

DEVELOPMENT AND PERFORMANCE ASSESSMENT OF REACTIVE MEMBRANES FOR NEW SELF-DETOXIFYING MATERIALS SYSTEMS FOR CB PROTECTIVE CLOTHING

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ABSTRACT

A new reactive membrane has been formulated from a commercially available copolymer and scaled up in processing trials. The water vapor permeability and the organic vapor barrier properties of this membrane have been measured after membrane humidity conditioning and are compared to other commercially available membranes. Recent evaluations of the reactivity of this new membrane have been difficult, but new sample extraction procedures have been successful, increasing extraction efficiencies for a reactive simulant and the hydrolysis products within the reactive membrane. Membrane formulation studies and performance assessments are discussed.

INTRODUCTION

Over the past 25 years, the Army and other services have intermittently studied the application of various reactive self-detoxifying materials concepts for use in chemical and biological protective clothing.¹⁻⁵ In the 1980s the U.S. Army Natick Research and Development Command funded efforts to synthesize reactive polymers for use in fibers, membranes and coatings.^{6,7} These reactive textile components were tested to determine their activity in the decontamination of nerve agents and surrogates with limited success. Problems that arose in the testing and confirmation of the reactive efficacy and the chemical fate of the reaction products eventually lead to inconclusive determinations and the suspension of reactive materials development for individual protection. In 2000, a new project was initiated to explore the use of new nanofiber fabrics as promising high surface area substrates for the incorporation of reactive chemicals and materials into self-detoxifying fabrics for chemical and biological protection. Since the inception of the research, materials synthesis, development and testing efforts have been conducted with many chemically and biologically reactive materials for liners and shell fabrics under three major areas of investigation: reactive membranes, reactive nanoparticles, and biocidal fabrics. The construction of the self-detoxifying fabric system is envisioned below in a construction that incorporates some of the most promising chemistries and materials that have been identified and studied in this effort.

Proceedings of and Presented at the 2006 Scientific Conference on Chemical & Biological
Defense Research, Nov 15, 2006 Hunt Valley, MD.

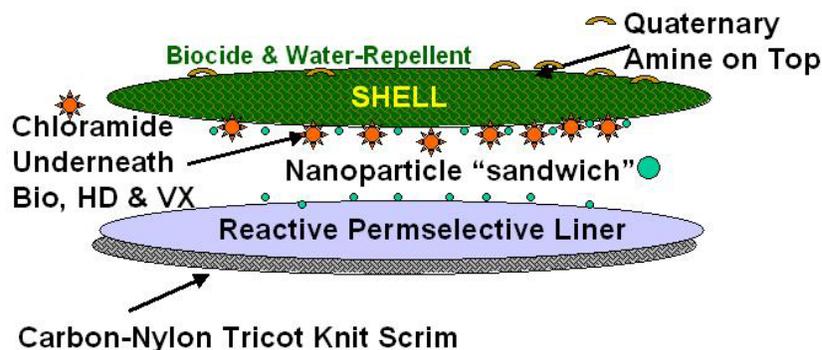


Figure 1. A concept for a reactive membrane-based fabric design.

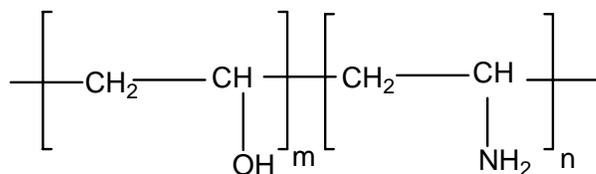
The purpose of the reactive membranes task was to make use of new reactive compounds that have been developed under basic research projects funded from 1980s through 2002 by the Army Research Office, the Army Medical Research and Materiel Command (AMRMC), and the Edgewood Chemical and Biological Command.

The initial intent of the reactive membranes research was to explore combinations of nanofiber layers with reactive compounds in order to determine the effect of fiber size and surface area on the reactivity of the chemically modified fibers and the utility of the nanofiber membrane in biological and chemical decontamination. Electrospun polyurethanes were combined with agent degrading enzymes, nerve agent reactive cyclodextrins, and mustard degrading catalysts, and reaction rates were found to be reduced only slightly by the incorporation of the reactive compound within the electrospun fiber. Electrospinning appeared to be a promising approach as a method of holding the reactive compound within a flexible, ultrafine fiber layer. However, the structure of the electrospun membrane was microporous, and this resulted in rapid vapor diffusion rates that exceeded the reaction times of the embedded catalysts. A membrane that slowed diffusion of toxic vapors and provided the reactivity needed to detoxify the contaminants was needed.

In order to achieve rapid reaction rates compared to vapor penetration rates for protective fabric systems, a new approach has been recently undertaken to increase residence time of the reactant within the reactive fabric layers - a thin reactive yet permeable film. This approach incorporates functional reactive layers within the protective clothing system through the use of a reactive, selectively permeable film.

PROCESSING AND CONDITIONING EFFECTS ON MEMBRANE PROPERTIES

A copolymer available from Celanese, called Erkol™ M12, has been under development to provide additional chemical protection within a layered protective fabric system through the ability of this copolymer to hydrolytically break down organophosphorus compounds such as pesticides and other nerve agents. The chemical composition of this copolymer is shown in Figure 2. The Erkol™ M12 copolymer has a composition of 12 mol% amine with a molecular weight range around 80 -140 kDa. Another copolymer available for membrane development is Erkol™ L12, or the low molecular weight copolymer of 30-35 kDa. The Erkol copolymer forms a pH 12 solution in water and functions as Lewis base when hydrated.



Polyvinyl alcohol-co-amine, PVA-Am

Figure 2. Chemical formula for Erkol™ M12 copolymer

A solution of Erkol™ M12 was used to prepare films of the copolymer, and a pH indicator was added to the solution. The pH indicator was blue within the film due to the high pH 12 of the solution. The dried film remained brilliant blue. Films of blue M12 were placed in vials and a water saturated disk of filter paper was added to adjust the humidity within the vial to approximately 90% RH. The blue color of the film lightened only slightly upon film humidification. Upon addition of a second disk of filter paper containing 5 mg of diisopropyl fluorophosphate, DFP, the blue film gradually turned colorless, and then gray over a period of one hour. The color change upon introduction of the DFP suggests that the acidic products of the hydrolysis of DFP vapor within the M12 film reacted after 10 min with the indicator to produce the marked color change (indicator m-cresol, purple to yellow transition at approximately pH 9), as seen in Figure 3.

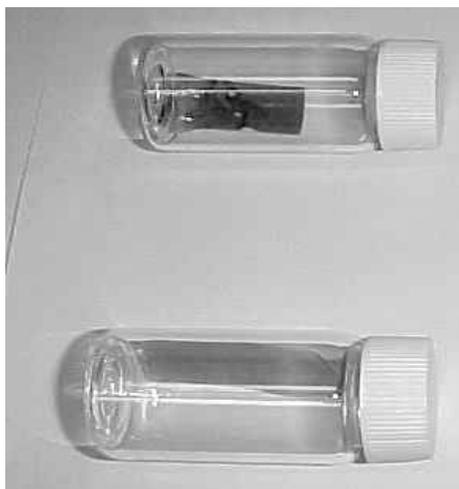


Figure 3. Top vial contains colored M12 film at 90% RH; bottom vial contains colorless M12 film at 90%RH after 10 min DFP vapor exposure.

These thin films of the Erkol™ M12 polyamine are permeable to water vapor, and this property is influenced by the thickness of the film, as illustrated in Figure 4. Here, we see that a 140µm film of Nafion exhibits a water vapor flux of around 13,000 g/m²-day, and that doubling the thickness of this film reduces the flux by only 1,000 g/m²-day, approximately an 8% reduction. The M12 polyamine film has flux values similar to the commercial selectively permeable membranes that are currently available for chemical protective garments – membrane C and membrane T. For

comparison, the Gore-Tex™ weatherproof liner material is presented and exhibits slightly lower flux than the permselective liners.

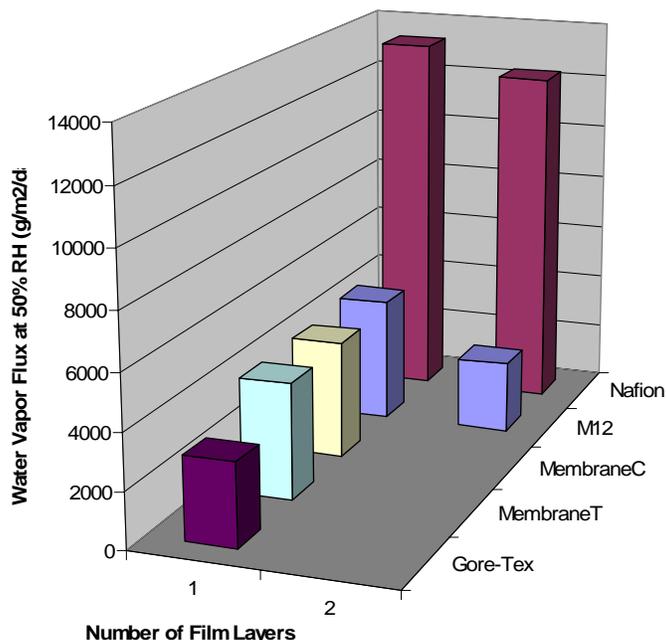


Figure 4. Water vapor diffusion resistance of thin films.

Diffusion of 2-CEES was measured by dynamic vapor permeation testing. The films were conditioned in a vapor diffusion cell for at least 4 hrs to the target humidity levels of 0, 50 and 80% RH. Humidified air was passed across the bottom of the film that was clamped in the cell exposing 3cm² of the film area to vapor conditioning. After conditioning, the top half of the cell was opened, and an open spacer mesh was placed on top of the film, followed by a disc of glass filter paper. Three μL of liquid 2-CEES was applied to the glass filter paper, and the top half of the test cell was stoppered, while the sweep stream across the bottom surface of the sample remained at the programmed humidity level during the test and flowed into an SRI 110 detector. The 2-CEES vapor diffusion through the film sample was monitored with a flame ionization detector over a 24-hour period in this manner.

Selective permeation is observed when we compare the high water vapor permeability of these films to the low organic vapor permeability of these films to 2-CEES vapor in Figure 5. The Gore-Tex™ weatherproof membrane is a hydrophilic polymer film that is not expected to provide any protection from organic vapors. On the other hand, thin films of dip coated Nafion® will allow some organic vapor transport at higher relative humidities, depending upon the thickness of the film. The dip coated Erkol™ M12 films allow some 2-CEES vapor to penetrate at the highest RH levels, but this is mitigated with two layers of M12 film, totaling less than 100 μm thick.

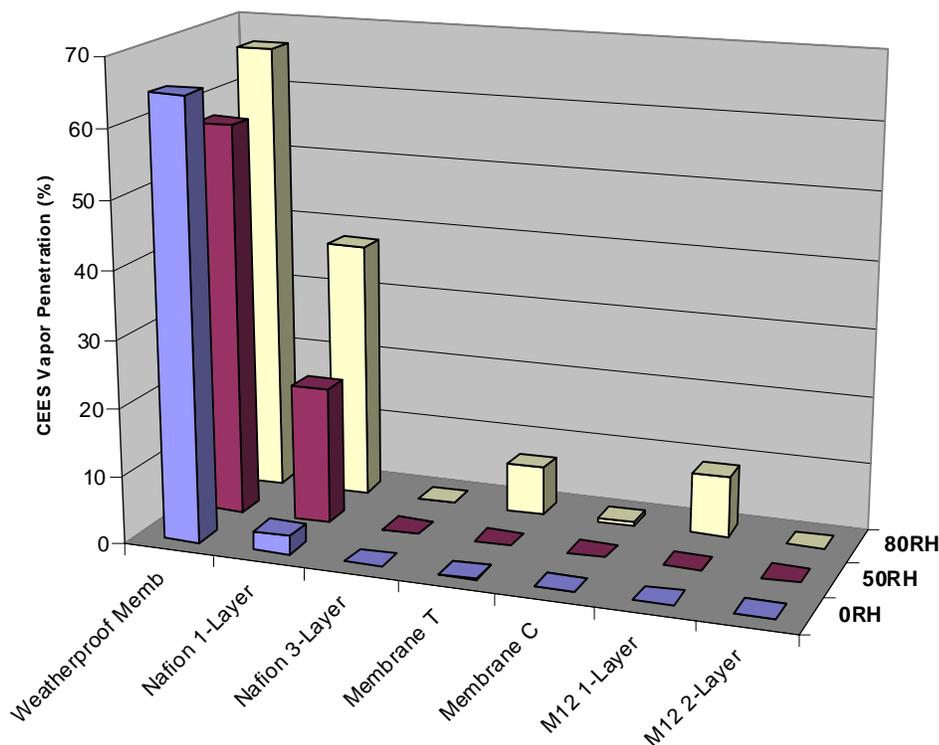


Figure 5. Penetration of 2-CEES vapor during dynamic vapor diffusion testing of dipped films conditioned to different relative humidities.

It can be seen from these vapor permeation studies with DFP and CEES that this new reactive membrane of poly(vinyl amine-co-vinyl alcohol) is hydrophilic and apparently capable of hydrolytically reacting with organophosphorus compounds. This film also possesses selective permeability; it is highly permeable to water vapor, but impermeable to organic vapors such as 2-CEES and will be able to provide acceptable comfort levels and high levels of vapor protection and detoxification of nerve agents. These studies are pointing to the development efforts in the direction of surface-treatments for fabrics that produce slow (hours) deactivation of chemical agent contaminations while requiring sufficient barrier properties (minutes) within the fabric system to provide on-contact protection. Faster reaction times coupled with adsorption features or barrier features for self-detoxifying materials systems are under development for future protective clothing applications.

Recently new composite membranes of Erkol™ polyamine infused into expanded PTFE (ePTFE, porous Teflon membrane) were produced on pilot lines by GE Energy Corp in Summit Hill, MO. Three levels of coating were applied and produced different polymer thicknesses within the composite structure. Vapor penetration testing showed that the “thick” coating was inconsistent and allowed chemical vapors to permeate too quickly, while the “thin” coating was better, yet not optimal, Table 1. The “thick” membrane was sandwiched into a double layer, to form a more uniform membrane without any of the residual porosity seen in Figure 6.

Table 1.
Differences between Processed Erkol M12 Membranes

Sample	Density (mg/cm²)	Water Vapor Flux 90%RH gradient (g/m²-day)
M12 Thick1	3.2	6321
M12 Thick2	2.6	9733
M12 Thin	1.6	4018
Expanded PTFE	2.0	10,002
M12 Thick1-2 Layer	6.4	1356
M12 Thin – 2 Layer	3.2	1601



Figure 6. Appearance of “thick” M12 membrane on the left and “thin” M12 membrane on the right.

A dynamic moisture permeation cell (DMPC) was used to measure the water vapor diffusion resistance of the M12 membranes. A comparison to similar commercially available breathable membranes was conducted. In this measurement, air at two different relative humidities flows over the two sides of the test sample held in the DMPC cell. By measuring the water vapor concentration at the exit ports of the cell, it is possible to measure how much water vapor crosses the sample. Results may be shown in terms of water vapor flux (grams/square meter/day) or in terms of *resistance* to the diffusion of water vapor (units of s/m). The resistance units make direct comparison of results obtained at different environmental conditions possible. The lower the diffusion resistance, the more water vapor gets through the material. The reason for doing the testing this way is that some materials (like Gore-Tex, Sympatex, etc.) have better water vapor transport properties in a humid environment than in a dry environment. Other materials, such as most textiles or microporous membranes, have a nearly constant water vapor diffusion resistance regardless of the environmental conditions

Figure 7 shows the water vapor diffusion resistance of the membranes. The data are measured at identical humidity gradients of 0.5 but an increasing mean relative humidity. Materials that are porous generally show the same resistance under these conditions, but materials

that contain a continuous hydrophilic polymer layer generally show a decreasing resistance to water vapor diffusion at the higher mean relative humidity, which corresponds to more water contained in the polymer layer.

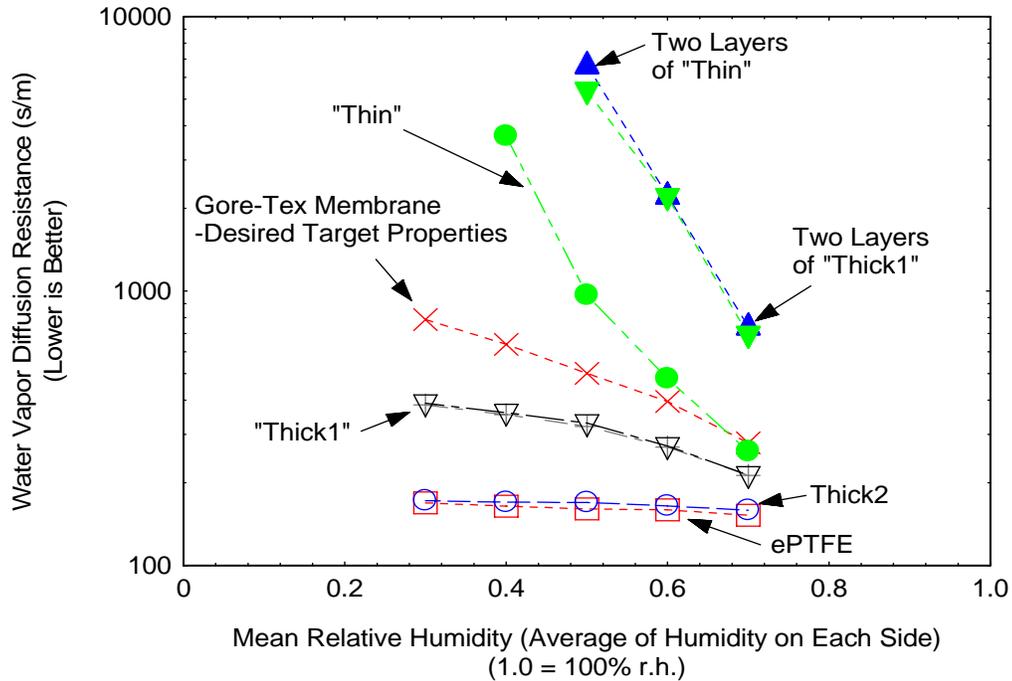


Figure 7. Water Vapor Diffusion Resistance with constant humidity gradient of 0.50.

The untreated ePTFE and M12 Thick-2 sample are nearly identical. The M12 Thick-1 membrane likely contains some very thin spots of polymer – this corresponds to an observation of white spots in the membrane that may be the result of nonuniformities such as small, untreated, porous regions. The “M12 Thin” treatment is much more uniform, and shows the humidity concentration-dependent behavior that is expected from a continuous polymer coating.

It was found that when the “thick” nonuniform samples were wetted, the white spots disappear and don’t return upon drying. Water might be redistributing the polymer in the ePTFE, resulting in a more continuous coating. This also suggests that the M12 polymer is not sufficiently crosslinked to provide membrane stability when wet. When the “thick” samples were wetted and adhered together, they become much more resistant to water vapor diffusion than would be expected from the original “thick” sample.

Data in Figure 7 and Table 1 show the water vapor transport properties for M12 membranes reinforced with ePTFE and similar, commercial membrane materials. Porous ePTFE exhibits the highest water vapor flux of 10,000, while the nonuniform “thick” M12 treatments also exhibit high flux values near 6,500. A commercially available Gore-Tex membrane possesses water vapor flux at 90%RH near 5,000, while the uniform “thin” M12 membrane reinforced with ePTFE has a flux of 4,000. The doubled sandwich of thick M12 causes flux to drop from 6,500 to 1,500, but washing of the doubled layer seems to remove enough M12 to increase the flux slightly to 1,800. Overall, we find that a thin layer of M12 infused into a reinforcing layer of ePTFE produces a reasonable breathable membrane that will allow up to 2.5

kg water vapor through one square meter of material at 90%RH over the course of one day. This is summarized in Figure 8.

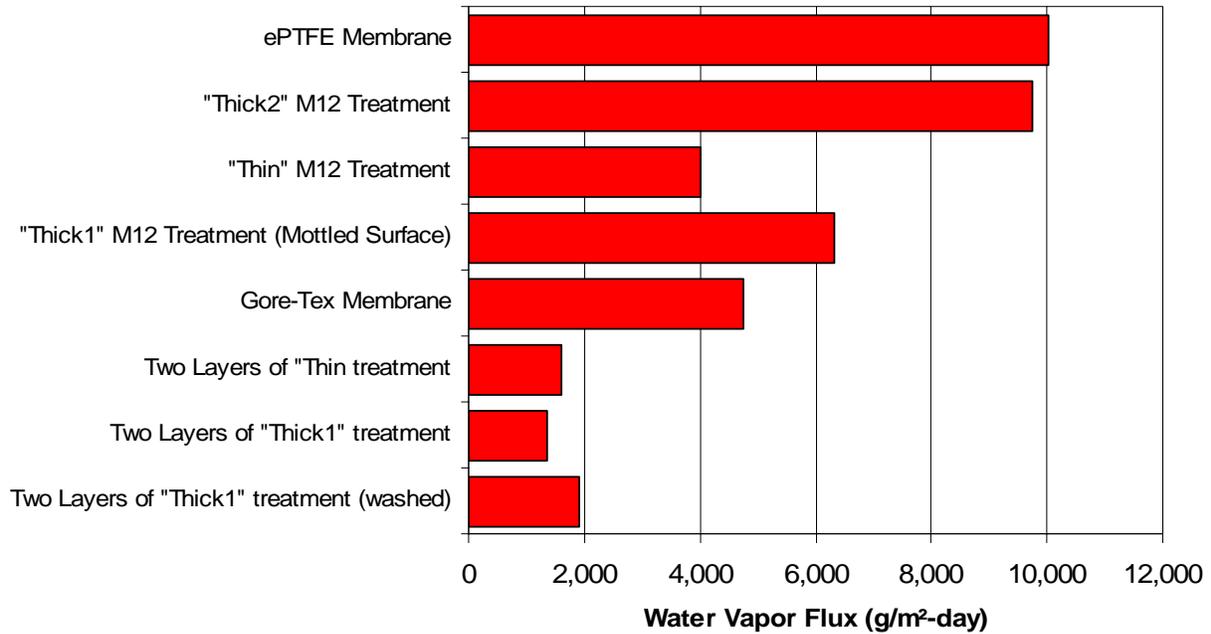


Figure 8. Water vapor flux of M12 membranes compared to commercial membranes.

In the production of a stable, permeable, reinforced membrane layer, the Erkol polyamine is crosslinked with a commercially available epoxide; both polymer and crosslinker are water soluble and film casting is accomplished from a mixture of water and isopropanol. Upon drying, the crosslinking reaction is completed with heating for 2 hours at 100°C. In the first pilot run of Erkol, the membranes were not sufficiently crosslinked for a clothing application. This is illustrated by polymer extraction in water, data in Table 2.

Table 2.
Water Extraction of Polyamine from ePTFE Substrate

“Crosslinked” Sample	Initial Weight (mg)	Final Weight (mg)	Weight Loss (%)
Lab Scale M12a	15.3	15.3	0
Lab Scale M12b	15.3	15.3	0
Pilot Scale M12	9.7	8.2	16

REACTIVITY DETERMINATIONS FOR MEMBRANE

Upon production of a stable M12 membrane, the reaction of the polyamine with diisopropyl fluorophosphate (DFP) was determined by a vapor exposure test. Three square centimeter samples were conditioned at 100%RH for 16 hours in a closed vial containing a wetted filter paper disc. Upon hydration of the M12 film, a filter paper disc was contaminated with 3uL DFP and added to the humidified vial. After specific test intervals, the contaminated M12 film was removed from the DFP vapor and analyzed for the presence of DFP and hydrolysis products on the polyamine membrane.

Hydrolysis products (such as DFP acid) were not initially apparent by GC of hydrolyzed DFP, as shown in Figure 9. Identification of the amount of DFP acid present in the sample was accomplished by first derivatizing the acid product by silylation. The method used was a standard reaction between BSTFA and the extracted acid product from the polyamine film. BSTFA is N,O-bis-(trimethylsilyl)-trifluoroacetamide with 1% trimethylchlorosilane (TMCS), available from Pierce Co. Because BSTFA can react with amines and hydroxyls, it was important to extract the acid from the polyamine film prior to derivatization.

The derivatization proceeded as follows. After humidity conditioning and DFP exposure, the contaminated film was removed from the vial and extracted with 1mL acetonitrile to remove unreacted DFP. The film was dried and then extracted with 1mL of a polar extraction solvent to remove the acid products that might have resulted from the hydrolysis of the DFP within the film. The DFP acid was derivatized by adding 5uL of BSTA directly to 50 uL of the the extract, heating to 60°C for 15 min, and injecting the solution directly into the GC. Cross analysis of the DFP and DFP-silyl acid peaks from the GC by mass spectrometry showed the expected silylated product from the acid reaction. We confirmed that the DFP alone would not silylate and contaminate the analysis. However, once the BSTA is added to the solution containing the hydrolyzed DFP, a silylated acid product can be seen in the (bottom) third chromatogram at a retention time of 9.8 min.

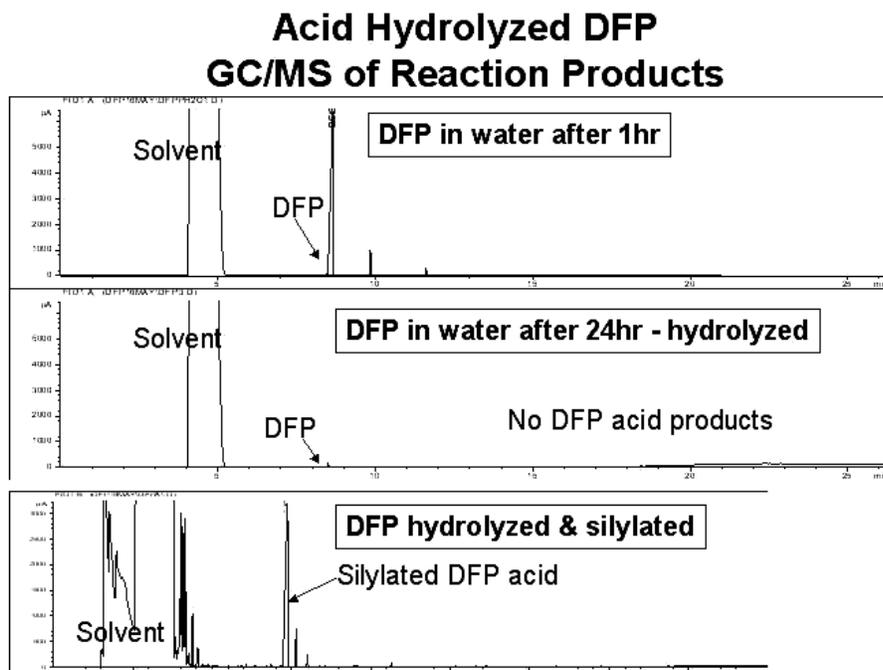


Figure 9. Mass Selective Detector (MSD) Chromatograms of Silylation Product of DFP acid at 9.2 min and DFP at 9.5 min.

Although we could detect the presence of the DFP acid after silylation, we could not initially extract the acid product from fabric or poly(vinyl amine-co-vinyl alcohol) film samples. After studying different extraction methods and solvents, extraction the acid products from the self-decontaminating material was successfully accomplished by extraction with dichloromethane/methanol/HCl mixture, followed by derivatization of the extracted reaction product acids by silylation. Dichloromethane was found to be a reasonably good solvent for the polyamine and was capable of diffusing into the bulk of the film as shown in Table 3. When combined with methanol and 1% HCl, the extraction efficiency was optimized, as discussed below.

Table 3.
Solvent Weight Gain by Crosslinked L12 Erkol Polyamine Film

Solvent	% Wt Gain	Comment
Methyl Tertbutyl Ether	0	nonsolvent
Isopropyl Alcohol	0	nonsolvent
Dioxane	0	nonsolvent
Tetrahydrofuran	0	nonsolvent
Acetonitrile	0.9	nonsolvent
Dimethyl Formamide	4.8	poor solvent
Dimethyl Acetamide	5.6	poor solvent
Dichloromethane	7.2	fair solvent
Water	13.3	good solvent
Dimethyl Sulfoxide	29.0	good solvent

Films of crosslinked polyvinyl amine (Erkol™ M12) with areas of 4cm² were exposed to 100% RH and then exposed to 5mg of DFP vapor for varied periods of time. The exposed films were extracted with different solvents and the extracts were silylated then injected into the GC. The silyated product peak heights were compared to determine the most efficient extraction solvent, shown below. It was found that a mixture of 90/10 dichloromethane and methanol alcohol with 1% HCl extracted the most DFP acid, and was the most efficient at removing even the lowest acid product levels from the polymer film, as seen in Figure 10. Dichloromethane was found to extract the most unreacted DFP from the exposed film.

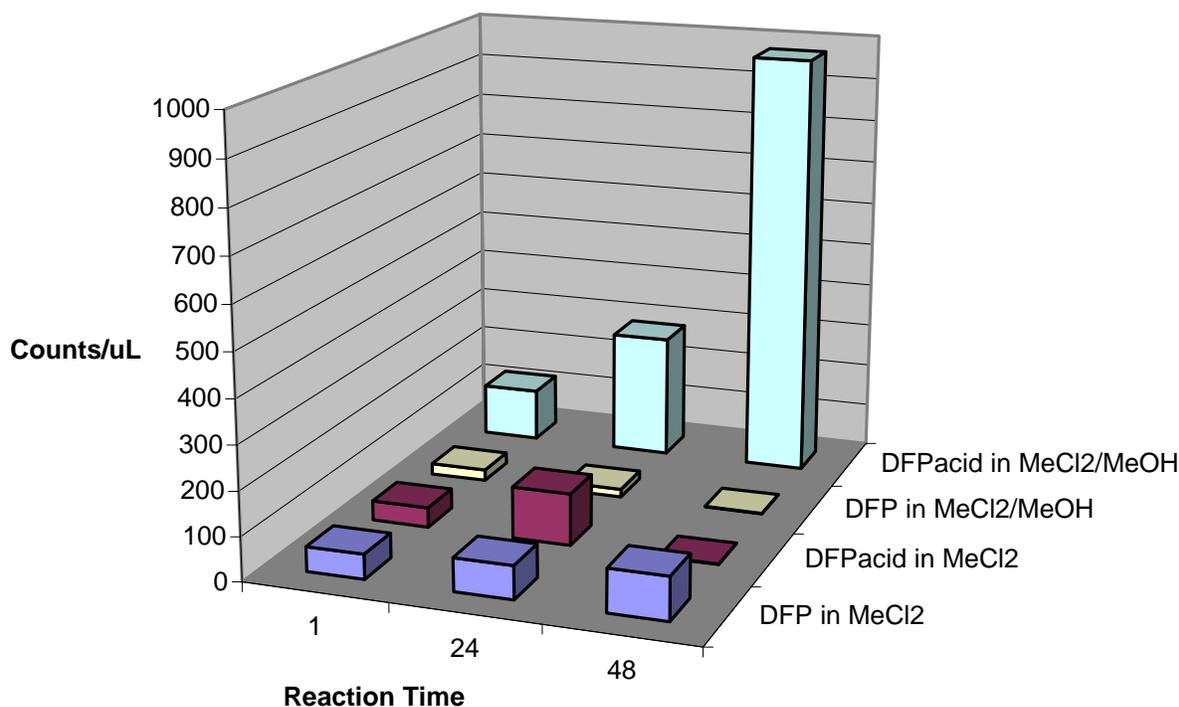


Figure 10. GC peak heights for extracted products from DFP reaction with hydrated M12 films over a range of reaction times.

DFP acid product measurements have been successful with GC analysis of extracts from reacted materials, however, confirmation of the hydrolysis reaction and the rate was pursued by solid state NMR using a phosphorus probe to improve detection sensitivity of DFP and its products. Samples exposed to surrogate vapor cannot be analyzed for residual reaction products, as the contamination levels are too low for good resolution in solid state NMR scans unless the materials are highly adsorbant. Therefore, in the case of membranes and treated fabrics, we have to rely upon liquid agent contamination methods for kinetics. Therefore, for complete reaction kinetics determinations of decontamination reactions on reactive fabrics and films, NMR results from *liquid contamination* methods will have to be coupled with GC/MS studies of *solid/vapor reaction* kinetics.

A small amount (150mg) of dry and humidity conditioned (100RH) powdered M12 poly(vinylamine-co-vinyl alcohol) sample was exposed to 50 mg liquid DFP by mixing to a thick paste and packing the contaminated sample into the rotor. The contamination level of the polymer was 1.5 times higher than the required exposure level of $10\text{g/m}^2\text{-day}$ for a fabric test. (A typical membrane fabric of M12 film contains approximately 50g/m^2 of polymer and the exposure level would be $10\text{g DFP per } 50\text{g M12}$, or 0.2mgDFP/mgM12 . We used an exposure level of 0.3mgDFP/mgM12 , which is almost two times more DFP per mass of M12 than required for protection. As a result, we would expect to see unreacted DFP.

NMR of Absorbed and Hydrolyzed DFP

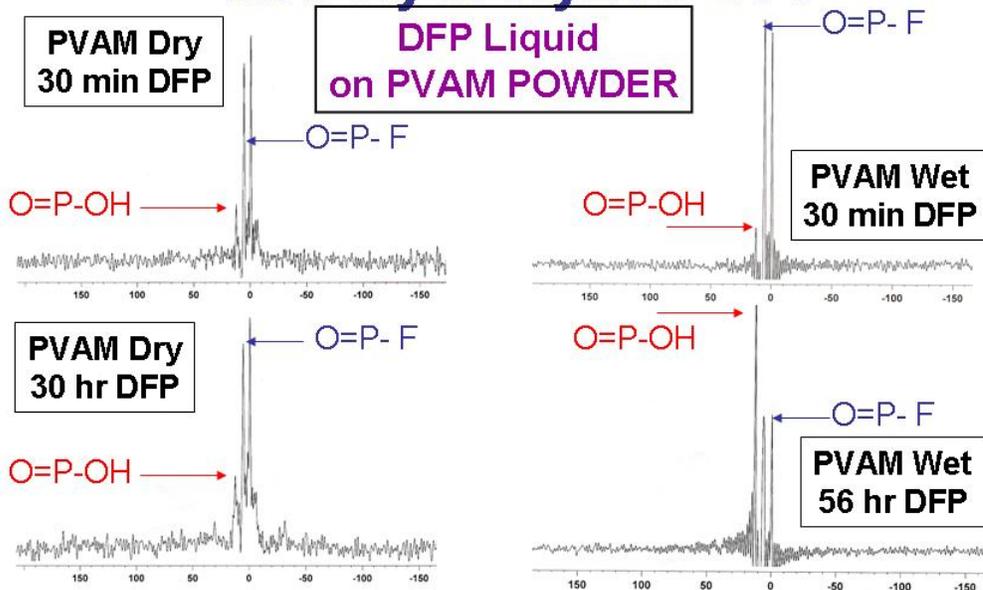


Figure 11. 300MHz Solid State (MAS) NMR with ^{31}P Probe used to measure the P-F peak of the DFP and the P-OR peak of the reaction product from the hydrolysis of DFP on M12 powder over time.

The NMR spectra in Figure 11 demonstrate the differences between DFP and the DFP reaction product. In untransformed DFP, a signature doublet phosphorus peak is observed at 0ppm, resulting from the P-F bond. Upon reaction, the removal of the fluorine from the phosphorus produces a singlet peak, shifted upfield, due to the substitution of the less electronegative hydroxyl substituent on the phosphorus. Differences between the hydrated and the unhydrated M12 powder properties are apparent. The hydrated powder adsorbs more liquid DFP as seen in the dry vs. wet NMR scans at 30 min. After 30 hours, there is no apparent depletion of the originally adsorbed DFP on the dry polymer, and no apparent production of DFP acid product. On the other hand, the hydrated (“wet”) M12 polymer produces a significant amount of the hydrolysis product after 56 hours of exposure to DFP liquid. Close to 25mg of DFP has been depleted by 150mg of the humidified M12 powder.

CONCLUSIONS

Studies of the Erkol™ copolymer M12 have resulted in favorable properties and further evaluations and formulations are underway for poly(vinylamine-co-vinyl alcohol) for reactive permselective membranes for future protective clothing applications. It has been found that the copolymer is very hydrophilic, and the hydration level affects the diffusion and adsorption of DFP by the copolymer. Without significant adsorption, there is little opportunity for hydrolytic

attack and reaction to deplete the DFP concentration within the membrane. In competition for this need to adsorb and react the contaminant, the copolymer exhibits selective permeability – keeping out chemical agents, even at high water concentrations within the membrane. Swelling of the membrane at conditions approaching 100% RH are needed to sufficiently adsorb simulants like DFP in order to accommodate subsequent reaction. The membrane can be reinforced by expanded PTFE porous membranes, enabling the use of extremely thin membranes in garment applications, but the processing and curing of the hydrophilic copolymer within the structure of the ePTFE is a key manufacturing issue that requires careful processing control. Analysis of the hydrolysis products of DFP within the copolymer membrane requires mixed solvents with minor protonation by acid in order to quantitatively remove the DFPacid from the polyamine matrix – this step must be followed by silylation derivitization for final GC analysis of this key product in the exposed membrane. GC analysis on vapor-exposed copolymer films show low level reaction of DFP to DFP acid within the first 24 hours, and significant increases in DFP acid production after 48 hours, and this is confirmed by solid state NMR testing of liquid-contaminated copolymer powder.

REFERENCES

1. Robbins, F.M., Andreotti, R.E., Walker, J.E., and Remy, D.E., “Preparation and Properties of a Metal Coordination Polymer Complex (U).” NATICK/TR-89/003L (1988).
2. Robbins, F.M., Walker, J.E., Andreotti, R.E., Evans, G., and Woodbury, C., “Metal Coordination Polymers for Chemical Protection (U).” NATICK/TR-89/004L (1988).
3. Kohlman, W.G., Preparation and Evaluation of Reactive and Adsorptive “Materials Systems for Chemical Protection.” NATICK/TR-93/016L (1993).
4. Seltzman, H.H.; Szulc, Z.M., “Chemically Modified Cyclodextrins as Catalytic Enzyme Mimics,” Medical Defense Bioscience Review Vol 1: 339-346 (1996).
5. Walker, J.E., Robbins, F., Andreotti, R., Woobury, C., Alabran, D., “Moisture Requirements for Chemical Agent Inactivation by Catalytic Protective Systems.” NATICK/TR-91/005L (1991).
6. Davis, R.B., Kramer, C.E., and Weinberg, J.S., “Improved Materials for Chemical Protective Clothing,” Final Report (Unpublished) for Contract DAAK60-82-C-0024 (March 1984).
7. GB Vapor Phase Reactivity Tests of Fabrics,” DPG-IR-85-202 (Dugway Proving Ground Internal Report, 1985).