tension of solutions than 3M's FC 120 (discontinued). These coatings were tested for efficacy against chemical contamination with CEES to compare the effects of Fluorolink 7004 and Zonly FSA. Each of the coatings was sprayed onto three replicate Nomex cloth discs. The samples were allowed to dry overnight and weighed the next day to determine the dried coating density. The samples were then contaminated with CEES at a target level of 30 g/m^2 and allowed to sit in a closed container for 1 hour. Next, the samples were rinsed using 300 mL of H_2O @ 5 psi delivered continuously, and extracted overnight in acetone prior to analysis of residual CEES by GC. Results in Table 7 suggest that in coatings containing the same PEI, Zonyl FSA results in better performance than Fluorolink 7004 against contamination, even at lower coating densities. We therefore selected Zonyl FSA as the fluorinated surfactant in our coating formulation.

Table 7. Chemical contamination performance of coatings containing Zonyl FSA and Fluorolink 7004.

Samples	Formulation	Coating Density (mg/cm2)	Mass CEES (g)	CEES Remaining %
1017-10,11,12	20% G20 + 0.5% FSA	5.360 ± 0.075	0.0403 ± 0.0011	4.48 ± 1.29
1017-1,2,3	40% G20 + 1% Fluorolink	6.296 ± 0.146	0.0343 ± 0.0043	6.65 ± 1.55
22,107 Average	Blank		0.0407 ± 0.0014	34.35 ± 1.37

4.3 Additives to Prevent Stickiness in High Humidity Environments

In our experimentation, we discovered that although coatings containing only Lupasol™ P and Zonyl FSA performed very well against contamination, they had a tacky feel in humid environments. As described in Table 4, the various poly(ethylene imine) products absorb water readily from humid air leading to this tacky feeling. We took various approaches to formulate a coating that had an acceptable look and feel without sacrificing chemical performance. Initially we looked into an assortment of solid particle additives, both organic and inorganic, that would sit on the surface of the coating acting as a small barrier that would alleviate stickiness. Various organic thickeners and film formers were also tried under the hypothesis that we could induce a barrier that would eliminate the tacky feel. We also investigated using perfluorinated carboxylic acids to form acid/amine complexes which would be much less hydrophilic than unmodified PEI. Finally, we investigated using other polymers with amine function groups both in place of and in combination with PEI; with this we hoped to find another water-soluble polyamine that was less hydrophilic/hygroscopic than PEI but would perform similarly when challenged with chemical agents.

4.3.1 Fillers and Film Formers

In an effort to alleviate the stickiness of the coating formulations in high humidity, we experimented with various inorganic and polymeric particulate additives that were expected to firm up the coating. To test an individual additive, a coating formulation containing the particular component was mixed and sprayed onto a small sample of butyl rubber, then allowed to dry overnight. Butyl rubber was chosen as a substrate because, being non-porous, it represented the worse case scenario for how the coating felt in high humidity. Next, it was placed into an environment with approximately 97% relative humidity at room temperature and allowed to equilibrate overnight. The high humidity environment was achieved by preparing a saturated potassium sulfate solution in a closed chamber. This chamber was designed to allow hand access to the samples without the humidity levels dropping significantly. Semi-quantitative observations were then made about the condition of the coating, such as the extent of phase separation in the liquid formulation, ease of mixing the formulation by shaking, ease of rinsing, and the extent of the stickiness for the dry coating in the humid environment. Fillers tested included organics such as polytetrafluorethylene (PTFE or Teflon™) and polyurea (Decosoft™), inorganics such as TiO_2, SiO_2 (Cellite and Novacite), Al_2O_3, bentonite and kaolin clays, wollastonite (Wollastocoat™), and powdered mica (Alsibronz 10, Alsibronz 39, and Magnapearl 1000).

Each of the above components were rejected as candidates for one or more of thefollowing reasons:

1. The coating was sticky in high humidity
2. The coating was difficult to rinse from the test substrate.
3. The dried coating would crack when the butyl rubber sample was bent or would easily brush off of the sample.
4. The additive would easily separate from solution and be difficult to remix with manual shaking.
5. The additive radically altered the visual appearance of the coating, i.e. the coating would be opaque when dried.
6. The formulation performed poorly against chemical contamination.

PTFE was rejected because the concentrations necessary would require a decrease in the amount of PEI present in the coating, thus decreasing the effectiveness of the coating against chemical warfare agents. For the most part, the clays, alumina, and various silica additives performed acceptably in high humidity but failed in tests that considered the chemical performance of the dried coating. The mica compounds performed well against humidity, but easily fell out of solution and brushed off when the coating was dry. In addition when coatings containing the mica products dried on sample substrates, the coating was entirely opaque. This characteristic made these additives impractical for final use. Coatings containing the titanium dioxide performed well enough to warrant further investigation, despite the obvious whitening of the coated substrate.

To alleviate problems with phase separation and the cracking of dried coatings, we began to experiment with various organic thickeners that were tested alone and in combination with the better performing fillers. Organic thickeners, in theory, would give the coating some flexibility when dried and would help keep inorganic fillers suspended in solution. Tests were performed with polyvinylpyrrolidone (PVP), carboxymethyl cellulose, polyvinyl alcohol (PVOH), and a polysaccharide called Dextran P. These thickeners were tested in coatings to determine if they relieved some the stickiness of the formulations. Coatings containing only PEI, surfactant and the thickeners were all sticky in high humidity with the exception of Dextran P, which did not significantly help keep the fillers suspended. PVOH and PVP were still considered for use to keep fillers in solution.

Various combinations of fillers and thickeners were tested in high humidity. One of the first formulations tested that had a combination of additives was 20% TiO_2, 5% PVP, 2% PEI (Lupasol Waterfree) and 1% surfactant (Zonyl FSA). This formulation performed well enough in high humidity to warrant testing against simulated chemical contamination. The indicated that less than 10% of the applied contamination remained after rinsing, but our goal was to have less than 1% remain. Contamination results also indicated that the TiO_2 provided some level of protection against the mustard simulant, 2-chloroethylethylsulfide (CEES). As the concentration of TiO_2 in the coating formulation decreased, the amount of CEES remaining increased. We hypothesized that the TiO_2 particle, being a plate shaped, provided a barrier to the CEES from reaching the Nomex test substrate. Ultimately the inorganic fillers were abandoned because formulations containing such species didn't provide adequate protection against contamination. They also changed the appearance of the coating, leaving an opaque residue that would interfere with camouflage coloring. In addition it was discovered that while such coating formulations rinsed from the butyl rubber substrate relatively easy, they did not rinse from the Nomex samples very well.

Since we were not particularly impressed with the performance of any of the coating formulations to date, we began to research other possible additives. The next additives belonged to a class of compounds called non-ionic film formers. The film formers tested included a variety of materials received from Air Products and Chemicals: Airflex 510 Emulsion Polymer, Aiflex 809 Vinyl Acetate-ethylene Emulsion Polymer, and Flexbond 325 Emulsion Polymer. These were tested in the same manner as the other candidates. Initially we tested the polymers (diluted to a concentration of 20% in water) without polyamine (PEI) or surfactant. The coatings did not brush off when dry. The polymers were not sticky when tested in the humidity chamber. Without other coating components, however, the films that were formed by the polymers were difficult to rinse from the butyl rubber substrate.

Next the film formers were included in formulations with the PEI (Lupasol Water-free) and fluorosurfactant (Zonyl FSA). These coatings were also very difficult to rinse from the rubber. Since the presence of the film forming polymers appeared to increase the amount of coating remaining (20-30% vs. 10-15% for control), and also the amount of chemical contamination remaining (e.g. 50%), work on these products was suspended.

The final inorganic filler experimented with was a commercially available glass flake 15 micron powder, called RCF015 (NGF Canada). We performed humidity tests with coatings containing the glass flake, PEI, and surfactant. Although much less opaque than coatings containing other inorganic fillers, these coatings did not perform well high humidity, brushed off of the sample substrate when dried, and separated out of solution easily. The coating rinsed off of the butyl rubber quite easily.

While testing the glass flake, we obtained a water-soluble polyurethane thickener, Polacryl BR 250. This product is normally used as a thickener in paints to increase the low-shear viscosity. The presence of the Polacryl kept the glass flake from settling out so quickly. To assist in preventing the dried coating from cracking, we went back to adding low amounts (~0.5%) of the film-forming polymer Flexbond 325. Coatings containing PEI, surfactant, RCF015, and Polacryl performed sufficiently in high humidity tests to warrant contamination testing. The formulations containing these additives performed poorly against CEES contamination (e.g. 44% CEES remaining after rinse). Since these coatings rinsed from the Nomex substrate as well as coatings containing only PEI and surfactant, we speculated that the fillers and additives effectively adsorbed the PEI and surfactant, preventing the coating from forming its protective barrier around the cloth fibers. It is also possible that the CEES was adsorbing onto the glass flake and the flake not rinsing fully away. To test these theories we made coatings of the individual components. These were sprayed onto Nomex samples and contaminated with CEES. While the analysis gave no indication which component was responsible for the decrease in performance, the results led us to believe that with fillers, thickeners, and film formers, the relative concentration of PEI may have been decreased beyond the point where it would be effective. In light of the fact that contamination performance is the critical feature of the coating, work with these additives was discontinued.

4.3.2 Perfluorinated Carboxylic Acids

The problem of high humidity is caused by the hygroscopic nature of PEI, to counteract the tacky feel of dried coating we tried adding fluorinated carboxylic acids to the PEI solutions. These acids have varying length carbon chains from 4 to 9 carbons long. The carboxylic acids react and complex with the amine groups in the PEI. These complexes are less hydrophilic than unmodified PEI. At a certain acid/amine ratios the complexes became insoluble in water and precipitated. We hoped that with slightly less acid, the complexes would be barely soluble and we expected that they would be less hygroscopic when dried, resulting in a less sticky coating.

We started by testing heptafluorobutyric acid (4 carbons), perfluorpentanoic acid (5 carbon), and heptadecafluorononanoic acid (9 carbons). Mixing ratios of to achieve equivalents of acid to PEI of 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 were calculated and a few milliliters of each solution was prepared. The heptadecafluorononanoic acid precipitated at a ratio of 0.1, the first drop of acid causing a solid precipitate to form upon contact with the amine solution. The heptafluorobutyric acid/amine solution became cloudy at an equivalents ratio of 0.6 (acid/amine) and a solid precipitate was visible at a ratio of 0.8. Both the 0.6 C4/amine and the supernatant from the 0.1 C9/amine were placed onto butyl rubber samples and placed into the high humidity chamber overnight. Both were sticky in the morning. The solid precipitates were not very hygroscopic and did not become sticky in high humidity. We suspect that the 9-carbon acid precipitated too easily to be effective, separating into fluorine-rich precipitate and an essentially unmodified supernatant, while the 4-carbon acid took too much to precipitate, effectively neutralizing most of the amine in the process (since only the free amine is expected to react with chemical agents). Based on these results we tried a seven-carbon compound, perfluorheptanoic acid. As with the other acids, we mixed various equivalents of acid and PEI hoping that a complex would be created that would be barely soluble and thus less hygroscopic and less sticky. However there was no ratio of acid to amine that was both water soluble and appreciably less sticky in high humidity than the blank PEI formulation. Although these perfluorinated acids may provide some small reduction of the polyamines' water absorption, they did not work well enough to be considered as a component in the final formulation.

4.3.3 Other Polyamines

Another angle that we chose to take concerning the high humidity issues with the PEI-based coatings, is to investigate other water soluble polymeric amines. The amine group is responsible for the chemical reactions that actually neutralize the chemical agents. We decided to test other polymers that may perform better in high humidity than PEI but still provide sufficient reaction with CEES. The polymers we chose to test were poly(allyl amine) (PAA) and poly(vinyl amine) (PVAm).

Coatings containing PAA and PVAm in high weight percentages relative to Lupasol P both had acceptable performance in high humidity. However, the polymers made it more difficult to rinse the coatings from the Nomex substrate. We performed rinse tests on coatings containing both polymers to quantify the coating remaining after rinsing. For these tests, each of the coatings was sprayed onto three replicate Nomex cloth discs. The samples were allowed to dry overnight and weighed the next day to determine the dried coating density. Next the samples were rinsed using the protocol (600 mL @ 20 psi), dried and weighed to determine the coating removed in rinsing. Table 8 shows that more than 75% of the coating applied remained after rinsing. Based on these results, it was clear that the coatings containing large fractions of PVAm and PAA were not rinsing as well as the coatings containing only PEI (e.g. 55 % coating remaining for Lupasol P and only 20% for Lupasol G20).

Table 8. Rinse test results of percentage of coating removed rinsing with 600 mL @ 20 psi.

Samples	Coating	Coating Density (mg/cm^2)	% Coating Removed
30 ABC	2.5 % PAA (65K) / 2.5% Lupasol P	4.61 ± 0.26	24.61 ± 5.63
31 ABC	10% PVAm (CF8106*) / 0.2% Zonyl FSA	2.62 ± 0.59	24.75 ± 2.64
41 ABC	2% Lupasol P / 8% PVAm (CF8106) / 0.2% Zonyl FSA	5.27 ± 0.33	18.27 ± 2.56
42 ABC	1% Lupasol P/ 9% PVAm (CF8106) / 0.2% Zonyl FSA	3.84 ± 0.71	22.91 ± 4.90

*PVAm Sample is Catiofast 8106 hydrochloride sample reacted with sodium hydroxide to obtain free amine and dialyzed to remove resulting salts.

4.3.3.1 Changes to rinsing method to allow comparison of more difficult-to-rinse samples

We decided to investigate making changes to the rinse protocol before moving on to testing PAA and PVAm formulations against CEES contamination. We first tested large samples of coated cloth rinsed with a garden hose to see if the PVAm coatings could be rinsed away in a reasonable time. Two Nomex samples measuring 900 cm^2 were coated with one of two formulations. The first formulation contained 20% Lupasol P and 0.2% Zonyl FSA. The second was from Table 8: 1% Lupasol P, 9% PVAm, and 0.2 % Zonyl FSA. The samples were dried overnight, then placed on a rack outdoors and rinsed with a garden hose. After rising each sample for a couple minutes, the samples were again allowed to dry over night. The sample coated with the Lupasol P formulation lost 92.7% of the coating mass during rinsing. The sample coated with the PVAm and P mixture lost 86.1% of its coating mass, suggesting that these coatings can be effectively rinsed away under field conditions.

Since the coatings containing PVAm and PAA did not rinse off with 600 mL water @ 20 psi, we decided to test different rinsing procedures to increased the fraction of coating – and presumably chemical contamination – removed from the substrates. Changing the rinse protocol should also give results with better correlation to field conditions because in the field equipment would be rinsed until 90+% of the coating was removed. First we adjusted the rinse apparatus by removing the spraying head so that a solid stream of water was used instead of a shower. Then we tested the following rinse protocols which varied the volume of water, the pressure, and the time pattern in which it was delivered:

A. 1 liter water @ 40 psi (about 14 second rinse)
B. 1 liter water @ 40 psi, stopping intermittently
C. 2 liter water @ 40 psi, stopping after 1 L
D. 2 liter water @ 40 psi, stopping intermittently
E. 1 liter water @ 40 psi, rinse for 3.5 sec, stop for 1 minute, 4 total rinse portions
F. 1 liter water @ 40 psi, rinse for 7 sec, stop for 1 minute, 2 total rinse portions.

The stops in rinsing were implemented in order to allow for the polymer to soak momentarily. Table 9 contains the results of the experiment.

Table 9. Rinse protocol adjustment with coating containing 1% Lupasol P/ 9% PVAm/ 0.5% Zonyl FSA.

Samples	Rinse Protocol	Coating Density (mg/cm^2)	% Coating Removed
50 ABC	A	4.28 ± 0.20	36.47 ± 5.76
51 ABC	B	3.94 ± 0.17	51.13 ± 1.95
52 ABC	C	3.50 ± 0.25	74.28 ± 1.70
53 ABC	D	4.06 ± 0.18	74.61 ± 1.10
54 ABC	E	3.48 ± 0.30	74.22 ± 3.57
55 ABC	F	3.47 ± 0.28	51.02 ± 3.29

In comparing protocols A - D, 2 liters of water rinses away more coating than 1 liter. With our apparatus, however, there is approximately a one-minute interval between the first and second liter while our 1 liter pressurized holding tank is refilled. The success of protocol E suggests that there is a strong kinetic component to polymer dissolution and rinsing, and that allowing the coating to soak briefly can dramatically increase the rinsing efficiency. In the field, this could be accomplished by first thoroughly wetting the entire ensemble, then returning for a second (and possibly third) pass to rinse away the loosened polyamine. Comparing the results from Table 9 with those from Table 8, we see that the fraction of coating rinsed off with protocol E, which we chose to use in further contamination testing, is nearly four times greater than the old protocol of 600 mL @ 20 psi.

The new rinse protocol was tested on formulations containing PAA and an older formulation containing only Lupasol P as a reference for the newer formulations. This formulation also contained a small amount of thymolphthalein as a color indicator. Each coating was sprayed onto Nomex coupons and allowed to dry overnight. The samples were rinsed with 1 liter of water at 40 psi, in 4 portions (rinse for 3.5 seconds, allow to sit for 1 minute, repeat for a total of

4 rinse portions). This procedure allows the sample to soak momentarily, making it easier to rinse the less hydrophilic polymers from the substrate. This rinse protocol is not intended to represent actual coating rinsing procedure in the field but is only used for experimental purposes so that tests of various coatings are comparable. Table 10 contains the results of the rinse test. Under the older rinse protocol (600ml @ 20 psi in one continuous stream), coating removal for 20% Lupasol P/ 0.5% Zonyl FSA from Nomex averaged 75% and coatings formulated with PAA averaged under 30% mass rinsed from the samples. The new protocol greatly increased the fraction of coating removed from the substrates.

Table 10. Rinse Test: Coatings with PAA or Lupasol P.

Samples	Coating	Coating Density (mg/cm^2)	% Coating Removed
64 ABC	10% PAA/0.5 % Zonyl FSA	3.98 ± 0.27	12.35 ± 4.02
65 ABC	9% PAA/1% Lupasol P/0.5% Zonyl FSA	4.12 ± 0.20	14.38 ± 4.52
66 ABC	20% Lupasol P/ 0.5% Zonyl FSA (ThyPht saturated)	7.77 ± 0.91	1.95 ± 0.59

4.3.3.2 Chemical performance of formulations containing PVAm or PAA

Once we developed a rinsing protocol that was appropriate for use with less hydrophilic polymers like PVAm and PAA we decided to move forward with testing coatings containing these polymers for efficacy against chemical contamination.

PAA was available commercially in molecular weights of 65,000 (20% solution), 17,000 (20% solution), and 24,400 (10% solution) (Nitto Boseki Co., Tokyo). In humidity studies the lower molecular weight were too hygroscopic/sticky to be viable alternatives to Lupasol P. Thus, only the 65K molecular weight polymer was used in coatings for contamination studies.

We also investigated poly(vinyl amine), PVAm. In our initial studies of PVAm, we used a sample (provided by BASF) of Catiofast PR 8106, a poly(vinyl amine) hydrochloride with an average molecular weight of 450,000. To obtain the free amine, we neutralized the material with sodium hydroxide and removed the salt product by dialysis prior to testing. Coating formulations were made containing a mixture of this PVAm, Lupasol P, and Zonyl FSA. Based on 10% total amine weight in the formulation, nine formulations were mixed, starting with 9% Lupasol P/ 1% PVAm/ 0.2% Zonyl FSA and ending with 1% Lupasol P, 9% PVAm, 0.2% Zonyl FSA. Each of these coatings was sprayed onto samples of butyl rubber, dried, then placed into the high humidity chamber. The two coatings that were the least tacky consisted of 2% Lupasol P, 8% PVAm, 0.2% Zonyl FSA and 1% Lupasol P, 9% PVAm, 0.2 % Zonyl FSA.

We also obtained two samples of free-amine (non HCl) PVAm from BASF. The first is Basocoll 8125, which has a reported molecular weight average of 250,000 (23% solution). The second is Basocoll 8139, which has a reported molecular weight average of 450,000 (23% solution). These Basocoll samples were prepared on the lab bench and could be readily prepared in pilot quantities by BASF. Unlike the Catiofast PR 8106, these solutions do not have to be neutralized and separated from the salts by dialysis. On the downside, these polymers did not perform as well under humid conditions as the Catiofast PR 8106, despite the fact that the Basocoll 8139 has the same nominal molecular weight as the Catiofast PR 8106. As discussed below, this difference in performance could well be due differences in the molecular weight distributions, with low MW components limiting the physical properties of the mixture.

We compared the viscosities of Basocoll 8125, Basocoll 8139, and Lupasol P at varying solution concentrations to see what concentrations of the new polyamines could be reasonably sprayed with our laboratory equipment. Figure 20 contains the results of the viscosity analysis. It was surprising that the Basocoll 8125 is more viscous than the other polymers since it has the lowest reported molecular weight average of the three. It is possible that the molecular weight distribution for Basocoll 8125 is broader than for the 8139, resulting in a higher viscosity (more strongly dependent on high MW fractions). More polymer in the low molecular weight fraction of Basocoll 8139 is also more likely to contribute to the hygroscopic effect of the polymer and may account for the physical differences between the Basocoll and Catiofast products in high humidity. We tried separating the low molecular weight fraction of Basocoll 8139 by dialysis to see if the polymer's performance in high humidity improved. The resulting polymer was not as tacky in humid conditions, so the dialyzed polymer was used in further testing.

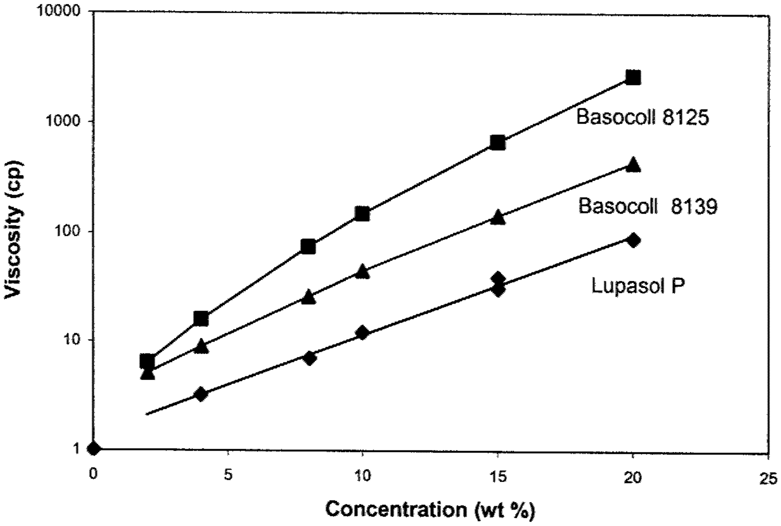


Figure 20. Viscosities of Basocoll 8125, Basocoll 8139, Lupasol P as a function of polymer concentration.

In a previous test, we discovered that multiple applications of a coating performed better than a single application of the coating. Since the coating formulations with PAA (65K) and PVAm (Catiofast 8106) were diluted to reduce viscosity and thereby facilitate the coating application, it was impossible to achieve our standard coating density of 5 mg/cm^2 in a single coat. Two methods of application were chosen. The first was to reach the desired density in as few applications as possible. The second method was to apply the coatings in many light coats. In addition to the normal density of 5 mg/cm^2, we also wanted to test heavier applications, in the range of 7.5 mg/cm^2. We also tested one of the formulations with a single heavy coat, regardless of the resulting (low) coating density. Each of the coatings was sprayed onto three replicate Nomex cloth discs. The samples were allowed to dry overnight and weighed the next day. This step was repeated until the density was at desired levels. The samples were then contaminated with CEES and allowed to sit in a closed container for 1 hour. Next the samples were rinsed using 1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods, then extracted overnight in acetone prior to analysis of residual CEES by GC. Table 11 contains the results of the analysis.

Table 11. Analysis of residual CEES after rinsing coatings from formulations containing 9/1/0.5 neutralized, dialyzed Catiofast PR8106/Lupasol P/Zonyl FSA and 10/0.5 PAA (65K MW) /Zonyl FSA.

Samples	Formulation	# of applications	Coating Density (mg/cm2)	Mass CEES (g)	CEES Remaining %
57 ABC	9% Catiofast /1% Lupasol P /0.5% FSA	5	4.70 ± 0.00	0.0122 ± 0.0023	3.17 ± 1.58
58 ABC	9% Catiofast /1% Lupasol P /0.5% FSA	4	7.00 ± 0.46	0.0101 ± 0.0008	1.97 ± 0.34
56 ABC	9% Catiofast /1% Lupasol P /0.5% FSA	3	5.13 ± 0.21	0.0091 ± 0.0013	2.38 ± 0.55
63 ABC	9% Catiofast /1% Lupasol P /0.5% FSA	1	1.48 ± 0.20	0.0108 ± 0.0028	9.42 ± 4.42
60 ABC	10 PAA (65 K MW)/ / 0.5 Zonyl FSA	5	4.50 ± 0.35	0.0111 ± 0.0024	2.52 ± 0.47
61 ABC	10 PAA (65 K MW)/ / 0.5 Zonyl FSA	4	7.73 ± 0.23	0.0071 ± 0.0007	1.61 ± 0.75
59 ABC	10 PAA (65 K MW)/ 0.5 Zonyl FSA	2	4.90 ± 0.30	0.0083 ± 0.0010	8.10 ± 1.67
62 ABC	Blank	-	-	0.0095 ± 0.0005	17.06 ± 10.00

Looking at specific samples, sample set 63 suggests that the lower densities don't provide adequate protection. Comparing set 59 to set 60, it is clear that more light applications perform better than fewer heavier applications. Presumably, this is because the coating distribution becomes more homogenous with successive coats. Coatings with higher densities, sets 58 and 61, don't perform much better than those with densities around 5 mg/cm^2. The low solids concentrations limit the application density, with at least three applications being required to achieve good chemical performance.

We continued testing formulations containing containing poly(vinylamine) (PVAm, Basocoll 8139) which had been dialyzed to remove low MW species. Since the PVAm-based coatings get more flexible and easier to rinse off of the substrates with increasing concentrations of Lupasol P, we wanted to test coatings containing a higher fraction of Lupasol P. (Pure PVAm was a brittle material when dry.) We targeted a coating formulation that would maximize the amount of Lupasol P present while maintaining the coating's non-stickiness in high humidity. A coating containing 8% PVAm/ 2% Lupasol P/0.5% Zonyl FSA performed moderately well in high humidity. A coating consisting of 7% PVAm/3% Lupasol P/0.5% Zonyl FSA was clearly much more hygroscopic and less physically robust in high humidity. Hoping to maximize the flexibility and ease of rinsing of the PVAm-based formulations while maintaining excellent resistance to chemical agents, we chose a formulation of 7.5% Basocoll 8139 / 2.5% Lupasol P / 0.5% Zonyl FSA to test against CEES contamination. We also tested a coating containing 20% Lupasol P / 0.5 % FSA to compare results with an older formulation. Each of the coatings was sprayed onto three replicate Nomex cloth discs. The samples were allowed to dry overnight and weighed the next day. This step was repeated until the density was at desired levels. The samples were then contaminated with CEES and allowed to sit in a closed container for 1 hour. Next the samples were rinsed with 1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods, then extracted overnight in acetone prior to analysis of residual CEES by GC. Table 12 contains the result of the analysis.

Table 12. Analysis of Residual CEES from formulations containing Lupasol P, and either PAA (65K MW) or dialyzed Basocol 8139.

Samples	Coating	# of Applic-ations	Coating Density (mg/cm^2)	CEES (g)	CEES Remaining %
68 ABC	7.5% Basocoll / 2.5% Lupasol P / 0.5% Zonyl FSA	3	5.10 ± 0.37	0.0127 ± 0.0064	1.80 ± 0.71
70 ABC	9% PAA / 1% Lupasol P / 0.5% Zonyl FSA	3	5.30 ± 0.38	0.0142 ± 0.0010	3.78 ± 0.42
69 ABC	20% Lupasol P / 0.5% Zonyl FSA (thymolphthalein saturated)	1	8.51 ± 0.63	0.0129 ± 0.0010	1.51 ± 0.32
71 ABC	20% Lupasol P/0.5% Zonyl FSA (thymolphthalein saturated)	2	4.76 ± 0.93	0.0141 ± 0.0010	3.72 ± 1.19
72 ABC	Blank	--		0.0137 ± 0.0019	19.47 ± 10.21

PVAm-based coatings appeared to provide similar if not better chemical protection than a similarly loaded sample containing only the Lupasol P polyamine. Coatings containing PVAm and PAA gave similar results in terms of physical properties, with PAA-based coatings being somewhat more flexible and easier to rinse away than their PVAm-based analogues, but the PVAm-based coatings demonstrated somewhat better chemical protection. We therefore decided to dicontinue formulation with poly(allyl amine)s. Even though the PVAm required dialysis or other separation to obtain the molecular weight distribution necessary to perform well in high humidity, it consistently performed better than PAA both in high humidity and against CEES contamination.

Both of the PVAm products would require additional processing before they could be used as coating components. Since neither Catiofast nor Basocoll could be used as sold, we began a head-to-head comparison to determine if either performed better than the other against chemical contamination. We tested a set of formulations containing neutralized/dialyzed Catiofast 8106 and Lupasol P in varying ratios and 10% of the total solution. We also tested the same formulations containing Basocoll 8139 PVAm, dialyzed to remove lower molecular weight fraction. In addition we tested formulations containing Arlasolve 200, a surfactant to be used as a visual indicator for coating removal (see section 4.5.2) and a film-forming emulsion of polyvinyl acetate (PVAc). The PVAc was added to the coating formulation in order to alleviate the problem with the coatings cracking in dry conditions. This compound also assisted in reducing tackiness of the coatings in high humidity.

Each of the coatings was sprayed onto three replicate Nomex cloth discs. The samples dried overnight and were weighed the next day. This step was repeated until the density was at desired levels. The samples were contaminated with CEES and allowed to sit in a closed container for 1 hour. Next, the samples were rinsed (1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods) and extracted overnight in acetone prior to analysis of residual CEES by GC. Table 13 shows the analytical results.

Table 13. Analysis of Residual CEES for coatings containg Catiofast 8106 and Basocoll 8139.

Samples	Coating	Coating Density (mg/cm^2)	CEES (g)	CEES Remaining %
77 ABC	7.5% Catiofast 8106 / 2.5% P / 0.1% FSA	5.14 ± 0.30	0.0123 ± 0.0005	2.31 ± 0.51
82 ABC	7.5% Basocoll 8139 / 2.5% P / 0.1% FSA	4.29 ± 0.31	0.0120 ± 0.0013	3.61 ± 0.52
84 ABC	7.5% Basocoll 8139 / 2.5% P / 1% PVAc / 0.1% FSA	4.69 ± 0.17	0.0112 ± 0.0011	6.36 ± 0.84
78 ABC	8% Catiofast 8106 / 2 % P / 0.1% FSA	4.34 ± 0.20	0.0129 ± 0.0008	2.10 ± 0.14
83 ABC	8% Basocoll 8139 / 2% P / 0.1% FSA	4.18 ± 0.27	0.0102 ± 0.0017	5.66 ± 1.36
85 ABC	8% Basocoll 8139 / 2% P / 0.25% Arlasolve / 0.25% FSA	4.80 ± 0.49	0.0093 ± 0.0017	7.64 ± 1.38
86 ABC	8% Basocoll 8139 /2% P / 1% PVAc / 0.25% Arlasolve / 0.25% FSA	4.33 ± 0.17	0.0114 ± 0.0020	4.02 ± 2.00
79 ABC	8.5% Catiofast 8106 / 1.5% P / 0.1% FSA	4.69 ± 0.40	0.0105 ± 0.0005	2.34 ± 0.79
80 ABC	9% Catiofast 8106 / 1% P / 0.1% FSA	4.12 ± 0.24	0.0135 ± 0.0002	2.69 ± 1.08
81&87 ABC	Blank	-	0.0096 ± 0.0014	18.67 ± 5.35

The results in Table 13 indicate that coatings containing Basocoll 8139 performed consistently worse than those containing Catiofast 8106 (77 vs. 82 and 78 vs. 83). While these two poly(vinyl amine)s have similar average molecular weights, they do not perform the same against CEES contamination. Additionally, it appears that the film-forming emulsion of PVAc drastically reduced the efficacy of the coating against contamination (82 vs. 84).

Based on these results, we investigated possible processing methods for Catiofast 8106 that could be applied on a small industrial scale. Initally we tried fractionation by precipitation: a procedure wherein the neutralized aqueous polymer solution is added to a water-miscible solvent in which the polymer is only slightly soluble, causing the higher molecular weight polymers to precipitate while leaving the low molecular weight fraction in solution. The high MW precipitate can then be filtered, redissolved in water and used as a coating component. This approach was partially successful. The polymer that precipitated upon addition of isopropanol was less sticky in high humidity than the commercial Catiofast product, but it was still much more hygroscopic than the dialyzed product and would be inadequate for use in a coating.

We investigated toll manufacturers that specialize in polymers to contract the purification of high MW PVAm for the final coating. This purification would involve the neutralization of Catiofast PR 8106, a PVAm hydrochloride, and removal of the low molecular weight polymer along with the aqueous salts produced by neutralization. We determined that the best way to remove the low molecular weight polymer is by ultra-filtration. Ultra-filtration would apply the same principles of membrane separation as dialysis, which has worked well on the laboratory scale, and in turn could be implemented on an industrial scale.

A variety of approaches were used to find a manufacturer that would be willing to do this work. We have contacted toll processors that specialize in polymers, companies that produce and sell ultra-filtration apparatuses, companies that buy ultra-filtration systems, universities and academics that specialize in this area, as well as the producers of Catiofast PR 8106, BASF. We found no parties interested in processing the quantity of high molecular weight PVAm that we need. While still hopeful that a processor could be found, we began investigating the addition of poly(vinyl alcohol) as an additive to the coating to replace PVAm.

4.3.4 Poly(vinyl alcohol)s

Poly(vinyl alcohol) PVOH is readily available commercially in varying molecular weights and extent of hydrolysis from the source poly(vinyl acetate). Coatings were prepared with ten PVOH samples at each of three concentrations. Nomex samples were coated with each formulation and tested in high humidity. Each coating was also rated for stiffness in a dry climate. Based on these results, two PVOH samples were chosen for rinse tests with the standard rinse procedure (1L H2O @ 40psi in 4 portions separated by 1 min soaking periods). Table 14 shows the results of these rinse tests. The coatings containing PVOH rinsed off far better than PVAm coatings, possibly leading to the improved chemical performance later observed.

Table 14. Results for Rinse Analysis of Coatings Containing Poly (Vinyl Alcohol).

PVOH Sample	Coating	Avg. Coating Removed
Mw 9,000-10,000 80% Hydrolyzed	7.5% PEI / 2.5% PVOH / 0.2%FSA/ 0.2%Arlasolve	98.43% (± 0.29)
	6.0% PEI / 4.0% PVOH / 0.2%FSA/ 0.2%Arlasolve	99.05% (± 1.07)
Mw 13,000-23,000 87-89% Hydrolyzed	7.5% PEI / 2.5% PVOH / 0.2%FSA/ 0.2%Arlasolve	96.65% (± 1.26)
	6.0% PEI / 4.0% PVOH / 0.2%FSA/ 0.2%Arlasolve	95.71% (± 1.20)

Comparative rinse evaluation and tests against chemical contamination indicated that the PVOH of molecular weight 13,000-23000 (88% hydrolyzed) was the best coating additive to counteract stickiness at high humidities without significantly sacrificing chemical performance. (The interaction between PVOH and PEI is very unusual, with the polymers slowly crosslinking each other to form solid-like gels at high concentrations; further academic of this association would be interesting to researchers.) Unlike poly(vinyl amine)s, PVOH is readily available on an industrial scale and requires no pretreatment. One may obtain large volumes of this particular PVOH at 24% concentration in water from Celanese Chemicals of Dallas, Texas as the commercial product Celvol 24203.

4.4 Coating Permeability

In our formulation efforts, we studied two aspects of coating permeability: permeability to simulants, which we desired to minimize, and permeability to water vapor, which we desired to maximize. Both types of permeability tests are described below.

4.4.1 Permeability to Simulant

We designed an apparatus that simultaneously tests the permeation rates of CEES through our coating in as many as 8 individual sample cells. This helped provide a mechanistic understanding of coating performance and allowed us to quickly evaluate the performance of multiple formulations.

Figure 21 shows a schematic of the proposed apparatus and a detailed view of a sample cell. The apparatus was plumbed with polyvinyl chloride (PVC) pipe and polyethylene tubing. Needle valves were used to precisely control the gas flow to the cells. The coating samples are applied to thin, translucent silicone rubber films used as permeable supports. A disc, approximately 2" in diameter, of the coated support is cut then dosed with a known amount of

CEES in an aerosol spray and mounted in a sample cell. In the sample cells the disc is compressed along the circumference to seal it against gas leaks and prevent loss of CEES from the sample cell. The effluent end of the permeable support were purged with a sweep gas to carry any CE ES vapor that permeates the coating to a sorbent sampling tube containing Anasorb® CSC, an activated carbon made from coconut shell charcoal. The carbon traps were then extracted in acetone and subsequently analyzed to yield a time-weighted-average concentration. Using the total area of the membrane, and the purge time for a specific sorbent tube, an average permeation rate (μg CEES/cm^2/min) of CEES through the coating can be calculated.

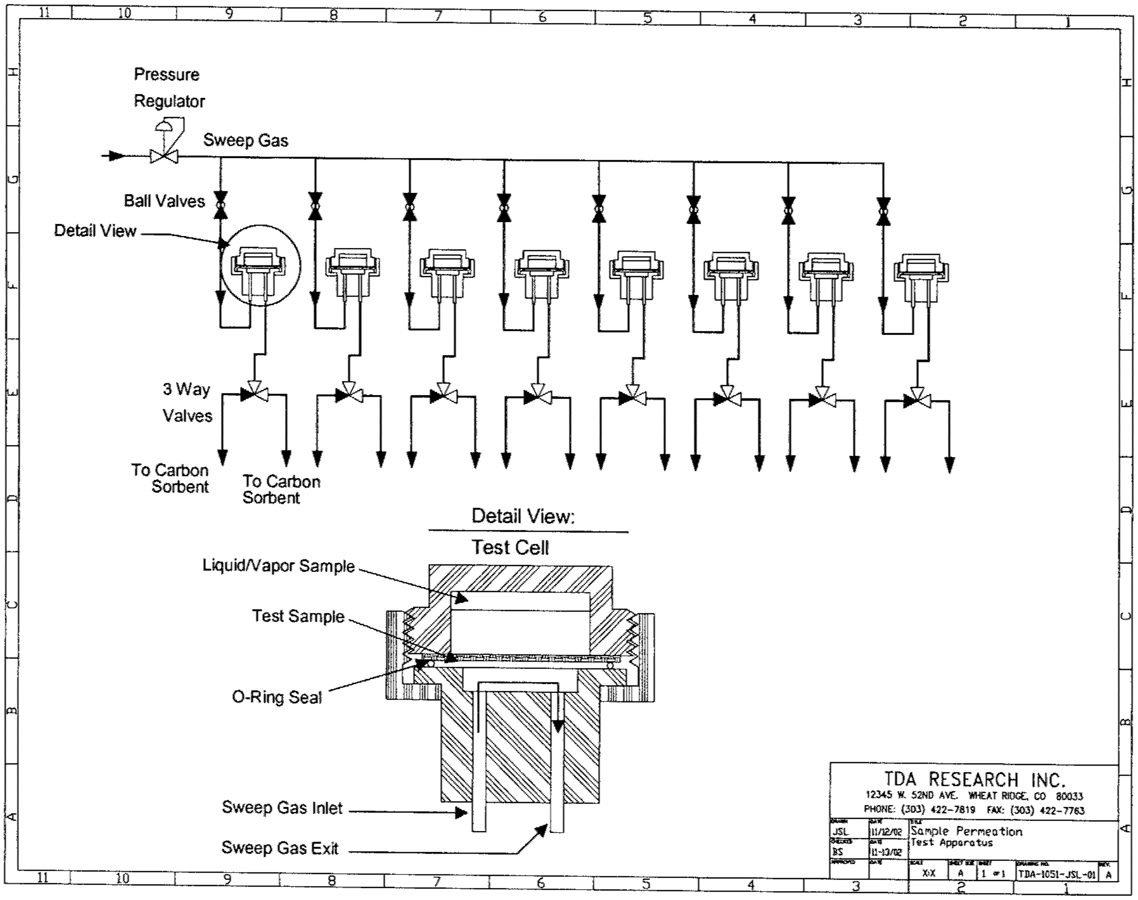


Figure 21. Test apparatus for parallel measurement of CEES permeation rates through coatings.

Once we obtained Sorbent Sampling Tubes containing Anasorb® CSC, experiments were done to establish the extraction efficiency (E_E) for desorbing CEES from the carbon. The E_E was 99%+ for CEES quantities less than 15 mg.

Figure 22 shows permeation data for a silicone coupon with coating, composition of 20%PEI and 0.5% FSA, compared with data from an uncoated silicone coupon. This data, which is the average data from three trials, indicates that the coated coupon is 200 times more effective at blocking CEES permeation than a blank coupon. The decrease in permeation rate with time is probably due to the exhaustion of the CEES supply on the contaminated side of the silicone.

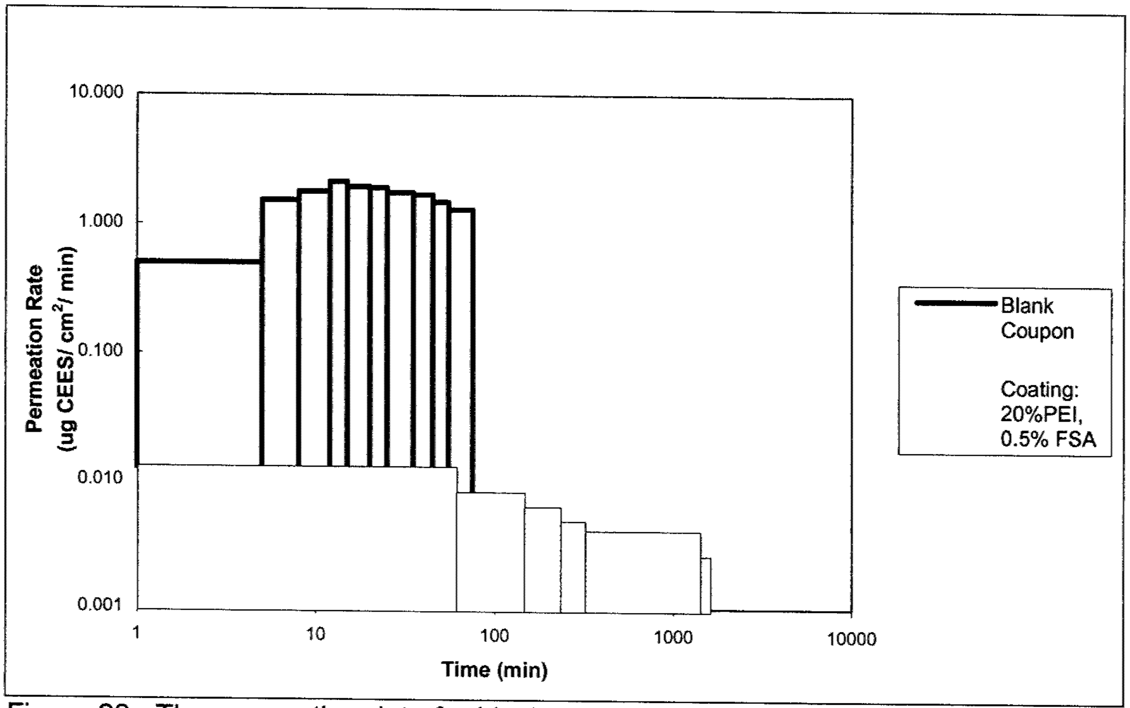


Figure 22. The permeation data for blank, uncoated coupons to the data from coupons coated with 20% Lupasol P, 0.5% Zonyl FSA. Data was obtained by adsorbing CEES onto carbon for a specified amount of time and calculating the average permeation rate over that time period. Each data set is the average of three trials with CEES loading averaging 0.297 mg/cm^2 for the blanks and 0.283 mg/cm^2 for the coating. The average coating density was 4.965 mg/cm^2 ± 5.4%, corresponding to an average thickness of about 50 um assuming the density of the coating is 1 g/cm^3. Note both axes have logarithmic scales.

Some differences to note between the testing of blank coupons and coated coupons are the time interval for each data point and the time span over which permeation was measured. There is a very deliberate reason for the differences in the time intervals for which each data point was sampled. Permeation of CEES through the blank coupon occurs very rapidly; in order to measure changes in the permeation rate each data point spans between 3 and 20 minutes of the test. In tests of the coating, the levels of CEES permeating are relatively low so the time allowed for sorption had to be at least one hour to be able to detect these levels of CEES. Even at these time intervals, the CEES concentrations were nearing the detection limit.

In order to determine of the effect fillers, such as Glass, Polacryl, and Flexbond, have on the permeability of a coating (Coating #48, described in figure caption) was tested against CEES permeation. The results, as seen in Figure 23, show that this coating was very poor at guarding against CEES permeation initially, only 20x better than a blank, and after 4 hours of CEES exposure the coating offered no more protection against permeation than a blank. Our hypothesis was that the small amount of PEI in coating #48 was rapidly overwhelmed by the applied CEES contamination.

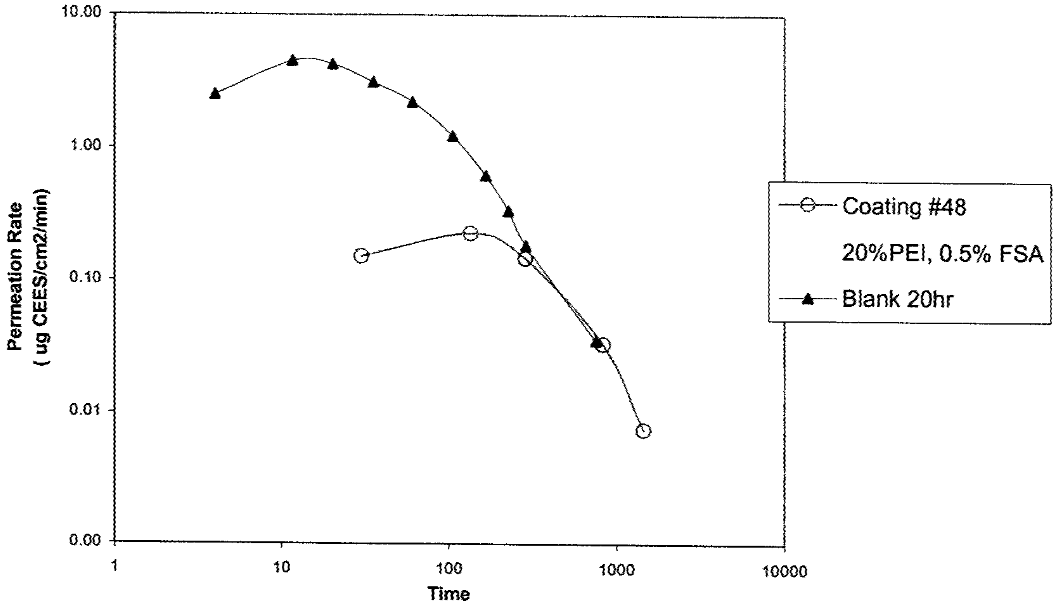


Figure 23: This figure compares permeation data of blank coupons to those coated with the 20%PEI, 0,5% FSA, average loading of 4.97mg/cm^2 ± 5%, and coupons coated with Coating #48 which contains 4%PEI, 20%Glass, 2.5% Flexbond, 4% Polacryl, 0.2%FSA, average loading 17.9mg/cm^2 ± 12%.

We also tried to observe what effect increased coating density (mass/area) would have on the CEES permeation rate for the 20% PEI, 0.5% FSA coating. The results, displayed in Figure 24, were surprising. We expected that increasing the loading, essentially making the coating thicker, would make it more difficult for CEES to permeate through the coating and the permeation rate would be consistently lower. However, the data shows that the thicker coating has, if anything, a slightly decreased resistance to permeation initially. The most likely scenario relies on the differences in the consistency of the two coatings. As previously demonstrated, the PEI coating is very hydrophilic and sticky. At higher loadings this problem is amplified, since thicker coatings take longer to dry. The coating with an average loading of 4.97 mg/cm^2 was dry to the touch, whereas the coating with average loading of 16.88 mg/cm^2 was still somewhat sticky before the experiment began. We believe that at the beginning of the experiment the coating with higher loading was acting more like a viscous liquid, which would have higher permeability than a solid film. As the experiment proceeded, the flow of dry nitrogen through the permeation cell, presumably, acted to dry out the thicker coating and make it more solid increasing its resistance to permeation.

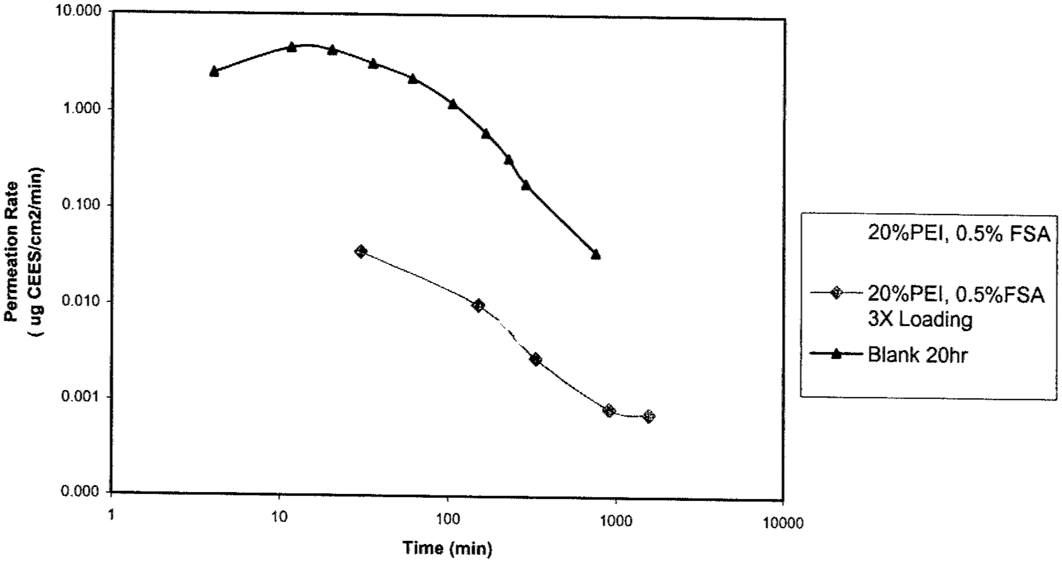


Figure 24: This figure shows the permeation results from silicone coupons coated with the 20% PEI, 0.5% FSA coating. The average loading for "20% PEI, 0.5% FSA" was 4.97 mg/cm^2 ± 5%. The average loading for "20% PEI, 0.5% FSA 3x Loading" was 16.88 mg/cm^2 ± 1%.

Other experiments support this theory of the nitrogen sweep gas drying out coatings as a permeation test progresses. We tested coatings containing 5% poly(allyl amine) (PAA) M.W. 60,000, 0.1% FSA for CEES permeation. A coating that was dry to the touch, but still flexible, on the silicone coupon would be cracked and peeling off the silicone when the permeation cell was disassembled. To verify that the peeling of the coating was caused by the coating drying out, a coated silicone coupon was placed in a desiccator and left over the weekend. Upon return, the coating exhibited similar cracking and peeling behavior as the coatings in the dry nitrogen stream.

In order to prevent this drying/cracking effect we decided to increase in the humidity of the sweep gas by bubbling the nitrogen through DI water before it entered the permeation cell. This approach did prevent the drying effect but also posed a new problem. The PAA coating proved to be very sensitive to humidity in these experiments and the coupon was slightly sticky when the permeation cell was disassembled. Additionally, the permeation data from the PAA coating with a humid sweep gas showed the coating acting liquid-like and no better at blocking CEES permeation than a blank coupon, see Figure 25. These results indicate a relationship between how dry, or solid, a coating is and its ability to resist permeation of CEES; if a coating is very highly swollen with water, it appears to offer almost no protection against chemical permeation.

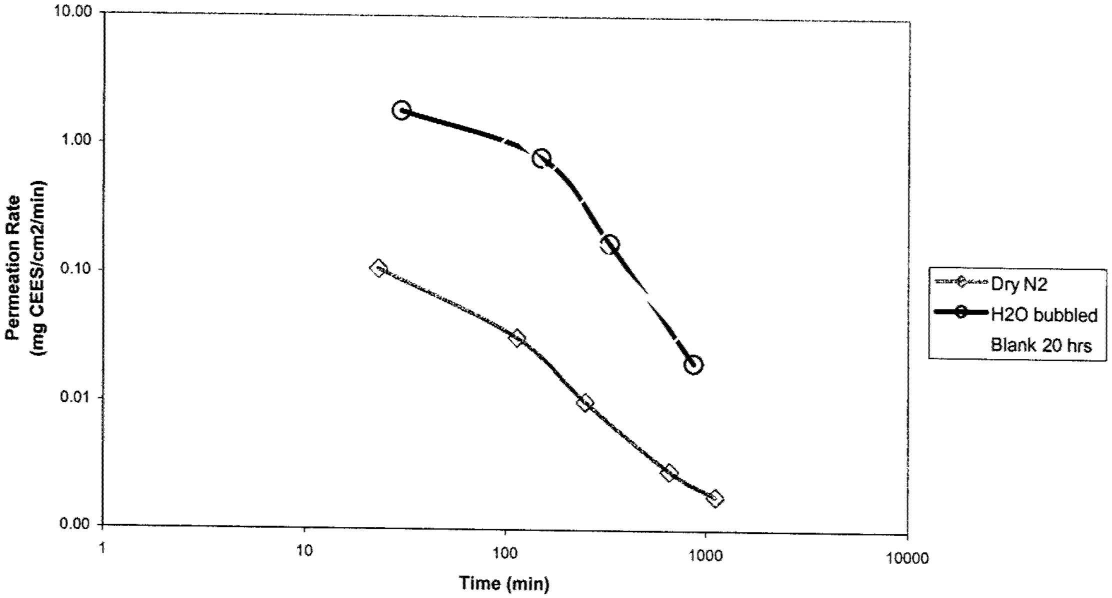


Figure 25: This figure shows the permeation data from the Poly(allyl)amine coating (5% PAA M.W. 60,000, 0.1%FSA) where the permeation cell sweep gas was either dry N_2, or N_2 bubbled through water.

4.4.2 Water Vapor Permeability

To make sure the coated cloth would not produce any additional heat stress on the wearer, we conducted a water vapor permeability analysis of the coating on Nomex cloth at varying densities. The experiment involved monitoring the mass change of a bottle containing desiccant (Drierite) subjected to 98% humidity. The bottle lid, which had a 4 cm diameter hole in it, was fitted over a piece of Nomex cloth creating a seal so that water had to permeate through the Nomex to reach the desiccant. The bottles were placed in a humidity chamber for a given time period, then removed, weighed, and place back in the chamber. The water weight gain was used to calculate the average permeation rate over that time period. Figure 26 shows the water vapor permeability of 2 samples of uncoated Nomex compared with 4 samples of coated Nomex with different coating densities. Typical coating densities for this sort of cloth are 4-6 mg/cm^2, and there appears to be very little if any added resistance to water vapor permeation at these coating densities. At very high coating densities (9.47mg/cm^2) there appears to be some drop off in the water vapor permeation. We believe that the data in Figure 26 do not indicate constant permeation rates because of the inability to maintain humidity in the test chamber given the rapid rate at which the desiccant is taking up water, not due to decreases in the water vapor permeability of the samples.

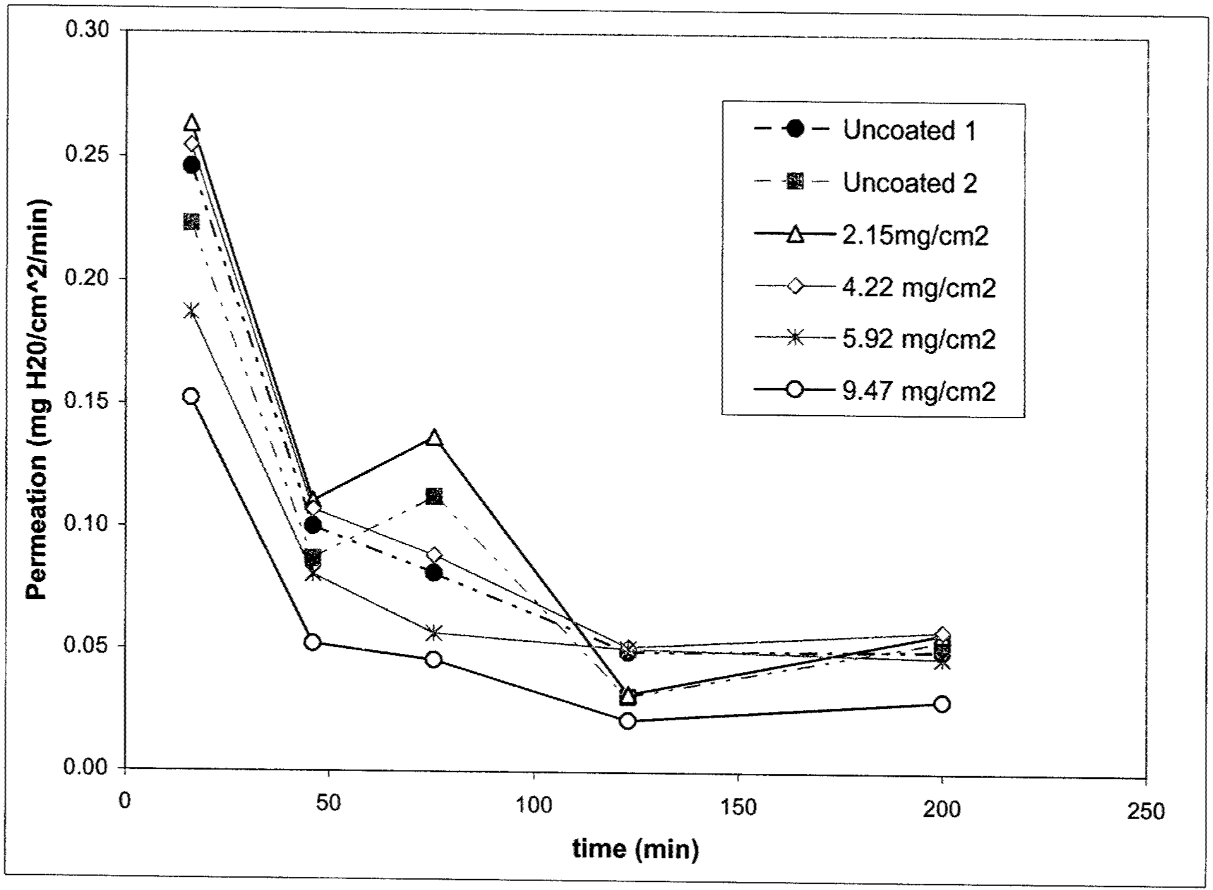


Figure 26. Water Vapor Permeability of Nomex Cloth. Permeability appears to decrease as a function of time presumably because the moisture absorption from the atmosphere is more rapid than replenishment from the stock solution, lowering the relative humidity in the chamber and thereby decreasing the apparent permeation rate during the course of the experiment.

4.5 Indicators for Coating Application and Removal

As a component of our formulation we sought to include a visual aide for users that indicates when the coating is rinsed off the substrate. We investigated colored dyes (disappearing inks) as well as additives that foam upon rinsing. Each of these is discussed in some detail below.

4.5.1 Colored indicators

As a practical matter, it would be very useful to have visual indications both of coating application density, so one could tell when the coating had been applied correctly, and of rinsing efficiency, so one could easily determine when an ensemble had been sufficiently rinsed by the disappearance of color in the rinse water. Initially we experimented with food-coloring dyes. These experiments proved that the coating could be colored, but the red dye, which gave the best visual indications of application and removal, gave coated substrates an obvious reddish tint. To alleviate this we experimented with acid-base indicators, including thymolphthalein, which would indicate the presence of wet coating. Thymolphthalein is a deep blue color in solutions with a pH above 9.4. As the water evaporates and the coating dries, the blue color fades so that there is no noticeable color change on the coated substrate. Experiments performed by drying out a coating containing Lupasol P and thymolphthalein indicated that the blue color would return when water was added. However in a test rinsing the coating off a substrate, the color proved too faint in the rinse water to be a good marker of coating removal.

4.5.2 Foaming Surfactant Indicators

We looked into the use of a surfactant combination in the coating that produces lots of foam during the rinsing process as a visual indication of coating removal. The person rinsing the gear would be able to know when the coating was sufficiently removed by the disappearance of foam in the rinse water. For this purpose we first tested coatings containing polyamine and a single surfactant. The coatings were sprayed on a sample of butyl rubber (12 cm^2) and on Nomex cloth (225 cm^2 sample) and allowed to dry overnight. The coating quality on butyl rubber was assessed to determine if foam, which occurs during spray application, would break and form a smooth coat without dried bubbles. These samples were rated on a scale 1 to 4, with 4 being a perfectly smooth coating and 1 being dried foam. Next, the dried Nomex samples were sprayed with a garden hose. The quantity and quality of the foam was observed and rated on a 1 to 4 scale (1 = no foam or bubbles, 4 = easy to see foam or bubbles). Each sample was rinsed for approximately 30 seconds after the foam was no longer evident and then allowed to dry. The percentage of coating remaining on the samples after rinsing was calculated. Table 15 shows the results of these experiments.

Table 15. Surfactant Testing of Coatings Containing a Single Surfactant at Two Concentrations.

PEI (wt%)	Surfactant Name (wt%)	Nomex Coating Density (mg/cm^2)	Coating Quality on Rubber (1-4)	Foam Rating when Rinsed (1-4)	Coating Remaining After Rinse %
Water-Free(10%)	Zonyl FSA (0.5 %)	2.9	3.5	1.5	15 %
Water-Free(10%)	Zonyl FSA (0.05 %)	2.9	3.5	1.5	18 %
Water-Free(10%)	Pluronic P84 (0.5%)	2.2	3.5	2	10 %
Water-Free(10%)	Pluronic P84 (0.05%)	2.6	4	2	11 %
Water-Free(10%)	Pluronic P65 (0.5%)	2.2	3.5	2	10 %
Water-Free(10%)	Pluronic P65 (0.05%)	2.2	3.5	2	10 %
Water-Free(10%)	Arlasolve 200 (0.5%)	1.6	3.5	2.5	7 %
Water-Free(10%)	Arlasolve 200 (0.05%)	2.3	4	2	9 %
Water-Free(10%)	T-Maz (0.5%)	2.4	3.5	1	18%
Water-Free(10%)	T-Maz (0.05%)	3.1	3.5	1	14%

Based on the results shown in Table 15, we chose to further investigate the Arlasolve 200 surfactant. We tried a combination of Arlasolve 200 with Zonyl FSA, the current surfactant used in coatings, and performed the same analysis that was done on the individual surfactants. Table 16 shows that the combined surfactants worked far better than either surfactant on its own for both the quality of the coating on rubber and the quantity of foam produced when rinsed resulting in more coating removal. The combination of Zonyl FSA and Arlasolve 200 produced a steady stream of bubbles until 95+% of coating was removed in laboratory tests.

Table 16. Surfactant Testing in Coatings Containing both Arlasolve 200 and Zonyl FSA.

PEI (wt%)	Zonyl FSA (wt%)	Arlasolve 200 (wt%)	Coating Density on Nomex (mg/cm^2)	Coating Quality on Rubber (1-4)	Foam Rating when Rinsed (1-4)	Coating Remaining After Rinse %
Water-Free(10%)	0.5 %	0.5 %	4.52	4	3.5	1.4 %
Water-Free(10%)	0.5 %	0.1 %	4.14	4	3	3.2 %
Water-Free(10%)	0.1 %	0.5 %	6.26	4	3	1.3 %
Water-Free(10%)	0.1 %	0.1 %	5.12	4	2.5	3.4 %

Technicians at Calspan/University of Buffalo Research Center (CUBRC) saw this coating and did not belive that the foam in the rinse water was sufficiently visible to be a good indicator. In order to further improve the foaming indicator, we tested coating formulations containing various concentrations of ethoxylated nonyl phenol and dodecyl sulfate, which are both known to be high foaming surfactants. We also added carboxymethyl cellulose, which acts to stabilize the foam, with base formulations containing either ethoxylated nonyl phenol or dodecyl sulfate. Table 17 and Table 18 show the coating formulations that were sprayed on Nomex squares (100 cm^2) then rinsed with tap water, until they stopped foaming. The foam was rated for quantity and stability. Coating removal was calculated for the coatings that showed the most promising foaming characteristics. Formulations 466-37-02, 466-37-03, 466-37-08, and 466-37-09 performed the best with the most visible and stable foam.

Table 17. Coating Formulations Containing Ethoxylated Nonyl Phenol.

Sample ID	PVA Wt%	Lupasol P Wt%	Zonly FSA Wt%	Arlasolve 200 Wt%	Ethoxylated Nonyl Phenol Wt%	Carboxy Methyl Cellulose Wt%	Percent Coating Remaining After Rinse
466-37-01	1.25	3.75	0.1	0.1	0.100	0.002	-
466-37-02	1.25	3.75	0.1	0.1	0.300	0.002	1.2 %
466-37-03	1.25	3.75	0.1	0.1	0.800	0.002	1.3 %
466-37-04	1.25	3.75	0.1	0.1	0.100	-	-
466-37-05	1.25	3.75	0.1	0.1	0.300	-	-
466-37-06	1.25	3.75	0.1	0.1	0.800	-	-

Table 18. Coating Formulation Containing Dodecyl Sulfate.

Sample ID	PVA Wt%	Lupasol P Wt%	Zonly FSA Wt%	Arlasolve 200 Wt%	Dodecyl Sulfate Wt%	Carboxy Methyl Cellulose Wt%	Percent Coating Remaining After Rinse
466-37-07	1.25	3.75	0.1	0.1	0.100	0.002	-
466-37-08	1.25	3.75	0.1	0.1	0.250	0.002	1.2 %
466-37-09	1.25	3.75	0.1	0.1	0.500	0.002	1.6 %
466-37-10	1.25	3.75	0.1	0.1	0.100	-	-
466-37-11	1.25	3.75	0.1	0.1	0.250	-	-
466-37-12	1.25	3.75	0.1	0.1	0.500	-	-

Next, we tested combinations of these formulations at lower concentrations for the final surfactant mixture. Surfactant rinse tests were performed with the ethoxylated nonly phenol and dodecyl sulfate at lower concentrations in order to finalize the concentrations of additional surfactants in the final coating mixture. Table 19 and Table 20 show the coating formulations and the fraction of coating remaining after they were rinsed until they stopped foaming. We also rated the foam for quantity and stability. All coatings performed fairly well, however those containing dodecyl sulfate and carboxy methyl cellulose had the most stable, visible foam. Based on these results we chose a final surfactant concentration of 0.01% dodecyl sulfate and 0.002% carboxy methyl cellulose for coatings containing 5% polymer.

Table 19. Coating Formulations Containing Ethoxylated Nonyl Phenol.

Sample ID	PVA Wt%	Lupasol P Wt%	Zonly FSA Wt%	Arlasolve 200 Wt%	Ethoxylated Nonyl Phenol Wt%	Carboxy Methyl Cellulose Wt%	Percent Coating Remaining After Rinse
466-43-01	1.25	3.75	0.1	0.1	0.0100	0.002	9.5%
466-43-02	1.25	3.75	0.1	0.1	0.0300	0.002	14.4%
466-43-03	1.25	3.75	0.1	0.1	0.0800	0.002	7.6%
466-43-04	1.25	3.75	0.1	0.1	0.0100	-	5.4%
466-43-05	1.25	3.75	0.1	0.1	0.0300	-	8.2%
466-43-06	1.25	3.75	0.1	0.1	0.0800	-	8.7%

Table 20. Coating Formulation Containing Dodecyl Sulfate.

Sample ID	PVA Wt%	Lupasol P Wt%	Zonly FSA Wt%	Arlasolve 200 Wt%	Dodecyl Sulfate Wt%	Carboxy Methyl Cellulose Wt%	Percent Coating Remaining After Rinse
466-43-07	1.25	3.75	0.1	0.1	0.0100	0.002	4.2%
466-43-08	1.25	3.75	0.1	0.1	0.0250	0.002	4.7 %
466-43-09	1.25	3.75	0.1	0.1	0.0500	0.002	6.1%
466-43-10	1.25	3.75	0.1	0.1	0.0100	-	9.6%
466-43-11	1.25	3.75	0.1	0.1	0.0250	-	9.5%
466-43-12	1.25	3.75	0.1	0.1	0.0500	-	9.7%

4.6 Fire Retardant Additives

Initially we conducted flammability tests on coated (7.5% PEI, 2.5% PVA, 0.2% Zonyl FSA, and 0.2% Arlasolve 200) Nomex samples. Tests were performed on a coated (density of approximately 6 mg/cm^2) 10 x 10 cm^2 Nomex sample. After the coatings dried, the corner of the fabric was ignited with a propane torch. Uncoated Nomex burns in the flame but self-extinguishes when removed from the flame. When coated Nomex was removed from the flame it did not self-extinguish. Initially, we believed the enhanced flammability of the coated Nomex was due to the poly (vinyl alcohol) (PVA), which is known to be flammable; however, Nomex coated with only (PEI) also did not self-extinguish.

A coating that increases the flammability of the substrate is obviously unacceptable, so we started to investigate the addition of flame retardants to the coating formulation in order to counteract the observed flammability. Some of the most common water-soluble flame-retardants contain bromide ions, phosphoric acid, phosphates, or boric acid. We experimented with potassium bromide, phosphoric acid, sodium phosphate salts, and boric acid in various loadings (5-20 weight % based on solids). We added the retardant chemicals to the base coating formulation containing 7.5% PEI, 2.5% PVA, 0.2% Zonyl FSA, and 0.2% Arlasolve 200. None of these additives appeared to significantly improve flame resistance. Additionally, we tried various commercial flame retardant mixes. Flame Safe Chemical Corporation's *FRT Add Mix*, *Fire poly FP757-I*, and *Polymeric Resin* did not to decrease flammability significantly. Manufacturers Chemicals' *Flame Retard* was used at concentrations of 5-50%. Although some improvement in flame resistance was observed with this product, it was not sufficient to be utilized as the sole fire retardant.

At this point we developed a consistent method for measuring the flammability of coated Nomex by which we could gauge the efficacy of various fire retardant additives on more than just a pass fail basis. Our method for testing the effectiveness of different fire retardant additives uses elements of ASTM Methods D6413 Standard Test Method for Flame Resistance of Textiles (Vertical Test), D1230 Standard Test Method for Flammability of Apparel Textiles, and F1358 Standard Test Method for Effects of Flame Impingement of Materials Used in Protective Clothing Not Designated Primarily for Flame Resistance.

Tests were performed on coated Nomex samples (7 cm x 16 cm) with a coating density of approximately 5 mg/cm^2. For a given test the coated fabric sample was held in a three-sided aluminum frame shown in Figure 27. The frame was fixed to a ring stand with clamps so that the fabric would rest vertically. The entire set up was housed in a fish tank inside of a chemical fume hood to minimize draft through the system during testing. A flame from a propane torch was applied to the center of the fabric at the bottom open edge for 3 seconds. The flame was then removed and the afterflame time (persistent flaming of the fabric after the ignitions source has been removed) was measured. If the fabric self extinguished, the char length (distance from the fabric edge, which is directly exposed to flame, to the furthest point of visible fabric damage) was recorded. Any melting, dripping, or shrinkage of the fabric was noted.

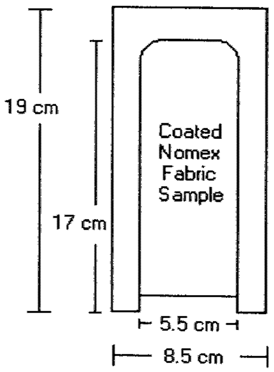


Figure 27. Aluminum frame for flammability testing.

Table 21 shows the flammability testing results for uncoated Nomex and coatings containing Manufacturers Chemicals' *Flame Retard,* ammonium hydrogen phosphate, and ammonium dihydrogen phosphate as flame retardants. We added the retardant chemicals to the base coating formulation containing 7.5% Lupasol P, 2.5% Poly(vinyl alcohol), 0.2% Zonyl FSA, and 0.2% Arlasolve 200. Each type of fire retardant additive was tested at several weight percentages based on total solids in the coating. Manufacturers Chemicals *Flame Retard* and ammonium dihydrogen phosphate were both effective flame retardants at relatively high loadings (≥ 35 wt% solids) and the coated fabric samples containing these fire retardants generally performed better than uncoated Nomex. These retardants left the coating with a moderate ammonia odor (from the phosphate), so we continued looking for other fire retardants which exhibited similar efficacy without this undesirable side effect.

Table 21. Flammability testing results for coatings with flame retardant additives.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm, cm)*	NOTES - Melting, Dripping, Shrinkage, etc.
Nomex	Uncoated Nomex	3	3.16	4.0, 7.0	-
466-52-A	20 wt% Flame Retard	3	infinite	-	continued burning, extinguished
466-52-B	30 wt% Flame Retard	3	infinite	-	continued burning, extinguished
466-52-C	40 wt% Flame Retard	3	2.97	3.5, 6.0	shrinkage
466-52-D	50 wt% Flame Retard	3	2.68	2.8, 5.0	shrinkage
466-48-A	50 wt% Flame Retard	3	4.75	3.5 , 7.0	shrinkage
466-48-B	60 wt% Flame Retard	3	1.78	3.0 , 4.5	shrinkage
466-48-C	70 wt% Flame Retard	3	instantaneous	2.5 , 3.5	shrinkage
466-47-6	10 wt% $(NH_4)_2HPO_4$	3	infinite	-	continued burning, extinguished
466-47-8	30 wt% $(NH_4)_2HPO_4$	3	infinite	-	continued burning, extinguished
466-50-1	10 wt% $(NH_4)H_2PO_4$	3	infinite	-	continued burning, extinguished
466-50-3	30 wt% $(NH_4)H_2PO_4$	3	infinite	-	continued burning, extinguished
466-52-E	35 wt% $(NH_4)H_2PO_4$	3	instantaneous	2.8, 3.5	shrinkage
466-52-F	40 wt% $(NH_4)H_2PO_4$	3	instantaneous	2.7, 3.5	shrinkage
466-50-4	40 wt% $(NH_4)H_2PO_4$	3	instantaneous	2.25, 3.75	shrinkage

*Char length is recorded as the distance that there is complete degradation of Nomex material followed by the distance that there is any blackened residue present on the Nomex.

Bases upon results from the flammability testing in Table 21, we chose 5 formulations to test against CEES contamination. Each sample was contaminated with CEES, allowed to sit for 1 hour in a closed container, rinsed (1L H2O @ 40psi in 4 portions separated by 1 min soaking periods), extracted, and analyzed. Table 22 shows the CEES contamination results for these coatings. The results of this round of contamination testing indicated that these flame retardant additives may inhibit the effectiveness of the coating to deactivate CEES.

Table 22. Residual CEES analysis results of coaitings containing Flame Retard and $(NH_4)H_2PO_4$.

Sample	Coating	Avg. CEES Remain
164 A,B,C	Base+40% Fire Retard	5.15%±3.20
165 A,B,C	Base+50% Fire Retard	7.14%±1.03
166 A,B,C	Base+60% Fire Retard	7.07%±2.05
167 A,B,C	Base+35% (NH4)H2PO4	13.46%±6.18
168 A,B,C	Base +40% (NH4)H2PO4	23.27%±0.71
169 A,B,C	Blank	26.46%±4.44

The next flame retardants tested were a group of products under the trade name Antiblaze, manufactured by Rhodia. These compounds are based on ammonium polyphosphates. We tested three different products from Rhodia: Antiblaze FSD, Antiblaze RD1, and Antiblaze LR4. We made three different coatings by adding each of the Antiblaze to the base coating formulation containing 7.5% Lupasol P, 2.5% Poly(vinyl alcohol), 0.2% Zonyl FSA, and 0.2% Arlasolve 200. Generally, the Antiblaze retardants exhibited much less ammonia odor, although this odor is still a potential problem. Table 23 shows the fire retardant results for these coatings.

Table 23. Flammability testing results for coatings containing Antiblaze products.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm, cm)*	NOTES - Melting, Dripping, Shrinkage, etc.
466 54 1	10 % Anti Blaze FSD	3	infinite	-	continued burning, extinguished
466 54 2	20% ”	3	infinite	-	continued burning, extinguished
466 54 3	30% ”	3	infinite	-	continued burning, extinguished
466 54 4	40% “	3	5.25	4.5, 9.0	shrinkage
466 54 5	50% “	3	5.27	1.5, 3.0	shrinkage
466 54 6	10% Antiblaze RD1	3	infinite	-	continued burning, extinguished
466 54 7	20% “	3	infinite		continued burning, extinguished
466 54 8	30% “	3	infinite	-	continued burning, extinguished
466 54 9	40% “	3	infinite	-	continued burning, extinguished
466 54 10	50% “	3	infinite	-	continued burning, extinguished
466 54 11	10% Antiblaze LR4	3	infinite	-	continued burning, extinguished
466 54 12	20% “	3	infinite	-	continued burning, extinguished
466 54 13	30% “	3	7.09	6.0, 8.0	shrinkage

The next set of samples tested contained coatings that had a mixture of *Fire Retard* and Antiblaze FSD in equal portions, as we were hoping for synergistic effects of the combined fire retardants. If chemical retardant concentration is 20% then the Fire Retardant concentration is 10% and the Antiblaze concentration is 10%. These were also added to the base mixture described above. In addition, we tested samples that contained the base mixture with phosphoric acid (H_3PO_4) added as a chemical fire retardant. Table 24 shows the results of these experiments. Mixing these two fire retardants did not significantly improve the overall fire protection. The use of phosphoric acid was promising, but we anticipated that the chemical performance of the coatings could suffer since the phosphoric acid neutralizes much of the basic character of the coating which is responsible, in principle, for the effectiveness of the coating in neutralizing chemical agents

Table 24. Flammabilty testing for coatings containing mixtures of retardants or H_3PO_4.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm, cm)*	NOTES - Melting, Dripping, Shrinkage, etc.
1	20 % Mixture	3	infinite	-	continued burning, extinguished
2	30% ”	3	infinite	-	continued burning, extinguished
3	40% ”	3	9.13	3.0, 5.5	shrinkage
4	50% “	3	9.29	3.0, 8.0	shrinkage
5	10% H_3PO_4	3	infinite	-	continued burning, extinguished
6	20% “	3	7.23	3.5, 7.0	shrinkage
7	30% “	3	2.12	2.5, 5.0	shrinkage
8	40% “	3	instant	2.5	Burned flame contact area only

After careful analysis of the ASTM methods we had modeled the procedure after, we made some slight modifications to our flammability testing method. Previously we were using a propane torch as the flame source which was applied to the front face of the fabric at the vertical center near the bottom of the sample. We determined that a propane torch is not the best model for a flame source. ASTM F1358 Standard Test Method for Effects of Flame Impingement of Materials Used in Protective Clothing Not Designated Primarily for Flame Resistance indicates that the flame (from a Bunsen burner or similar source) should be 1 ½" in length with ¾" of the flame in direct contact with the fabric. Additionally, the flame should be positioned so that it is beneath the fabric sample pointed in the direction of the fabric. To be more faithful to ASTM methods, we changed the flame source to a butane lighter with an adjustable flame. We also began testing each coating in replicates of at least 5 and averaging the results to minimize any inconsistencies in the method. We do not believe that this change in method affected the relative effectiveness of the fire retardants.

Table 25. Fire Tesistance Testing for Uncoated Nomex.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.62.1	Uncoated Nomex	3	25.81	11.50	Self extinguished after long burn
466.62.2	Uncoated Nomex	3	26.02	16.00	sample slipped/ blown out
466.62.3	Uncoated Nomex	3	1.90	1.00	-
466.62.4	Uncoated Nomex	3	1.92	2.00	-
466.62.5	Uncoated Nomex	3	34.12	16.00	sample slipped/ blown out
466.62.6	Uncoated Nomex	3	2.02	2.50	-
466.62.7	Uncoated Nomex	3	40.35	16.00	blown out, burned entire coupon
466.62.8	Uncoated Nomex	3	2.33	2.00	-
466.62.9	Uncoated Nomex	3	1.02	1.00	instant out
466.62.10	Uncoated Nomex	3	1.90	1.50	-
466.62.11	Uncoated Nomex	3	3.22	3.00	-
		AVG	12.78	6.59	
		StdDev	15.39	6.71	

The first samples tested with this modified method was a set of 11 uncoated Nomex coupons. Data for uncoated Nomex is shown in Table 25. Out of the 11 samples tested, 3 had to be extinguished, 1 burned 25.8 s after the flame was removed then self-extinguished, and 7 self extinguished in 3.2 s or less. The data shows that 36% of the samples tested had considerable after flame times and char lengths.

Table 26. Fire Resistance Testing for containing 15 wt% based on total solids Phosphoric Acid.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.63.A01	15% H_3PO_4	3	13.62	16.00	blown out
466.63.A02	"	3	0.00	0.00	
466.63.A03	"	3	1.78	0.50	
466.63.A04	"	3	15.11	16.00	blown out, burned entire coupon
466.63.A05	"	3	2.15	0.00	
		AVG	6.53	6.50	
		StdDev	7.22	8.67	

Various coatings containing phosphoric acid, H_3PO_4, were tested with the new procedure. Three of the 5 samples (40%) with 15 wt% H_3PO_4, Table 26, self-extinguished rapidly. Table 27 shows that all of the samples with 20 wt% H_3PO_4 extinguished rapidly with an average after flame time of 1.2 s. Coatings with 25 wt% phosphoric acid performed well with all but one sample self extinguishing (Table 28).

Table 27. Fire Resistance Testing for containing 20 wt% based on total solids Phosphoric Acid.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.63.B01	20% H_3PO_4	3	1.54	0.20	
466.63.B02	"	3	1.15	0.20	
466.63.B03	"	3	1.20	0.30	
466.63.B04	"	3	0.90	0.40	
466.63.B05	"	3	1.20	0.50	
		AVG	1.20	0.32	
		StdDev	0.23	0.13	

Table 28. Fire Resistance Testing for containing 25 wt% based on total solids Phosphoric Acid.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.63.C01	25% H_3PO_4	3	0.00	0.20	
466.63.C02	"	3	1.45	0.40	
466.63.C03	"	3	0.00	0.20	
466.63.C04	"	3	1.36	0.50	
466.63.C05	"	3	18.60	16.00	blown out, burned entire coupon
		AVG	4.28	3.46	
		StdDev	8.03	7.01	

The next series of samples tested contained Octoguard, a fire retardant mixture comprising of 20% antimony trioxide and 80% decabromodiphenyl oxide, DBDO. Table 29 shows data for coating containing 5 wt% Octoguard; 60% of the samples had to be extinguished. Table 30 shows that when the Octoguard concentration was increased to 10 wt% all of the samples self extinguished with an average after flame time of 6.47s. Samples were also tested with 15% H3PO4 and 5% Octoguard, shown in Table 31; this formulation improved on the performance of both individual components with an average after flame time of 3.54 s and a char length of 0.64 cm.

Table 29. Fire Resistance Testing for containing 5 wt% based on total solids Octoguard Mix.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.63.E01	5% Octoguard	3	12.80	16.00	blown out, burned entire coupon
466.63.E02	5% Octoguard	3	27.52	16.00	blown out, burned entire coupon
466.63.E03	5% Octoguard	3	13.97	16.00	blown out, burned entire coupon
466.63.E04	5% Octoguard	5	4.96	2.40	*ignition time 5s
466.63.E05	5% Octoguard	3	3.68	2.00	
		AVG	12.59	10.48	
		StdDev	9.52	7.56	

Table 30. Fire Resistance Testing for containing 10 wt% based on total solids Octoguard Mix.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.63.F01	10% Octoguard	3	11.68	6.50	
466.63.F02	10% Octoguard	3	8.30	4.00	
466.63.F03	10% Octoguard	3	2.46	0.70	
466.63.F04	10% Octoguard	3	3.91	3.00	
466.63.F05	10% Octoguard	3	6.00	2.00	
		AVG	6.47	3.24	
		StdDev	3.65	2.19	

Table 31. Fire Resistance Testing for containing 15 wt% Phosphoric Acid and 5 wt% based on total solids.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.63.G01	15%H3PO4 5%Octoguard	3	3.44	0.40	
466.63.G02	15%H3PO4 5%Octoguard	3	3.08	0.30	
466.63.G03	15%H3PO4 5%Octoguard	3	5.79	1.50	
466.63.G04	15%H3PO4 5%Octoguard	3	3.15	0.30	
466.63.G05	15%H3PO4 5%Octoguard	3	2.25	0.70	
		AVG	3.54	0.64	
		StdDev	1.33	0.51	

The last group of coatings contained the Octoguard component DBDO with phosphoric acid replacing antimony trioxide in the same mole ratio.

Table 32 shows results for this combination with 5 wt% total fire retardant additives. The coating performed poorly and all of these coupons had to be extinguished. Table 33 shows results for samples with the fire retardant combination at 10 wt%, three of which self extinguished rapidly.

Table 32. Fire Resistance Testing for containing 4.6 wt% Decabromodiphenyl oxide and 0.4 wt% Phosphoric Acid based on total solids.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.69.A01	4.6%DBDO 0.4%H3PO4	3	13.78	16.00	blown out, burned entire coupon
466.69.A02	4.6%DBDO 0.4%H3PO4	3	14.68	16.00	blown out, burned entire coupon
466.69.A03	4.6%DBDO 0.4%H3PO4	3	13.00	16.00	blown out, burned entire coupon
466.69.A04	4.6%DBDO 0.4%H3PO4	3	13.00	16.00	blown out, burned entire coupon
466.69.A05	4.6%DBDO 0.4%H3PO4	3	15.47	16.00	blown out, burned entire coupon
		AVG	13.99	16.00	
		StdDev	1.08	0.00	

Table 33. Fire Resistance Testing for containing 9.2 wt% Decabromodiphenyl oxide and 0.8 wt% Phosphoric Acid based on total solids.

SAMPLE NUMBER	SAMPLE DESCRIPTION	FLAME APPLICATION TIME (s)	AFTER FLAME TIME (s)	CHAR LENGTH (cm)	NOTES - Melting, Dripping, Shrinkage
466.69.B01	9.2%DBDO 0.8%H3PO4	3	1.90	1.00	
466.69.B02	9.2%DBDO 0.8%H3PO4	3	3.65	1.40	
466.69.B03	9.2%DBDO 0.8%H3PO4	3	13.56	16.00	blown out, burned entire coupon
466.69.B04	9.2%DBDO 0.8%H3PO4	3	3.83	0.90	
466.69.B05	9.2%DBDO 0.8%H3PO4	3	14.66	16.00	blown out, burned entire coupon
		AVG	7.52	7.06	
		StdDev	6.08	8.16	

We continued to test coatings that contained decabromodiphenyl oxide (DBDPO) and phosphoric acid, H_3PO_4, in combination as flame retardant additives. The base coating for the first batch of flame testing consisted of 7.5% Lupasol P, 2.5% Poly(vinyl alcohol), 0.2% Zonyl FSA, 0.2% Arlasolve 200, 0.008% Carbxoy Methyl Cellulose, and 0.1% Dodecyl Sulfate. The total concentration of flame resistant additives was either 10% or 20% of total solids. Within those parameters the concentrations of DBDPO and H_3PO_4 was 70% and 30% or 85% and 15%, respectively. Table 34 contains the results of the first set tests.

Table 34. Flame Resistance Test for Coatings containing 10% total DBDPO & H_3PO_4(70/30).

Sample	Flame Retardant Concentration (DBDPO/H_3PO_4)	Flame Application time(s)	After Flame Time(s)	Char Length (cm)	Notes - Melting, Dripping, Shrinkage
A1	10% Total(70/30)	3	10.96	10.5	Manually Extinguished
A2	"	3	1.53	0.4	Instant Out, self extinguish
A3	"	3	5.08	3.5	Self Extinguish
A4	"	3	1.75	1.3	"
A5	"	3	3.61	1.5	"
		AVG	4.59	3.44	
		StdDev	3.84	4.11	

Individual results for this coating are very good with the exception of the first sample. The next batch tested also contained 10% total flame retardant but with concentrations of 85% and 15% for DBDPO and H_3PO_4 respectively. Initially we tested 5 samples, however, since the coatings performed well, we tested an additional 5 samples, totaling ten, to be sure of the results. Table 35 contains results for these tests.

Table 35. Flame Resistance Test for Coatings containing 10% Total DBDPO & H_3PO_4(85/15).

Sample	Flame Retardant Concentration (DBDPO/H_3PO_4)	Flame Application time(s)	After Flame Time(s)	Char Length (cm)	Notes - Melting, Dripping, Shrinkage
B1	10% Total(85/15)	3	6.41	3.0	Self Extinguished
B2	"	3	4.27	0.8	"
B3	"	3	1.33	1.4	"
B4	"	3	2.58	1.3	"
B5	"	3	4.24	2.5	"
B6	"	3	6.53	3.7	-
B7	"	3	3.77	0.3	"
B8	"	3	3.49	0.2	"
B9	"	3	20.00	16.00	Burned to end
B10	"	3	6.96	2.5	Self Extinguished
		AVG	5.96	3.17	
		StdDev	5.25	2.50	

This formulation performed very well. Even though sample B9 burned to the end of the Nomex (16 cm), it burned slowly and only in the middle of the sample. The entire sample was not consumed. This is similar to the performance of an uncoated Nomex sample. The results with sample B9 removed yielded an average after flame time of 4.40 s ±1.91 and an average char length of 1.74 cm ± 1.24. Next we flame-tested this formulation with variations in coating density. Table 36 contains the results of this analysis.

Table 36. Flame Resistance Testing for Coating with 10% total DBDPO & H_3PO_4. (85/15) Variable Coating Density.

Sample	Coating Density (mg/cm^2)	Flame Application time(s)	After Flame Time(s)	Char Length (cm)	Notes - Melting, Dripping, Shrinkage
B11	2.5	3	1.21	1.0	Instantly out
B12	2.6	3	1.73	0.8	"
B13	4.1	3	3.95	1.0	"
B14	4.2	3	1.99	1.0	"
B15	4.6	3	0.91	0.3	"
B16	5.4	3	13.59	16.0	Burned to end, Mid of sample
B17	7.4	3	7.21	0.5	Self Extinguish
B18	6.6	3	15.58	9.5	"
B19	9.7	3	17.77	12.4	"
B20	8.9	3	12.86	2.6	"

These results indicate that at coating densities below about 5 mg/cm^2 the flame instantly extinguishes, while coatings with higher densities generally burn for a longer time but still self-extinguish. Sample B16 was the only example of the flame burning the length of the sample, but again it only burned the middle of the sample not the entire piece and this performance was similar to that of untreated Nomex. We also tested a coating that contained the same base formulation with 20% flame retardant additives on total coating solids. The concentrations of the DBDPO and H_3PO_4 were again 85/15% or 70/30% respectively. While these coatings performed well in flame testing, they were discounted from further consideration because of a white residue left on the samples upon drying.

The fire retardant formulation of 85% DBDPO and 15% H_3PO_4 from Table 36 had satisfactory flammability testing results and was tested for efficacy against chemical contamination with two base formulations at 1 wt% total fire retardants on total liquid formulation. The first base formulation, B(0.1), contained 7.5% Lupasol P, 2.5% Poly(vinyl alcohol), 0.2% Zonyl FSA, 0.2% Arlasolve 200, 0.008% Carbxoy Methyl Cellulose, 0.1% Sodium Dodecyl Sulfate. The second formulation, B(0.02) reduced the Sodium Dodecyl Sulfate to 0.02%. We tested each coating with and without Sandia Decontamination foam. For each sample receiving the decon foam, 2 squirts of foam were applied to the contaminated sample and the allowed to set for 5 minutes (this corresponds to approximately 1.5 times the manufacturers recommendation). Next the coupons were rinsed (1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods), extracted in acetone, and analyzed by gas chromatography. The results are shown in Table 37.

Table 37. Residual CEES Analysis for Coatings B(0.02) & B(0.1).

Samples	**Coating**	**Foam**	**Avg CEES Remain.**
1,2,4	B(0.02)	None	1.15%±0.17
8,9,12	"	2 sqrt/5 min	0.06%±0.05
3,5,6	B(0.1)	None	1.51%±0.84
7,10,11	"	2 sqrt/5 min	0.09%±0.02
13,14,15	Blank	None	10.40%±7.49
16,17,18	"	2 sqrt/5 min	1.30%±1.06

Based upon these results, we chose coating B(0.02) as the candidate for our pilot batch. The coating performed as well or slightly better than B(0.1) and still possessed the desired foaming qualities despite having a lower concentration of sodium dodecyl sulfate.

4.7 Final Coating Formulation

We settled on a final coating formulation and prepared a 23 lb test batch at TDA. This test batch was shipped to Ian Gecker and Associates for aerosol packaging a labeling consultation. The final formulation, shown in Table 38 provides a nice balance of chemical efficacy with acceptable feel on cloth substrates and sufficient flame retardancy.

Table 38. Final formulation prepared in pilot batch.

Component	**Wt % solids**
Lupasol P, Poly(ethylene imine)	12.0 %
Celvol 24-203, Poly(vinyl alcohol)	4.0 %
Zonyl FSA	0.32 %
Arlasolve 200	0.32 %
Sodium Dodecyl Sulfate	0.032 %
Carboxy Methyl Cellulose	0.006 %
Decabromodiphenyl Oxide	1.57 %
Phosphoric Acid	0.27 %
Water	81.482 %

4.8 Testing of Soiled Substrates

We tested the final coating formulation on Nomex samples that were soiled by Scientific Services with a dust/sebum mixture intended to model ring-around-the-collar oil and dirt. The "B(0.02)" coating formulation contained 7.5% Lupasol P, 2.5% Poly(vinyl alcohol), 0.2% Zonyl FSA, 0.2% Arlasolve 200, 0.008% Carbxoy Methyl Cellulose, 0.02% Sodium Dodecyl Sulfate, and 1% total flame retardants (consisting of 85% DBDPO and 15% H_3PO_4). We tested the coating with and without the application of the Sandia Decontamination (MDF, from Modec Inc. Denver, CO) foam before rinsing. For each sample receiving the decon foam, 2 squirts of foam were applied to the contaminated sample and the samples were allowed to set for 5 minutes (this corresponds to approximately 1.5 times the manufacturers recommendation). Next the coupons were rinsed (1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods), extracted in acetone, and analyzed by gas chromatography. Table 39 shows the results, which suggest that the coating will be most effective when applied to a clean substrate. We also plan to test the performance of the coatings when soiled after application.

Table 39. Residual CEES Analysis for Coated Soiled Samples.

Samples	**Coating**	**Foam**	**Avg CEES Remain.**
186 A,B,C	B(0.02)	2 squirt/ 5 min soak	3.00%±0.14
187 A,B,C	"	None	16.52% ±4.19
188 A,B,C	Blank	2 squirt/ 5 min soak	20.54% ±3.03
189 A,B,C	"	None	38.44% ±3.15

4.9 Freeze-Thaw Testing

To test the freeze-thaw stability of the coating formulation, we subjected formulations to daily freeze-thaw cycles for one week. The freeze-thaw tests accelerated polymer gelation, but did not cause additional effects beyond the PEI/PVOH gelation that would be observed upon storage of concentrated mixtures. These freeze-thaw tests allowed us to identify a maximum total solids concentration (ca. 15%) that would not gel even on prolonged storage. At this concentration, the brominated fire retardant does settle out over time, so the formulations will need to be mixed or resuspended before application.

4.10 Shelf Stability of Coating Performance

In the final 3 months of the project, we performed several contamination tests to determine the effectiveness of the final coating formulation. One set of analysis was performed in order to determine which spray nozzle was most effective in applying the coating to the chosen substrate. These samples yielded results of 0.49%±0.09 CEES remaining. A final analysis was performed to confirm the previous results. Table 40 shows the results, which indicate that more than 99% of contamination is removed from the substrate coated with approximately 5 mg/cm^2 of the coating formulation from Table 38.

Table 40. Residual CEES Analysis Final Coating Formulation.

Sample	Coating	Avg. %Remain
C 1,2,3	Pilot Batch #3	0.40%±0.06
D 1,2,3	Blank	14.16% ±5.94

In terms of cost effectiveness and ease of use, it would be ideal for the coating to be effective for an extended period of time after application. In early December 2002, Nomex coupons were coated and stored for later analysis. Contamination tests were performed on these samples on December 26, 2002 and March 21, 2003 with the shelved coated samples. Table 41 contains the results of both analyses.

Table 41. Residual CEES Analysis, Applied Coating Shelf Life.

4.10.1 Sample	4.10.2 Test Date	4.10.3 Avg. %Remain
96 A,B,C	12/2002	3.74% ± 0.52
96 D,E,F	03/2003	1.13% ± 0.22

While we are unable to hypothesize as to why samples D, E, F performed better than A, B, C (newer), the tests clearly demonstrated that the coating did not lose any effectiveness over a period of three months. When used in the field, reapplication of the coating would not have to occur on a day-to-day basis.

5. Large-Scale Decontamination Testing

After developing the coating largely based on the results of small swatch tests, we wanted to demonstrate the coating performance on a larger scale than we could test with available equipment. We therefore designed and constructed an apparatus capable of contaminating and rinsing a mannequin torso wearing a variety of aircrew equipment. Tests conducted in this large-scale contamination apparatus with CEES were compared to analogous swatch tests, leading us to ultimately conclude that the testing of these coatings on a large scale with hazardous chemicals was not representative of their expected ultimate performance. We had initially planned to conduct live agent testing on actual aircrew equipment in this apparatus, but canceled that testing in light of the simulant results.

We first describe the large-scale contamination apparatus and the results of testing, then compare these data to the more familiar 'control' experiments on swatches cut from aircrew items.

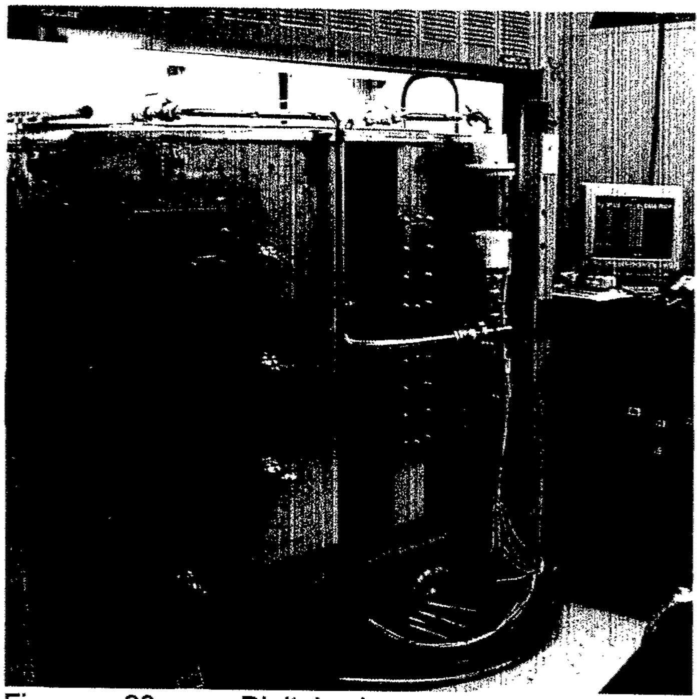


Figure 28. Digital Image of Large-Scale Contamination/Rinsing Apparatus.

Figure 28 shows a digital image and Figure 29 shows a schematic of the large-scale contamination apparatus. The apparatus consists of two chambers: one for contamination and one for rinsing. All walls in the apparatus, including the doors between the two chambers, were made of stainless steel and all joints were welded to ensure that the box was air-tight. Access from the outside of the apparatus was through a hinged door in the contamination chamber. This door sealed against a compressible neoprene gasket and was held with clamps. Additionally, we had visual access to the inside of the apparatus through five glass windows: three in the rinsing chamber and two in the contamination chamber. The mannequin sits on a platform which has a spinning motor inside so that rotation of the mannequin can be controlled electronically from the outside of the box. The entire platform is on a set of tracks that enables movement of the mannequin between the chambers. These tracks have a small break between them to allow space for the door that separates the chambers so that the chambers could be completely sealed off from each other. Each chamber has a drain, which can be opened or closed with a ball valve. The drain lines for both chambers combine and used a peristaltic pump to add a metered amount of bleach to the rinse water, which will then go into the septic system. Water for rinsing came from a tap water supply and was fed in to six water nozzles in the rinsing chamber. The nozzles were broken into three groups of two (top, middle, and bottom) and had ball valves to control the flow of water to each set. Two blowers (REGB-01, 02) were used to pull air through the chamber; having the air pulled through the chamber eliminates the risk of over pressurizing the apparatus. Each heater and heat pad, used to keep air in the box at 70 °C during the thermal desorbtion to recover residual CEES, has a thermocouple for individual control (TC 01-12, TIC 01-12). All electrical operations for this apparatus were controlled with Control EG software.

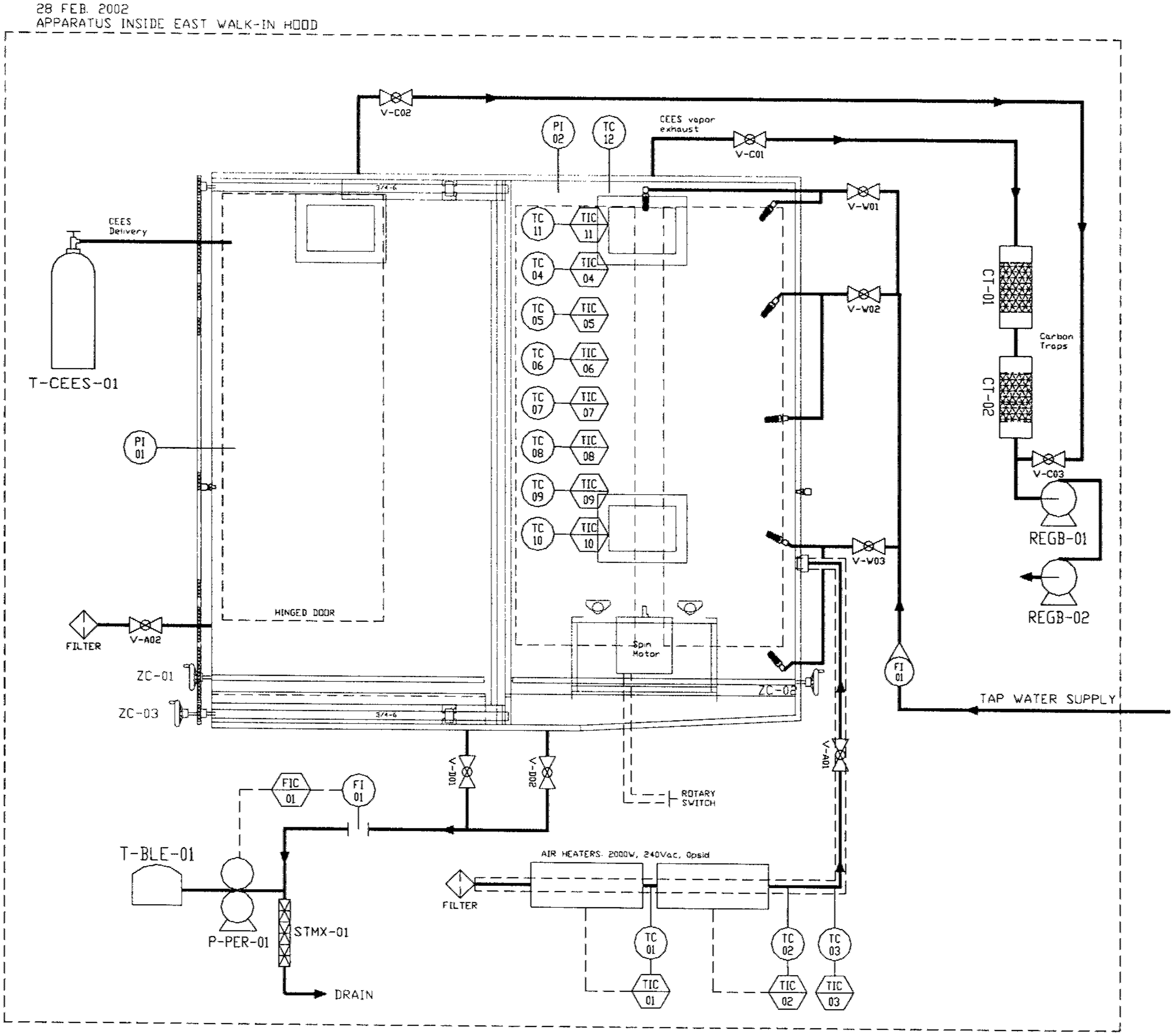


Figure 29. Schemiatic of Large-Scale Contamination Apparatus.

Preliminary testing was done on a scaled down version of this apparatus to nail down the appropriate air temperature and flow rate to thermally desorb CEES for analysis. When the appropriate conditions were determined, we began troubleshooting on the large apparatus. This apparatus has a complex heating system to allow for the thermal desorbtion and quantification of CEES from contaminated clothing. This system involves eight wall heaters and three heaters for the air flowing into the apparatus. We wrote a control program which brings the heaters to temperature and sustains those temperatures. This requires oscillating power between different sets of wall heaters and the air heaters so as not to overdraw from the circuits. This program was tested for 1.5 hours to ensure its ability to sustain the temperatures needed for CEES desorbtion over a long time period. Adjustments involving rinsing nozzle placement and pressure were made to the water rinsing system in the apparatus to ensure that we would be able to thoroughly rinse the coating from the contaminated clothing worn by the mannequin. Next, we finalized the system to apply the CEES to the mannequin delivered in a uniform, reproducible aerosol to simulate chemical agent contamination. This was particularly challenging because the limited space in the contamination chamber made it difficult to disperse a "cloud" of simulant before it came into contact with the mannequin. With the contamination, heating, and rinsing sequences resolved, testing was begun.

The first tests were designed to quantify the CEES adsorbed onto to the mannequin. For this, the mannequin was dressed in an uncoated bomber jacket and sealed in the contamination chamber. Next, 5 g of CEES was propelled into the chamber through two aspirators to create and aerosol cloud of simulant. Upon completion of the contamination cycle, the mannequin was transferred to the rinsing chamber where it sat for one hour. The water rinsing sequence was skipped since the objective of these tests was to establish and baseline for contamination. Next, the heating sequence was activated and allowed to run for 5 hours to facilitate the thermal desorbtion of CEES from the mannequin and clothing. When the heating cycle finished, the carbon trap (4 x 100g sections of carbon) was extracted with acetone (625 mL for each 100g of carbon) and analyzed for CEES by GC. Table 42 shows that on average 35.98 ± 0.28 percent of the challenge mass of CEES deposits on the mannequin. (The extracts from both the third and fourth carbon layers contained no measurable CEES, suggesting that adequate sorbent was used.) The quantity of CEES recovered in the rinsing tests will be compared with this number to determine the efficacy of the coating.

Table 42. Quantification of CEES on Mannequin Without Water Rinse.

Experiment ID	Mass CEES Challenge (g)	Mass CEES on Mannequin (g)	Percent of Challenge on Mannequin (%)
466.94	5.0169	1.7913	35.70%
466.95	5.0400	1.8275	36.26%
		Average	**35.98% ± 0.28**

Next, we tested coated clothing in the large-scale contamination apparatus. For the first experiment the mannequin was dressed in the jumpsuit, pressure vest, and utility vest. The procedure used followed the one outlined above, adding in the water rinse before CEES recovery. To rinse the mannequin, the water was directed through 6 spray nozzles, broken into groups (top, middle, and bottom) so that only 2 nozzles were in use at any given time. The water was pressurized to approximately 50 psi and delivered at a rate of 3.5 gallons per minute. Water rinsing persisted until there was no visible foam in the rinse water. Table 43 shows that, after rinsing, 10.41% of the CEES expected contamination mass remained after rinsing. Anticipating that the difficulty of rinsing coating off through 3 layers of clothing contributed to the high CEES recovery, a second experiment was performed where the mannequin was dressed in only the jumpsuit and utility vest. Table 44 shows that under these conditions 5.61% of the CEES remained after rinsing.

Table 43. Mannequin in Coated Jumpsuit, Pressure Vest, and Utility Vest.

Experiment ID	Mass CEES Challenge (g)	Estimated Mass CEES on Mannequin (g) (35.98% of Challenge)	Mass CEES Recovered After Rinse (g)	Percent of CEES Remaining After Rinse (%)
466.97	5.0370	1.8123	0.1886	10.41%

Table 44. Mannequin in Coated Jumpsuit and Utility Vest.

Experiment ID	Mass CEES Challenge (g)	Mass CEES on Mannequin (g) (35.98% of Challenge)	Mass CEES Recovered After Rinse (g)	Percent of CEES Remaining After Rinse (%)
466.98	5.0339	1.8112	0.1017	5.61%

Although this was an improvement over the experiments with three clothing layers, the data did not correlate particularly well with results from the small swatch tests. In the swatch tests, there was less CEES left on the coated, rinsed coupons (~1%). We hypothesized that the coatings were not penetrating the seams of the garments and that a test of a simple seamless Nomex poncho would yield results more comparable to those observed in swatch tests. We believed that these tests would either confirm that the coating was not working as well on real garments as expected, or indicate that there was a more complex problem that made our large-scale contamination results incomparable to the small swatch tests.

Table 45 shows the test results from the poncho experiments where a 9-minute rinse time was used. These experiments did not show any advantage of a seamless garment with 7.2 % and 12.4 % CEES remaining on a coated and uncoated poncho. For a final experiment we contaminated the mannequin without dress, using a 9-minute rinse time, to determine if there was interaction between CEES and the exposed "skin" that could account for the CEES that remained after rinsing. Results shown in Table 46 indicate that the interaction with the mannequin "skin" may partly account for the remaining CEES from previous experiments. The unclothed mannequin behaved similarly to the uncoated poncho with more CEES remaining on the poncho probably linked to CEES buried in the fabric weave being more difficult to rinse than if it were sitting on a smooth surface.

Table 45. Mannequin in Poncho**.

Experiment ID	Coating Details	Mass CEES Challenge (g)	Mass CEES on Mannequin (g) (35.98% of Challenge)	Mass CEES Recovered After Rinse (g)	Percent of CEES Remaining After Rinse (%)
466.100	Coated	5.0095	1.8024	0.1304	7.2 %
535.03	Uncoated	5.3026	1.9079	0.2378	12.4 %

**Total rinsing time is 9 minutes

Table 46. Mannequin, No dress**.

Experiment ID	Mass CEES Challenge (g)	Mass CEES on Mannequin (g) (35.98% of Challenge)	Mass CEES Recovered After Rinse (g)	Percent of CEES Remaining After Rinse (%)
535.07	5.0959	1.8335	0.1824	10.0 %

**Total rinsing time is 9 minutes

The collective results from the large-scale contamination tests show that there is little correlation between these tests and the smaller swatch tests with simple Nomex coupons. We believe that this is probably due to inadequacies in the rinsing system, which do not allow for coating removal without use of exorbitant amounts of water. For tests using the ensemble garments, 122 gallons of water were used in rinsing and, even then, there was indication of some coating still in the clothes. This is probably a result of our inability to direct the rinse stream and move the mannequin so that difficult to reach areas can be sufficiently rinsed without just continually pumping water into the chamber. This excessive pumping of water may over-rinse areas with maximum water contact and result in effectively stripping CEES off the uncoated attire. In practice the coating would be washed off the garments after they have been removed from the wearer so that the clothes may be moved around and the water stream can be adjusted to provide ample coating removal without excessive water use. In order to carry out a better analysis of coating performance on garments with seams, folds, and zippers, we decided to perform smaller scale swatch tests on coupons cut from the ensemble garments.

We contaminated coated and uncoated samples cut from articles of a flight ensemble obtained from Flight Suits. Round samples (6 cm diameter) were cut from a Nomex jump suit, a survival vest, and a pressure vest. In the case of the jump suit, samples were cut to include a portion of a zipper in each sample. We cut the pressure vest sample from the air bladder inside the vest to see how the coating performed on substrates other than Nomex. The samples from the pressure vest did not contain the Nomex covering, only the plastic bladder material. The coating dried on the surface of these samples (as opposed to wicking into the nylon cloth). Each of the coated samples was coated with the final formulation (Table 38) at approximately 7 mg/cm^2 (5 mg/cm^2 on the plastic from the pressure vest) and contaminated with approximately 10 g/m^2 CEES. After storing for one hour in confined headspace, the coupons were rinsed (1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods), extracted overnight in acetone, and analyzed by gas chromatograph. Table 47 shows the results of the analysis.

Table 47. Residual CEES Analysis Equipment Samples.

Equip	**Sample**	**Coating**	**Avg CEES Remaining**
Pressure Vest	A,B,C	Final	56.74%±12.91
	D,E,F	Blank	78.11%±3.28
Jump Suit	G,H,I	Final	13.47%±1.81
	J,K,L	Blank	32.95%±5.90
Survival Vest	M,N,O	Final	13.03%±0.42
	P,Q,R	Blank	43.93%±22.23

The results for this experiment were disappointing. When hit by the spray of CEES, samples A thru F curled up, indicating a physical reaction with the chemical simulant (probably simple adsorption/swelling of the plastic bladder). The coating may not have adhered to the jump suit zippers as well as it did to the Nomex. In addition there may have been small spaces were there was no coating present and the CEES was able to adsorb onto the zipper. The situation was similar for the survival vest. While made of Nomex, it was a more coarse weave and CEES may have reached spaces where the coating was thin or not present.

We suspected that some of the poor results could be attributed to inefficient rinsing of the coating from the sample substrate, so we tested the rinsing efficiency on a new set of coated samples. Table 48 shows the results from the rinse test.

Table 48. Rinse Test of Flight Equipment Swatch Samples.

Equip	**Sample**	**Avg. Coating Removed by Rinse**
Jumpsuit	S,T,U	86.70%±2.65
Survival Vest	V,W,X	45.49%±2.89

Rinse results for the jump suit were very similar to results of rinsing the coating from Nomex samples. The coating on survival vest was less easily removed, but the results were consistent. More and/or longer rinsing may reduce the amount of residual CEES remaining on the substrate, but these rinsing results do not explain the rather poor performance of the coating on the jump suit swatches containing pieces of zipper material.

Although these tests were imperfect and used only samples of items exposed to chemical simulants, the results suggest that even thoroughly rinsing a coated flight suit, for example, might remove about 90% of an insoluble agent that was initially present as heavy contamination (ca. 10 g/m^2). Compared to our minimal target of 99.9% removal of chemical agents, it appears that the coating formulation at the end of this Phase II project has fallen rather short of our goal.

6. Live Agent Testing

Throughout the project, we contracted for several rounds of live agent testing of our developing formulations. In some of these tests, we also evaluated the efficacy of the Sandia decon foam (MDF provided by Modec, Inc., Denver, CO) both in comparison to and in conjunction with our decon-aid coating. We also compared the live agent results with the oxidizing Sandia formulations to similarly treated samples using only simulant (CEES) contamination.

All Phase II testing with live agents was conducted by Calspan in Buffalo, NY, formerly a division of Veridian Engineering, now Calspan/University of Buffalo Research Center, under Bailment Agreements DAAD13-00-H-0008 and DAAD13-01-H-0001. Samples, containing 5 mg/cm^2 of 40% Lupasol G20 with 1% Zonyl FSA, were contaminated with agents GB, HD, and VX (nominally 10 g/m^2), stored for 1 hour before rinsing (with 150 or 300 ml water at about 2 psi), extraction and analysis. In these tests, both the test coupons and the rinse water were analyzed to determine whether the agents were neutralized in the rinse water or simply removed from the substrate.

In these tests, we found that agent GB is readily removed from the substrate and decontaminated, with coated samples retaining only 0.0016% of the original contamination, compared to 0.015% for the uncoated controls. The rinse water for both the uncoated and coated samples contained no measurable agent (25/75 hexane/chloroform extract). Based on these results, shown in Figure 30, we did not conduct further live agent testing with G-agents.

Tests with agents HD and VX suggested that this early coating formulation was not effective at facilitating removal of the agent from the substrate, and that the agents were not rapidly detoxified in the rinse water. Further tests on these agents were conducted in subsequent studies on more advanced formulations.

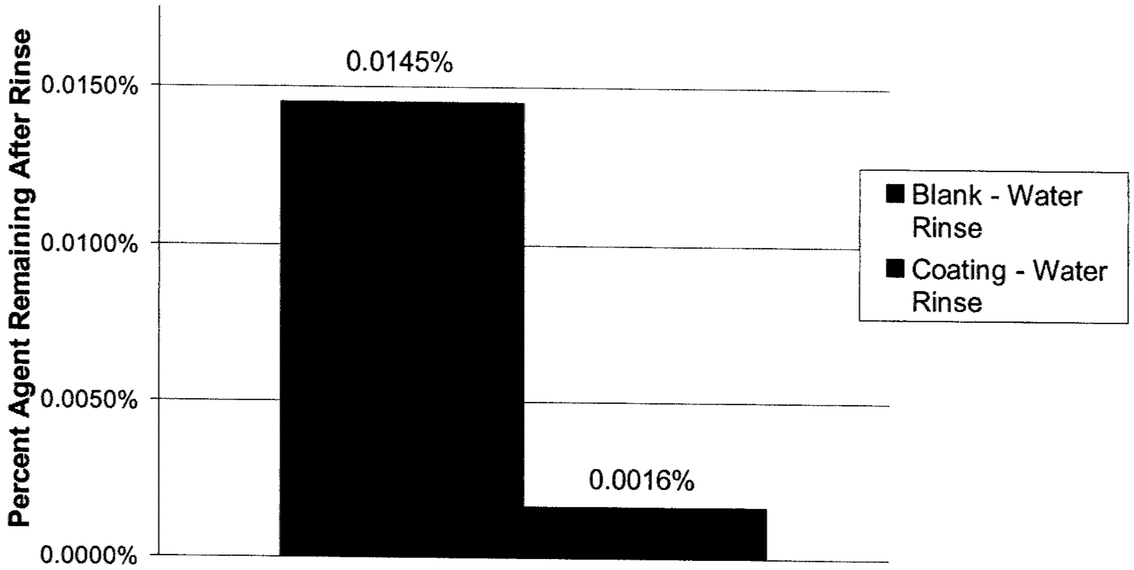


Figure 30. Agent GB remaining on coupons after rinsing gently with 150 ml water.

For the second batch of live agent testing, we used formulation B25 (7.5% Lupasol P solids, 2.5% PVOH solids, 0.1% Zonyl FSA, and 0.1% Arlasolve 200). The PVOH was Celvol 205 with a molecular weight of 13,000-23,000 and 88% hydrolyzed from the acetate. We coated the samples at TDA and sent them to Buffalo for contamination with VX and HD. In addition, a sample of Sandia Decon Foam in a two-component hand pump from Modec Inc. was sent with the samples.

The coating was tested against VX and HD in replicates of five. Each coupon was contaminated with approximately 10 g/m^2 of liquid agent and allowed to sit while covered for one hour. A set of five replicates for each agent was sprayed with the decon foam prior to rinsing. For each sample receiving decon foam, 2 squirts of foam were applied and the sample was allowed to set for 5 minutes (this corresponds to approximately 1.5 times the manufacturers recommendation). Next the coupons were rinsed (1 L H_2O @ 40 psi in 4 equal portions separated by 1 minute soaking periods).

Table 49, Figure 31, and Figure 32 show the results of the analysis. These results clearly indicate that the coating offers substantial protection against agent HD compared to uncoated Nomex. In addition, the decon foam increases the protection significantly against agent VX.

Table 49. Preliminary Results Live Agent Testing Batch #2.

Coating	Decon Method	Avg HD Remaining	Avg. VX Remaining
B25	Rinse	0.68% ± 0.25	1.73% ± 0.60
B25	Foam+Rinse	0.51% ± 0.19	0.32% ± 0.28
Blank	Rinse	69% ± 22	1.9% % ± 1.3
Blank	Foam+Rinse	40% ± 14	0.45% ± 0.07

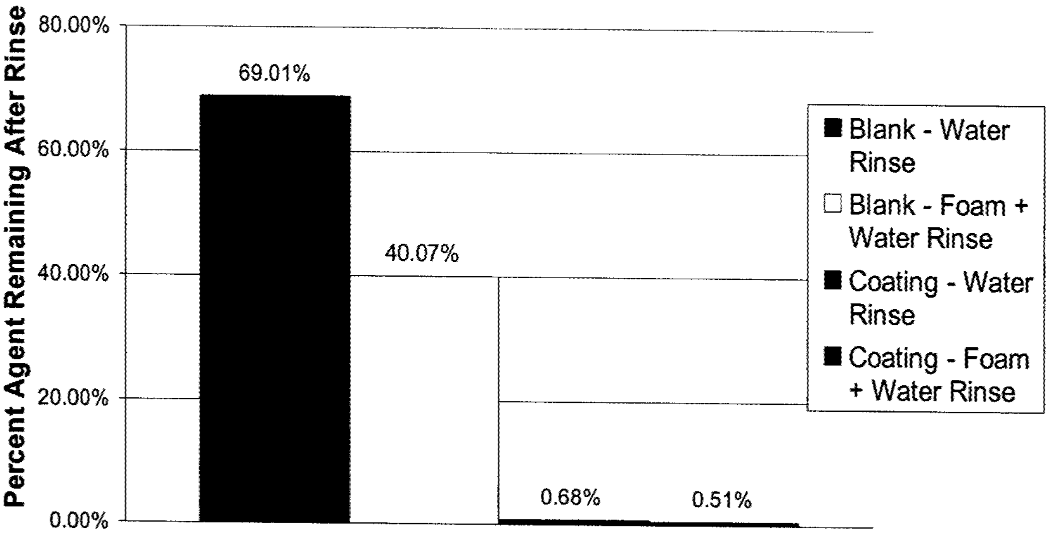


Figure 31. Agent HD remaining on rinsed Nomex coupons.

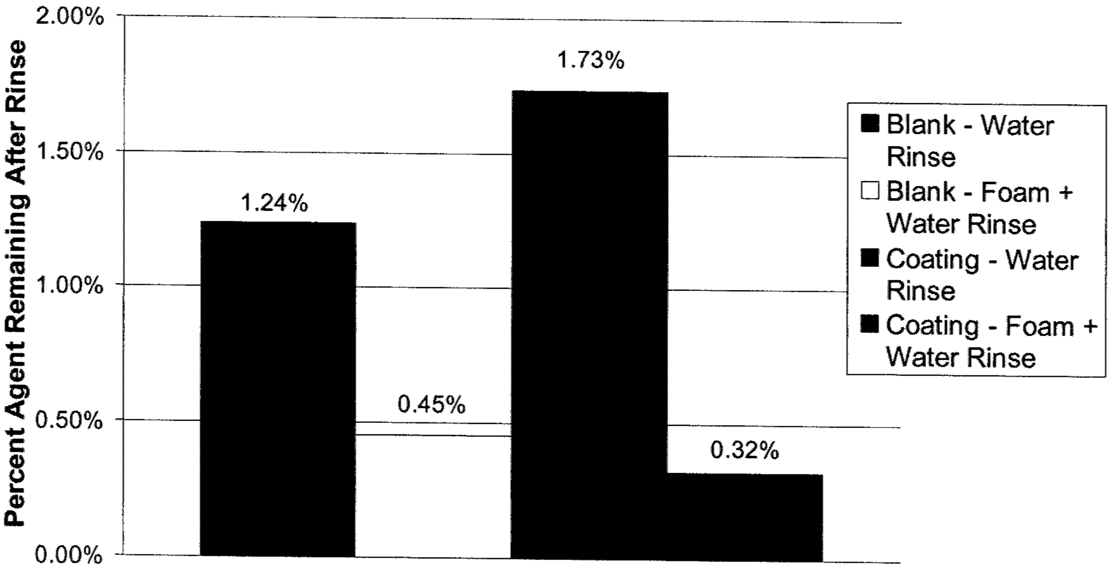


Figure 32. Agent VX remaining on rinsed Nomex coupons.

For several samples, the staff at CUBRC collected the rinse water and extracted it to determine the effectiveness of the foam and the foam/coating combination in detoxifying the chemical agent. For each sample type, a 1 liter rinse volume was split into two 500 mL portions. One was extracted immediately following the rinse step, and the other was extracted 1 hour later. Results indicate that against HD, the amount of agent present in the rinse portion after 1 hour decreases on average by 97%, with coating/foam combinations having lower agent concentrations. However, against VX, the concentration of agent decreases only by an average of 14% in one hour.

These results for mustard do not correlate particularly well with what we had expected based on simulant testing with CEES in our laboratory. The same coating tested against HD and VX immediately above (formulation B25) was also tested against CEES in conjunction with the MDF decontamination spray. Based upon instructions provided by Modec, Inc., it was necessary to apply 0.25 ml of the decontamination foam to our samples using a two-component pump trigger sprayer. Initially, we decided that two squirts of the foam would be applied to each Nomex sample, resulting in an application of approximately 0.43 ml of foam per sample, or almost twice the manufacturer's recommendation.

The first set of testing involved comparison of samples with foam applied against samples without a foam application. The samples were contaminated with CEES and allowed to sit in a closed container for 1 hour. Samples that received the decontamination foam were squirted and allowed to set for 30 seconds or 5 minutes. Next, the samples were rinsed (1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods) and extracted overnight in acetone prior to analysis of residual CEES by GC/ELCD. The amount of foam applied was either 2 squirts or 4 squirts while the time for the foam to soak on the samples was either 30 seconds or 5 minutes. Table 50 contains the results of this analysis.

Table 50. Residual CEES Analysis for Varied Foam Application & Soak Time.

Samples	Coating	Method	Avg. CEES Remain.
150 A,B,C	B25	2 squirt, 30 sec.	1.17% ± 0.16
151 A,B,C	"	4 squirt, 30 sec.	1.22% ± 0.46
152 A,B,C	"	2 squirt, 5 min	0.56% ± 0.09
153 A,B,C	"	4 squirt, 5 min	0.62% ± 0.08
154 A,B,C	Blank	2 squirt, 30 sec.	29.61% ± 6.13
155 A,B,C	"	4 squirt, 30 sec.	28.61% ± 2.71
156 A,B,C	"	2 squirt, 5 min	12.59% ± 2.36
157 A,B,C	"	4 squirt, 5 min	15.40% ± 3.28

Results in Table 50 indicate that while doubling the amount of foam applied to the samples does not result in a significant decrease in the amount of CEES remaining, the increased soaking time does decrease the amount of CEES remaining. Based on these results, we decided that there was essentially no benefit to applying more than 2 squirts of foam.

For the next set of analysis, we used the final formulation from Table 38 with a coating density on Nomex of approximately 7 mg/cm^2, applying two squirts of MDF and letting it work for 5 minutes before rinsing (1 L H_2O @40 psi in 4 equal portions separated by 1 minute soaking periods). Figure 33 shows the results of the analysis. Unlike what we observed in the case of agent HD, we the combination of MDF and the decon-aid coating appears to provide some additional protection compared to either alone. In the case of HD, on the other hand, the Sandia foam (MDF) was not particularly effective alone and did not contribute significantly to the protection offered by the coating.

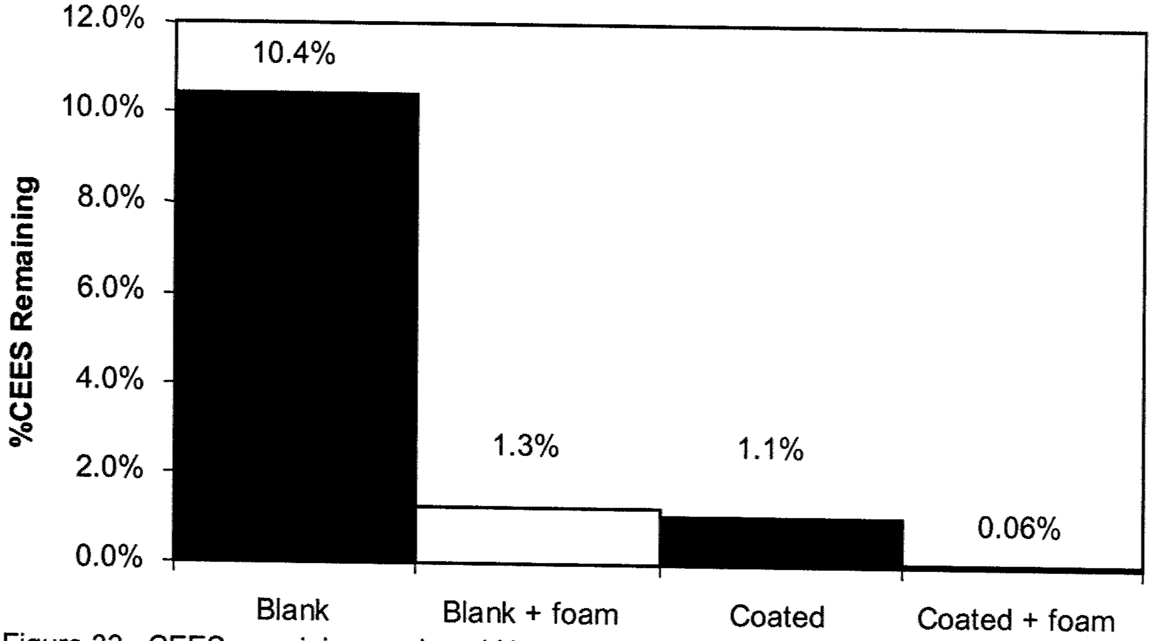


Figure 33. CEES remaining on rinsed Nomex coupons.

7. Corrosiveness and Dermal/Ocular Irritation Testing

We contracted InVitro International (Irvine, CA) to test our final coating (Table 38) with their Corrositex® test method and their Irritection® Assay system. The Corrositex® test method was performed to determine the corrosive potential and to designate the DOT Packing Group classification of the coating. The Corrositex® test, Figure 34, measures the time it takes for the coating mixture to permeate through or destroy a synthetic biobarrier, with a color change in the chemical detection system marking the endpoint. The results of this test showed a classification of Noncorrosive.

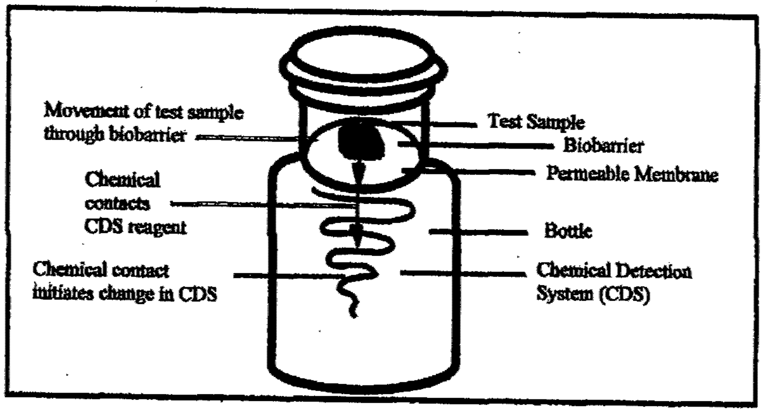


Figure 34. A Schematic Diagram Depicting the Biobarrier and Chemical Detection System of the Corrositex® Test Method.

The Irritection® Assay system is a method proven to be useful for reliably and reproducibly predicting the potential of chemical mixtures to cause ocular and dermal irritation, and has greater fidelity to human responses than the more common Draize testing with laboratory animals (Gordon et al., 1995) The Dermal Irritection® assay is based on the principle that chemical compounds will promote measurable changes in target biomolecules and macromolecular structures which mimic the protein denaturation and disaggregation that occurs when these types of irritants are applied to the skin. Similarly, the Ocular Irritection® Assay measures changes in relevant macromolecules to predict acute ocular irritation. Results from these tests classified the coating as a minimal-to-mild ocular irritant and a borderline dermal non-irritant/irritant.

8. Packaging

We contracted Ian Gecker & Associates, LLC (Las Vegas, NV) to work with us in developing the packaging for the coating. A test batch containing 16 wt% polymer solids was sent to begin packaging tests. The first test batch of packaged coating was prepared in nominal 20 oz size containers pressurized to 100-110 psig w/ nitrogen and containing 12 oz coating. Ian Gecker & Associates diluted the supplied concentrate with 33% deionized water. While checking the performance of these packaging samples we observed that only the first 60% of the liquid dispensed in a spray. The remaining 40% came out in a stream. Additionally, the diluted coating was insufficient to provide the desired coating density in a single application. We worked to address these issues but we re unable to find a suitable aerosol package that could deliver enough coating to coat an entire ensemble with the desired density in a single application and an acceptable coating appearance. Higher nitrogen pressures allowed atomization of higher solids concentrations in the coatings, but higher nitrogen pressures also resulted in the appearance of a dried foam in applied coatings.

In our next approach we tried a barrier packaging where, contained in a single can, the propellant is separated from the coating. We believed that this would prevent the foaming problem, by not allowing the propellant to dissolve in the coating, and thereby make for a useable product. The barrier packaging was successful at delivering the proper coating density with an acceptable coating appearance, but only a small volume of coating could be packaged in commercial barrier packs. These barrier packages may be suitable for packaging coating intended for use on smaller items such masks.

We also evaluated delivering the coating with simple, hand-operated trigger sprayers. With a coating concentration of 10 wt% polymer solids there is adequate delivery to achieve the desired density in one application. Impact (Toledo, Ohio) makes a line of chemical-resistant spray heads that worked very well to deliver the coating in a uniform spray. Tests were done to ensure that the trigger sprayers did not seize during use when coating an entire ensemble. The sprayers (Trigger Sprayer, Contour, Chem. Resistant, 8 1/8 inch, gray, supplied by Straight Representation, Inc, Aurora, CO) performed well at delivering the proper coating density, and the coating appearance was better than any seen with aerosol delivery. The trigger sprayers appear to be the best option for coating packaging. Use of these sprayers allows us to prepare the coating in 16oz., 24 oz., or 32 oz. packages. We prepared a pilot batch of 24 oz. samples, at a concentration of 10.66% total polymer solids (PEI + PVOH) from the formulation in Table 38 (formulation diluted to improve application), using these trigger sprayer heads for atomization.

9. Conclusions

In this project, TDA successfully developed and demonstrated a safe and effective prophylactic coating to achieve very effective decontamination of porous substrates with a water wash. The coating is particularly effective against G-agents (virtually complete protection), and is also very effective against sulfur mustard, agent HD, reducing heavy (10 g/m^2) HD contamination by over 99.5% when rinsed with water. The coating is not particularly effective against agent VX. The coating does require considerable water to rinse and would therefore not be applicable for forward-deployed forces, but may be useful to maintain operations in, for example, a contaminated air base.

The formulation is inexpensive, uses commercially available ingredients, and can be efficiently applied by a hand-operated trigger sprayer. It is non-corrosive by DOT standards, and is a minimal-to-mild ocular irritant and a borderline dermal non-irritant/irritant. It is non-flammable and self-extinguishing, having very similar flame retardant properties to Nomex cloth. Once applied, the coating remains effective indefinitely, with no degradation in performance upon storage of coated items for at least three months; prolonged storage should also not degrade coating performance.

The present formulation does have some limitations. While it is colorless, it is not optically clear and therefore cannot be applied to visors, night vision goggles, etc. The coating is designed to wash off of the substrate while rinsing under moderate pressures and would therefore need to be reapplied after rinsing. Even though we greatly reduced the tackiness of the reactive component (the poly(ethylene imine)), the formulation can still feel slightly tacky on non-porous substrates in exceptionally humid environments (>90% r.h.). We were unable to conduct a suitable field test to determine how durable the coating might be under conditions of normal use, but we would expect the durability to be an inverse function of the ambient humidity.

10. References

Brown, W.H. (1995), *Organic Chemistry*, Saunders College Publishing, Fort Worth, TX.

Compton, J.A.F. (1988), *Military Chemical and Biological Agents: Chemical and Toxicological Properties*, Telford Press, Caldwell, NJ.

Day, S.E (1996), *DS2: Development, Improvements, and Replacements*, ERDEC-TR-263.

Di Sioudi, B.D., C.E. Miller and J.R. Wild (1999a). "Rational design of organophosphorus hydrolase for altered substrate specificities." *Chemico-Biological Interactions* **119/120**, 211.

Di Sioudi, B.D., J.K. Grimsley and J.R. Wild (1999b). "Modification of Near Active Site Residues in Organophosphorus Hydrolase Reduces Metal Stoichiometry and Alters Substrate Specificity." *Biochemistry* **38**, 2866.

Gordon, V.C., J.D. Harvell, and H.I. Maibach (1995). "The SKINTEX System: an *In Vitro* Biomacromolecular Assay to Predict *In Vivo* Dermal Irritation," in In Vitro *Skin Toxicology: Irritation, Phototoxicity, Sensitization*, 47-57, A. Rougier, A. Goldberg, and H. Maibach, eds. Mary Ann Liebest, Inc.

Koper, G.J.M., et al. (1997), "Protonation Mechanism of Poly(propylene imine) Dendrimers and Some Associated Oligo Amines," *J. Am. Chem. Soc.* **119**, 6512-6521.

Newkome, G.R., C.N. Moorefield and F. Vögtle (1996), *Dendritic Molecules -- Concepts, Syntheses, Perspectives*, VCH Weinheim.

Schwarzenbach, R.P., P.M. Gschwend, and D.M. Imboden (1993). *Environmental Organic Chemistry*, John Wiley & Sons, Inc, New York.

Yang, Y.-C., L.L. Szafraniec and W.T. Beaudry (1995). "Autocatalytic Hydrolysis of V-type Nerve Agents." Proceedings of the Scientific Conference on Chemical and Biological Defense Research, Edgewood, MD, Nov. 14-17.

Yang, Y.-C., F.J. Berg, L.L. Szafraniec, W.T. Beaudry, C.A. Bunton and A. Kumar (1997). "Peroxohydrolysis of nerve agent VX and model compounds and related nucleophilic reactions." *J. Chem. Soc., Perkin Trans 2*, 607-613.

Wartell, M.A., M.T. Kleinman, B.M. Huey and L.M. Duffy, Editors; Division of Military Science and Technology, National Research Council (1999). *Strategies to Protect the Health of Deployed U.S. Forces: Force Protection and Decontamination.* Washington, DC: National Academy Press.