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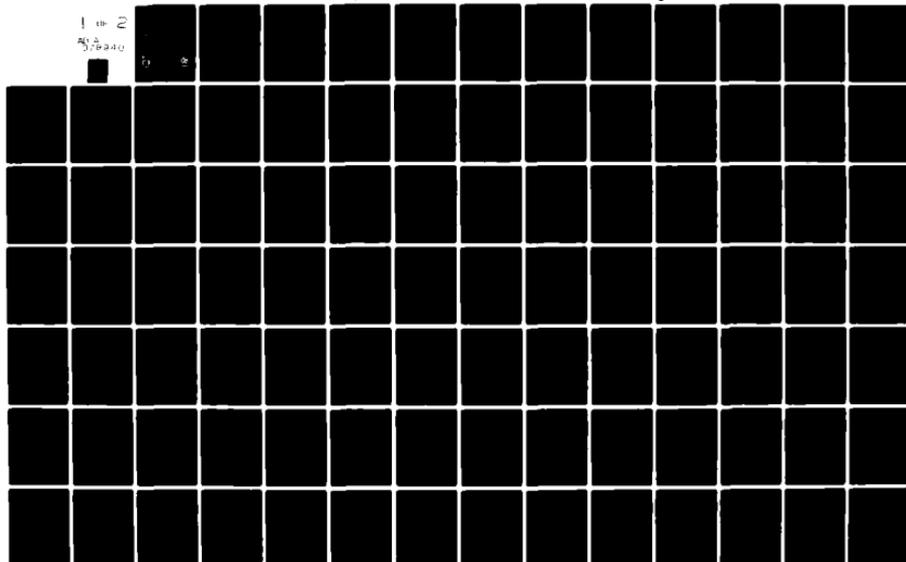
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A STUDY OF AGENT-REACTIVE FABRICS
FOR USE IN PROTECTIVE CLOTHING

FINAL REPORT

by

Gerald Zon

December 1979

ANDRULIS RESEARCH CORPORATION
7315 Wisconsin Avenue
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A broad investigation has been carried out in order to obtain modified fabrics which exhibit catalytic activity toward hydrolytic decomposition of chemical warfare agents. The major areas of study included the development of chemically modified Nomex and cotton-blend fabrics, mechanistic inquiries with regard to factors which control simulant/agent hydrolysis, and the design and construction of a suitable fabric testing apparatus for comparative evaluation of candidate fabrics.			

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Chelating fabrics
Catalyst evaluation

PREFACE

This experimental project was authorized by contract DAAK11-78-C-0060, with the same title as that of this report. It was carried out from May 1978 through July 1979.

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1. OBJECTIVE

The goal of this project was to investigate modifications to synthetic fibers and/or synthetic fabrics so as to impart catalytic reactivity towards G-, V-, and H-agents. The long-term or ultimate objective associated with this goal is to obtain a permeable modified fabric which offers the wearer adequate protection from these chemical warfare (CW) agents. Ideally, such a fabric should be physiologically harmless and should be effective against all of the reactive agent types. Other factors which indirectly influence the long-term development of the proposed fiber/fabric modifications are garment durability, comfort, regular cleaning, decontamination, and "shelf-life".

2. BACKGROUND

In connection with defense against CW agents, it is generally recognized¹ that it is much more difficult to provide the same high level of protection to a person's skin as to the respiratory tract, or, at least, to do so without encumbering the person to the point of military uselessness. The oilcloth used to protect against vesicant agents in World War I was impermeable to "mustard gas," but, as well as being heavy and uncomfortable, it was also impermeable to air and water vapor, so that the wearer quickly became overheated and exhausted. Consequently there has been an intensive search for clothing materials impermeable to CW agent but permeable to air and water vapor.^{2,3} There have been some promising approaches to this formidable problem, but none has been more than partially successful, as heat loss is always impaired to some extent, and the effective lifetime of the clothing is never long.¹

¹"Medical Protection against Chemical-Warfare Agents", Stockholm International Peace Research Institute (SIPRI), Almqvist and Wiksell International, Stockholm, Sweden, pp. 1-21 (1977).

²"Chemical and Biological Warfare. Part 2. Protection, Decontamination, and Disposal", Search Period 1964-Nov. 1977, U.S. Dept. of Commerce, National Technical Information Service, Springfield, VA.

³"Protective Clothing. Part 3. Survival, Aircraft, and Combat Environments", Search Period 1964-April 1977, U.S. Dept of Commerce, National Technical Information Service, Springfield, Va.

A recent version of the British chemical/biological protective suit, which is a permeable overgarment, is made of a nonwoven synthetic textile coated on the outside with a liquid repellent (both hydro- and lipophobic) and having a layer of activated charcoal bonded to the inside. Several liquid repellents are available: highly fluorinated hydrocarbons and Werner-type chromium complexes with perfluoroalkanoyl acido-groups. The outer coating impedes penetration of liquid agents into the cloth, while the inner charcoal layer absorbs any agent vapor that might still get through. The major defects of this suit, however, seem to be its limited "shelflife" and poor tear resistance.¹ A new material known as "carbon cloth", a woven activated carbon-containing fabric that is strong and tear resistant has been studied,¹ but some are of the opinion that a more promising tack involves clothing impregnants that destroy rather than merely absorb invading chemicals. One of the earliest developments in this area was the U.S. production in the late 1920's and early 1930's of a clothing-impregnating process based on the impregnant sym-bis-(chloro-2,4,6-trichlorophenyl)urea (CC-2), which chemically decomposed V-agent nerve gases, although not the G-agents (see Figure 1) The U.S. CC-2 process was used throughout World War II and has been subsequently modified to yield XXCC-3, a micronized-powder form containing 10% zinc oxide stabilizer.¹

A serious limitation with CC-2 or other stoichiometrically-reactive chloroamides is the large amount of impregnant that must be incorporated into the cloth. Thus, there has been an active search¹⁻³ for materials capable of catalyzing the air-oxidation, autoxidation or hydrolysis of invading CW agents, and there remains a definite need for a modified fabric which overcomes the aforementioned drawbacks but which otherwise meets the idealized criteria previously stated in the objective.

3. RATIONALE

3.1 Analysis of the General Modes of Agent Decomposition

The modification of synthetic fibers and/or fabrics so as to incorporate protective agent-reactive functional groups (ARFGs) should be approached by a systematic and critical consideration of the general modes of agent interception that are feasible within the scope and limitations of chemical reaction theory.

<u>Molecular Structure</u>	<u>Trivial Name</u>	<u>Agent Type</u>
$\text{ClCH}_2\text{CH}_2 - \text{S} - \text{CH}_2\text{CH}_2\text{Cl}$	Sulfur Mustard	Agent H
$ \begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_2\text{CHO} - \text{P} - \text{F} \\ \\ \text{CH}_3 \end{array} $	Sarin	Agent GB
$ \begin{array}{c} \text{O} \\ \\ (\text{CH}_3)_3\text{C} - \text{CH}(\text{CH}_3) - \text{O} - \text{P} - \text{F} \\ \\ \text{CH}_3 \end{array} $	Soman	Agent GD
$ \begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O} - \text{P} - \text{CN} \\ \\ \text{N}(\text{CH}_3)_2 \end{array} $	Tabun	Agent GA
$ \begin{array}{c} \text{O} \\ \\ \text{CH}_3\text{CH}_2\text{O} - \text{P} - \text{SCH}_2\text{CH}_2\text{N}[\text{CH}(\text{CH}_3)_2]_2 \\ \\ \text{CH}_3 \end{array} $		Agent VX

Figure 1. Molecular structures and trivial names for various CW agents.

For the particular H-, G-, and V-type CW agents pictured in Figure 1, the recognized general classes of agent destruction (decomposition) are the following:

- oxidation by surface-associated oxygen
- unimolecular fragmentation
- hydrolysis by surface-associated water

Granted the reasonable assumption that an ARFG should operate by a catalytic rather than stoichiometric process for maximal efficiency, viz, one ARFG facilitating the destruction of n agent molecules (n > 1), it is necessary to evaluate the relative feasibilities of the three general destruction modes.

Catalytic oxidation is attractive in that the available amount of air-oxygen for either direct chemical "activation" by fiber-attached ARFGs, or participation in an ARFG-initiated catalytic oxidation, would be rather insensitive to the molecular composition of the fabric, due to the small size and non-polarity of the O_2 molecule. That chemical "activation" of O_2 is necessary in the first of these approaches stems from the fact that while the agents under consideration are unreactive toward normal (ground state) triplet O_2 , the two electronically excited singlet O_2 molecules which are ca. 20 to 40 kcal/mol higher in energy would most likely participate in sulfur, nitrogen, C-H, and/or P=O oxidation reactions with the agents.⁴ These favorable points are, on the other hand, outweighed by the relatively indiscriminate chemical behavior of singlet O_2 that would most likely lead to degradative-type oxidation reactions with the fiber per se. The ARFG could, in principle, be designed so as to simultaneously bind the agent and produce singlet O_2 for exclusive agent oxidation; however, precedent for such complexes having substrate-selective reactivity is unknown to us.

Along these lines it is also conceivable that synthetic analogs of biological cytochrome P-450 mixed-function oxidases could be used to effect agent-specific monooxidations of the C-H to C-OH type and thereby mimic in vivo liver detoxification

⁴C.S. Foote, Accounts Chem. Res., 1, 104 (1968).

processes; however, such systems require a coupled redox system, and are therefore not truly catalytic. Also, a considerable amount of data on Fe(II)-based model systems reveals very little substrate selectivity.⁵ Problems with spontaneous dimerization and the need for a redox system also confront Co(II) and other M(II)-Schiff base complexes with a nitrogenous base, which are known to bind molecular O₂ at room temperature but rapidly form super dioxo-bridged complexes of the type M(III)-O₂-M(III).⁶

The second approach mentioned above, *viz.*, the involvement of molecular oxygen in an ARFG-initiated, catalytic, co-oxidative reaction with the agents has already been studied⁷ during previous contract work between the Department of the Army/Edgewood Arsenal and W. R. Grace & Co. It was shown that cooxidative initiators (e.g., *t*-butoxy radicals) effectively abstract hydrogen from sulfur mustard and the GB and GF agents; however, the resultant agent radicals, if involved in chain propagation, failed to provide an overall catalytic process that was effective at ambient temperature.

Unimolecular fragmentation of each agent in Figure 1 is possible, in principle, by means of the mechanisms illustrated in Figure 2. While the 1,2-elimination pathway for sulfur mustard (Agent H) has not to our knowledge been reported, γ -alumina is known⁸ to cause fragmentation of sarin to yield propylene which may also be formed from sarin at significantly higher temperatures⁹ without the intervention of a surface catalyst such as gamma alumina; however, even the "facile" gamma alumina process is extremely slow at normal temperatures. Note that the vinyl chloride (CH₂=CHCl) expected in the case of sulfur mustard is now widely recognized to be a potent carcinogen. These factors and the absence of reasonable (*i.e.*, lower energy) alternate fragmentation pathways or other useful precedent forces one to reject the unimolecular fragmentation approach as a generally applicable solution to the problem under consideration.

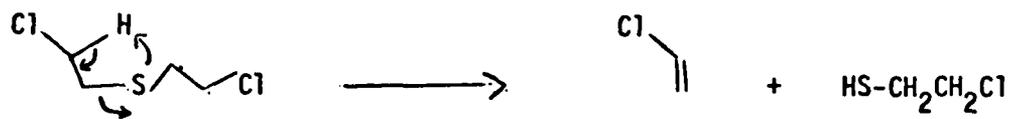
⁵For a lead ref. to such oxidations in organophosphorus mustard compounds, see D. L. Hill, "A Review of Cyclophosphamide", Charles C. Thomas, Publisher, Springfield, Ill. (1975).

⁶E. Tsuchida and H. Nishide, "Polymer-Metal Complexes and Their Catalytic Activity" in *Adv. in Polymer Sci.*, 24, 2-87 (1977).

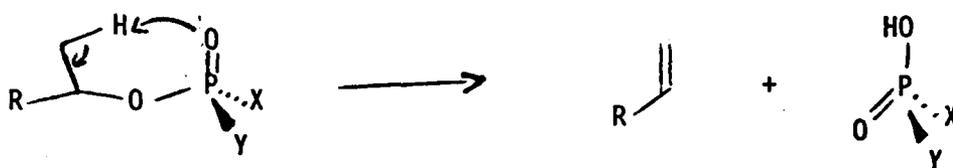
⁷G.J. Braude (W.R. Grace & Co., Clarksville, Md.) Contract No. DA-18035-AMC--287(A).

⁸A. E. T. Kuiper, J.J.G.M. van Bokhoven, and J. Medema, *J. Catalysis*, 43, 154 (1976).

⁹R.W. Baier and S.W. Weller, *I & E Process Design and Development*, 6, 380 (1967).



Agent H

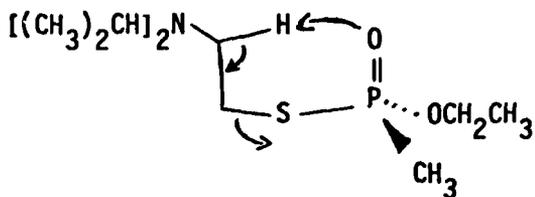


Agent GB: $\text{R} = \text{CH}_3$, $\text{Y} = \text{CH}_3$, $\text{X} = \text{F}$

Agent GA: $\text{R} = \text{H}$, $\text{Y} = \text{N}(\text{CH}_3)_2$, $\text{X} = \text{CN}$

Agent VX: $\text{R} = \text{H}$, $\text{Y} = \text{CH}_3$, $\text{X} = \text{SCH}_2\text{CH}_2\text{N}[\text{CH}(\text{CH}_3)_2]_2$

Agent GD: $\text{R} = \text{t-Bu}$, $\text{Y} = \text{CH}_3$, $\text{X} = \text{F}$



Agent VX

Figure 2. Unimolecular fragmentation mechanisms for H-, G-, and V-type agents.

and implies that further acceleration by a catalyst is not needed. This set of circumstances is rather fortunate, as an accelerated S_N2 step would require metal ion (Lewis acid) assisted chloride ionization; however, to do so without a rate-decelerating metal ion-interaction with the sulfur lone pair is an improbable task. In any event, one is therefore primarily concerned with decreasing the rate of sulfur mustard passage through fabric and the availability of fabric-associated water and/or fabric-associated groups to "activate" water via general base catalysis, which together would cause irreversible hydrolysis of sulfur mustard.

Compared to sulfur mustard, the hydrolysis of the four remaining agents are significantly more complex, due to (a.) the variable nature of the best leaving group¹⁰ in each case [GB and GD: fluoride; GA: cyanide in alkaline media, dimethylamino in acidic media; VX: thioalkyl], (b.) the variable molecular structure about phosphorus, which can influence the hydrolysis rate and mechanism,¹² (c.) the inherently complicated nature of the potential energy surface ("reaction manifold") for nucleophilic substitution processes at tetracoordinate phosphorus, which includes formation of pentacoordinate phosphorane intermediates of variable stability,¹⁵ (d.) strict geometric (stereochemical/electronegativity control factors,¹⁵ and (e.) oftentimes dramatic pH effects on the overall hydrolysis rate and/or mechanism of reaction.¹⁰ In view of these complicating factors, it has been necessary for us to adopt a heuristic (and admittedly oversimplified) mechanistic assumption wherein all of the G- and V-type agents have a generalized $ROP(O)R'X$ structure akin to sarin and soman, as well as $[(CH_3)_2CHO]_2P(O)F$ (DFP), for which a substantial volume of catalytic hydrolysis data exists.^{10,11} This approach assumes that the obvious steric inequities about phosphorus, which are indeed present, give rise to relatively small rate differences for back-side attack by water/hydroxide and that the various leaving groups (X) are roughly comparable to fluoride. Equating of leaving group ability is certainly justifiable for fluoride vs. cyanide, but less so for fluoride vs. thioalkyl. In any event, the initial simplified conceptual procedure is to regard the agents as comparably sized molecules having similar "solubility" properties and a moderately good leaving group. Thus, it is now possible to concentrate on the literature data for catalytic hydrolyses of sarin and DFP with the intention of deducing those general types of catalysts which are relatively efficient and moreover, lend themselves toward fabric attachment.

¹⁵For a review dealing with general aspects of nucleophilic substitution at tetracoordinate phosphorus, see G. Zon and K. Mislow, Topics in Current Chemistry, 10, 6, (1971).

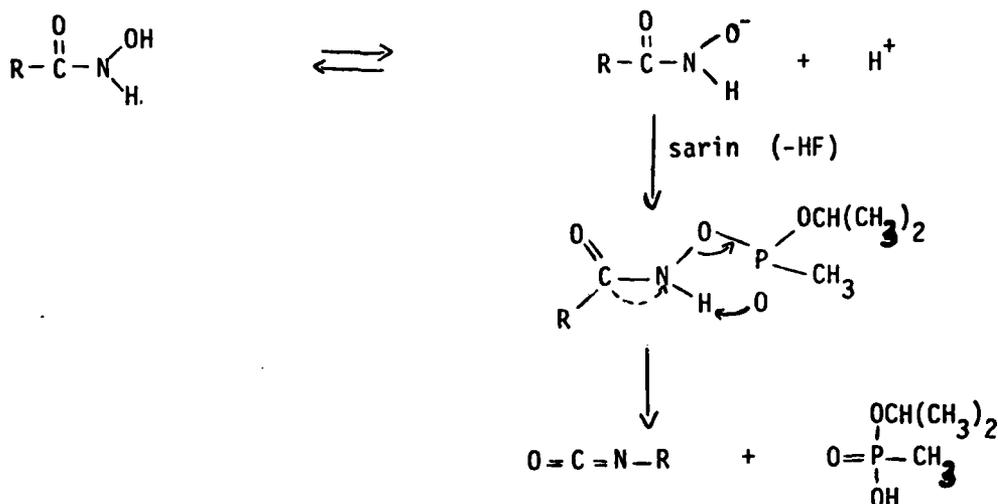
3.3 Catalytic Hydrolyses of H-, G-, and V-Type Agents

In view of the fact that the text by Bruice and Benkovic¹⁰ contains a comprehensive review of pioneering work in the area of catalytic hydrolyses of CW-related organophosphorus compounds, the following summary is meant to highlight selected literature data available to us.

A variety of substances including chlorine, nitrogenous organic compounds, various metal ions, and metal chelates have been shown to accelerate the hydrolysis of DFP and sarin.¹⁴ Dissolved chlorine provides an equilibrium-controlled concentration of hypochlorite as the active phosphorus nucleophile. The fact that the hydrolysis reaction with chlorine is stoichiometric together with our belief that chlorine/hypochlorite would not be suitable for use as an ARFG on fabric eliminate it and the peroxide nucleophile from further consideration. On the other hand, the role of nitrogen bases (*i.e.*, amino acids, imidazole, and primary amines) is truly catalytic. While the magnitudes of the rate enhancements provided by these bases are relatively modest, Epstein and co-workers¹¹ have shown that the hydrolysis of sarin is first order in free amino nitrogen. The latter work¹¹ has also demonstrated that nucleophilic attack on phosphorus by the amine nitrogen leading to PN bond formation is not catalytically important, as only isopropyl methylphosphonic acid is produced, and that the absence of an "alpha" or "charge" effect is consistent with a general base-catalysis mechanism.

As a class of nitrogenous organic compounds, hydroxamic acids $RC(O)NHOH$ have been of interest as reactivators of poisoned cholinesterases. However, the acceleration of the hydrolytic decomposition of sarin which is observed for hydroxamic acids does not arise from the general base catalysis mechanism, and instead involves stoichiometric (equimolar) amounts of $RC(O)NHOH$. This "pseudo-catalysis" phenomenon results in co-destruction of the hydroxamic acid promoter-molecule and is believed to occur by the mechanism outlined below, wherein initial fluoride ion displacement is followed by a combined alpha, elimination/Lossen-type rearrangement¹⁸ to afford the sarin hydrolysis product and an isocyanate (RNCO), which may then undergo the normal hydration/decarboxylative-fragmentation characteristic of RNCO species in aqueous media.

¹⁸M. A. Stolberg, R. C. Tweit, G. H. Steinberg, and T. Wagner-Jauregg, J. Am. Chem. Soc., 77, 765 (1955).



Among the most effective catalytic agents known to accelerate the hydrolysis of sarin and DFP are metallic ions and, especially, metal ion chelates. Studies with sarin have shown that chromate, molybdate and tungstate anions exert some catalytic effect.¹⁹ Sarin hydrolysis is also accelerated by a few simple hydrated metal ions, with the following catalytic order being in evidence:^{20,22} Cu(II) Ce(II) Mn(II) Mg(II). Similar studies of tabun hydrolysis revealed an effective catalytic order of Cu(II) Pd(II) Au(III) Ag(I) Ni(II) Co(II) Zn(II).²² Interestingly, rare earth metal ions which are known²³ to strongly catalyze the hydrolysis of organophosphate esters²³ are not very effective against sarin or DFP; however, some effect has been cited for the uranyl ion.²⁰

It is important to note that chelated metal ions are even more effective as hydrolysis catalysts than the corresponding hydrated metal ions. In view of the problem under consideration this is a circumstance to take advantage of, as the desired metal catalyst can be attached to fabric via the organic chelating group. Wagner-Jauregg and collaborators were the first to report catalysis by metal chelates.

¹⁹L. Larsson, Acta Chem. Scand., 12, 1226 (1958).

²⁰J. Epstein and D. H. Rosenblatt, J. Am. Chem. Soc., 89, 3596 (1958). J. Epstein and W. A. Mosher, J. Phys. Chem., 72, 622 (1968).

²²J. Epstein and W.A. Mosher, J. Phys. Chem., 72, 622 (1968).

²³K. B. Augustinsson and G. Heimburger, Acta Chem. Scand., 9, 383 (1955).

²⁴T. Wagner-Jauregg, B. E. Hackley, Jr., T.A. Lies, O.O. Owens, and R. Proper, J. Am. Chem.

In these studies with DFP, they reported that Cu(II) chelates were much more effective than those of Ni(II) or Co(II), and that Fe(II) and Mn(II) chelates did not apparently serve to catalyze the hydrolysis. Among the amino acids and amine ligands investigated, and the ligand/metal ratios employed in bicarbonate buffer at pH 7.6, the best results were obtained with the 1 : 1 complex formed between Cu(II) and bipyridyl, with the half-life of DFP being reduced from 2500 min to 4.5 min.²⁴ In related work on sarin hydrolysis, Courtney, *et al.*,²⁵ investigated an impressive array of chelates involving ten metals. Once again the chelates of Cu(II) produced the largest rate enhancements. Somewhat less effective catalytic activity was also found for some of the chelates of VO₂(VI), ZrO(IV), and MoO₂(IV), while La(III), Mo(II), Fe(III), Cr(III), Ti(IV) and Sn(IV) chelates, provided either low or no measurable activity.

From a mechanistic viewpoint the catalysis observed for the aforementioned metal chelates could arise *via* formation of an initial complex between the substrate and metal center, followed by rate-determining nucleophilic attack by hydroxide at phosphorus.²⁴ According to this view, the electropositive metal withdraws charge density from the phosphorous and therefore facilitates nucleophilic attack. An alternative mechanism emphasizes the ability of the metal center to lower the transition state energy for P-F bond cleavage in the rate-determining step. Accordingly, the metal center is involved in a "push-pull" situation wherein it acts as a Lewis acid to facilitate the formation of fluoride ion, while simultaneously donating a hydroxyl group.^{20,26,27}

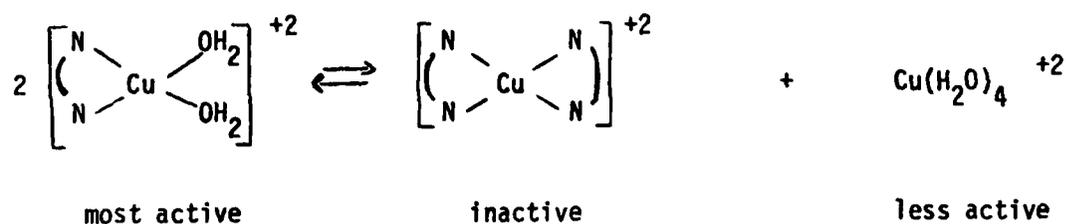
Considerable effort has been directed toward determining the factors influencing the hydrolytic reactivity of Cu(II) chelates. Those complexes, which exhibit the greatest catalytic activity, all contain bidentate nitrogen donor ligands and have water and/or hydroxy ligands occupying the remaining positions in the square-planar first- coordination sphere, as compared to complexes containing tridentate, tetradentate or bis-bidentate nitrogen ligands. Somewhat lower activities result when the third and fourth coordination sites are filled by oxygen donors appended to the bidentate nitrogen ligand, due to effects associated with the hydrolytic behavior of the complexes. Lowered activity also

²⁵R. C. Courtney, R. L. Gustafson, S. J. Westerback, H. Hyytiainen, S. C. Chaberrk, Jr., and A. E. Martell, *J. Am. Chem. Soc.*, 79, 3030 (1957).

²⁶R. L. Gustafson and A. E. Martell, *J. Am. Chem. Soc.*, 84, 2309 (1962).

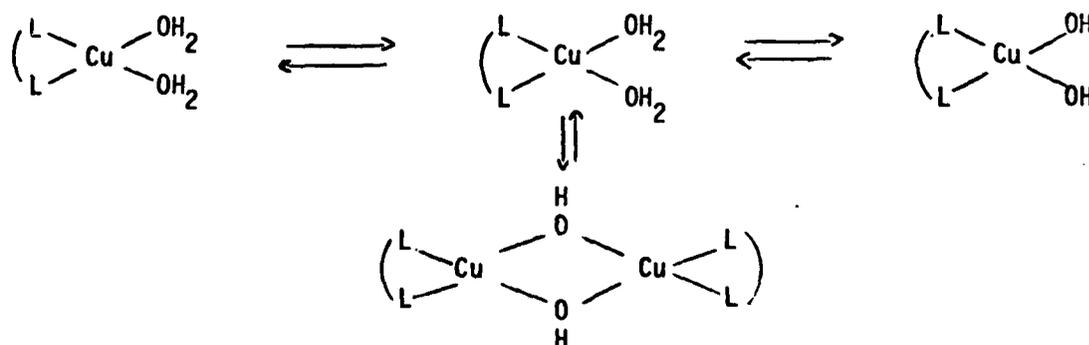
²⁷F. M. Fowkes, G. S. Ronay, and L. B. Ryland, *J. Phys. Chem.*, 62, 867 (1958).

occurs when the positive charge of the complex is decreased by the presence of anionic donors other than hydroxide. Hence, the generalizations appear to be that catalytic activity decreases with increasing negative charge of the chelate as well as with increasing stability of the complex.²⁴⁻²⁶ The latter phenomenon has been explained^{25,26} by the increased tendency for Cu(II) chelates to disproportionate as a function of increasing Cu-N bond strength, as pictured below.



Of the many ligands studied, the superiority of N,N,N',N'-tetramethylethylenediamine (TMEN) is understandable in that the Cu-N bonds are sufficiently strong to provide a high value for $K_{\text{formation}}$ while the steric bulk of the geminal methyl groups precludes disproportionation to the inactive chelate bis(TMEN)Cu(II).²⁵

The role of pH is also quite important. The catalytic activity appears to generally increase with pH, as this factor determines the relative concentrations of the Cu(II) species which are present in the following equilibria:



Although each of the species in the equilibrium mixture contributes to the overall catalytic effect, they do so to varying degrees. Thus, while the hydroxy-bridged dimer possesses negligible activity,²⁶ the influence of pH can be rationalized by postulating

that the diaquo monomer is less active than either the hydroxy aquo monomer or the dihydroxy chelate.^{25,28} In this regard, a study which correlates DFP hydrolytic rate data with carefully measured dipyriddy Cu(II) equilibrium data at various pH values led Fowkes, *et al.*,²⁷ to conclude that (a.) in the neutral region the principal catalytic species is the diaquo chelate, (b.) in the alkaline region the principal catalyst is the dihydroxy species, and (c.) the catalytic contribution of the hydroxy aquo monomer is much less than previously supposed.²⁹

In concluding this section, it is instructive to briefly review relevant experimental findings and suggestions from the work of W. R. Grace & Co.³⁰ on protection from and decontamination of the CW agents presently being considered. More specifically, a non-catalytic approach involving agent decontamination by metal salts and organo-metallic compounds was studied and, *inter alia*, the following was reported.

- (a.) Some derivatives of copper (I), molybdenum (V), tungsten (VI), and niobium (V), particularly phenolates, were highly effective for agent GF in non-aqueous solution.
- (b.) IR and NMR data for aryloxy metal chloride-GF and DFP complexes were indicative of GF-metal binding *via* P=O.
- (c.) Decomposition of GF by aryloxy metal chlorides was not accompanied by formation of detectable amounts of fluoride ion.
- (d.) Synthetic sweat treatment made the metal derivatives largely ineffective as agent decontaminants, and urea was identified as an inactivating component in sweat.
- (e.) Sulfur mustard is, relative to the other agents, much more difficult to bind by metal compounds; molybdenum complexes are effective in solution, but as a fabric impregnate the complexed mustard can be displaced by addition of an amine.
- (f.) Removal of mustard from heptane solution could also be accomplished with Ag(I), Bi(III), Cd(II), Ce(IV), Pb(II), Pd(II), Pd(IV), Sb(III), Sb(V), Sn(IV), Te(IV), and W(IV). In general, it appeared that mustard complexation is favored by metal ions with substantially filled d- and f-orbitals, as opposed to

²⁸L.L. Pytlewski has found (see Contract DAAA1575-C-0195) that activated carbon impregnated with copper may lead to the formation of a hydrolytically active copper species.

²⁹J.T. Hoppe and J.E. Pure, *J. Chem. Soc.*, 1775 (1957).

³⁰Contract DA18035-AMC-287(A).

outermost metal orbitals having p- or s-electrons.

- (g.) Of the metals tested as fabric impregnants, e.g., Mo(I), Mg(II), Nb(V), Sb(III), Sb(V), Sn(IV), and Te(IV), only mercury salts were completely effective against sulfur mustard.

It was concluded that Mo(V), Nb(V), and Hg(II) showed some promise for decontamination and retention of both the nerve agent and mustard in nonaqueous media; however, all of the metal compounds are "poisoned" by sweat and the toxicity problems of such heavy metals must be considered.

3.4 Factors Related to Bonding of Catalytic ARFGs to Fiber/Fabric

The foregoing discussion was concerned with soluble (homogeneous) catalysts that are uniformly dispersed in aqueous reaction media and provide, in effect, a virtually infinite number of nucleophilic solvent molecules. In extending such chemical reactivity concepts to catalysts which are bonded to a fabric surface, it is necessary to exercise some caution, especially with regard to relative polymerbound vs. model monomer reactivities and the relative availability of a fabric's surface-associated water molecules. Consequently, both of these aspects will now be evaluated in detail, drawing primarily upon data that has been very recently reviewed by Tsuchida and Nishide⁶ and by Kuitake and Okahate.³¹ The former review deals with polymer-metal complexes and their catalytic activity in general, while the latter review is specifically concerned with contemporary advances in catalytic hydrolysis by synthetic polymers.

Polymeric acids e.g., poly(styrenesulfonic acids) and polymeric ammonium ions e.g., poly(vinylbenzyltriethylammonium hydroxide) can "moderately" catalyze the hydrolysis of esters, amides, and ethers due to a local proton concentration in the polymer domain which is higher than that of the bulk phase. However, when substrate molecules are attracted to the polymer molecule by electrostatic and hydrophobic forces, the catalytic efficiency increases by up to 100-fold, relative to mineral acids or alkalis.

³¹T. Kunitake and Y. Okahata, "Catalytic Hydrolysis by Synthetic Polymers" in Adv. in Polymer Sci., 20, 161-221 (1976).

Studies of imidazole-containing polymers indicate that poly(vinylimidazoles) show some enhanced reactivities toward simple phenyl esters relative to monomeric analogs, which are caused by possible multifunctional catalysis and by substrate attraction due to secondary valence forces. Remarkable rate enhancements were found when long-chain substrates were used, and this was attributed to increased hydrophobic interactions. Combinations of hydrophobic and electrostatic interactions at the catalytic site produced further increases in the catalytic efficiency, and the pyridine group e.g. poly(vinylpyridine) has been found to show catalytic activity similar to that of imidazole.

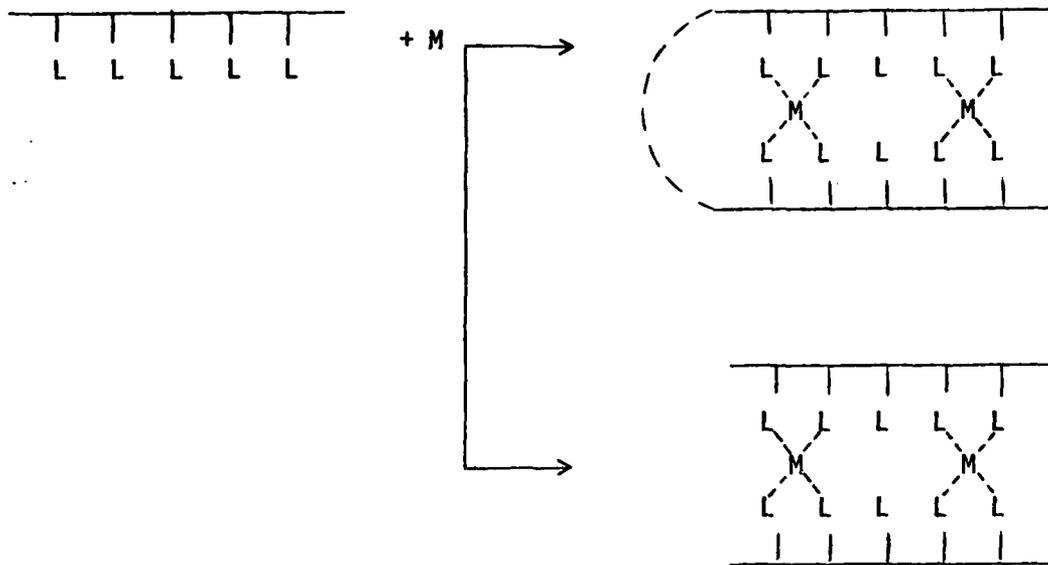
Anionic nucleophiles such as hydroxamate, oximate, and thiolate retain this type of reactivity in polymeric systems, and pronounced acceleration, relative to monofunctional polymers, has been obtained via bifunctional polymers such as a mixed hydroxamate-imidazole.

Poly(ethyleneimine) exhibits "moderate" catalytic effects on several hydrolysis reactions, and very large efficiency enhancements were obtained, as noted above, by use of bifunctionality, viz. an ethyleneimine-imidazole modified polymer, which has been referred to as a "synzyme" (synthetic enzyme) on the basis of its structural characteristics and catalytic activity that is comparable to hydrolytic enzymes.

While poly(amino acids) are attractive catalytic systems because of backbone similarities to enzymes, rate accelerations obtained to date have been unimpressive.

Polymer-metal complexes of the five basic types illustrated in Figure 3 are defined as complexes composed of a polymer ligand and metal ions (M) in which the metal ions are attached to the polymer ligand by a coordinate bond. It is generally understood that a polymer ligand is a polymeric substance that contains coordinating groups or atoms (L; usually N, O, and S), obtained by polymerization of monomer containing coordinating sites, or by the chemical reaction between a polymer and a low molecular weight compound having coordinating ability.

(A) Polymer-Metal Complexes



(B) Coordinate Polymers

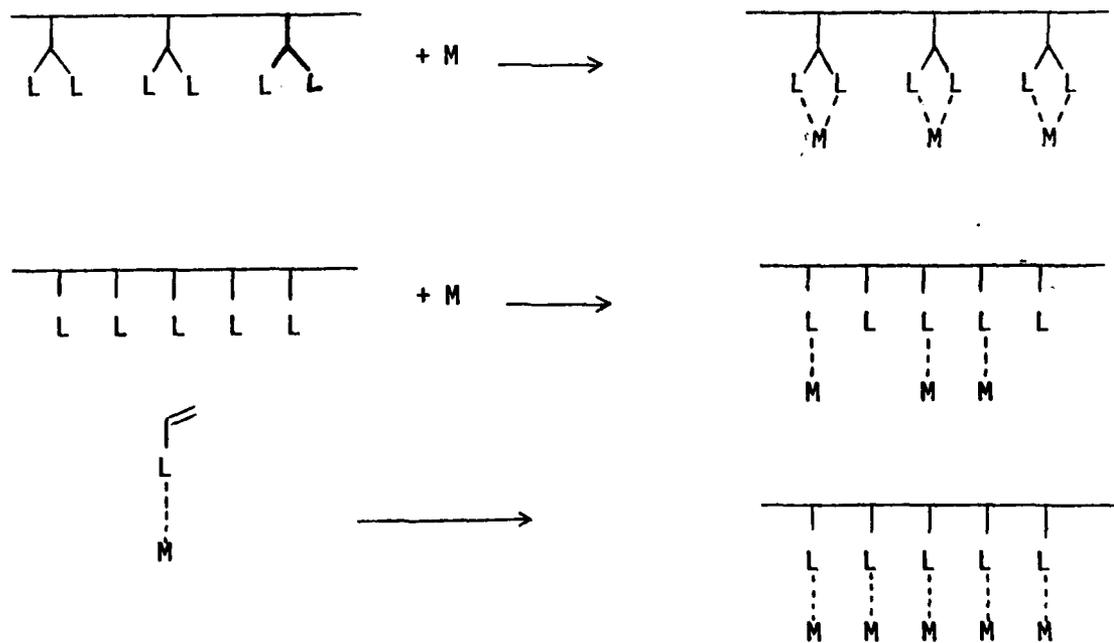


Figure 3. Schematic representations of synthetic routes to the five different types of polymer-metal complexes.

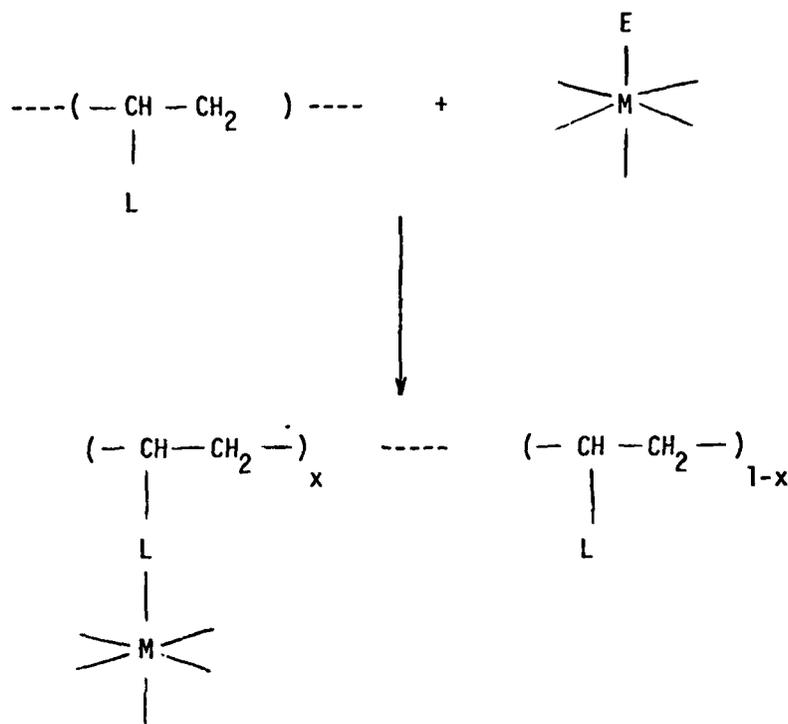
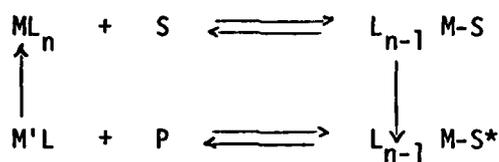


Figure 4. Synthesis and general structure of pendant-type polymer-metal complexes

A considerable amount of work has been carried out with pendant-type polymer-metal complexes which are obtained when a polymer ligand is made to coordinate to a reactive site of a previously prepared, stable, low-molecular weight metal complex (Figure 4). It is important to note that the structure and, hence, functions of the metal complex are regarded as undergoing only minor variations by attachment to the polymer ligand. In this connection it is of interest that the hydrophobic character of, for example, stearyl and perfluoroalkyl groups has been translated into waterproofing of cellulosic material, rayon, polyamides, and synthetic protein fibers by attachment of preformed "Werner-type" stearato and perfluoroalkato-Cr(III) complexes to each polymer via coordination bonds to available polymer ligands.

When a "naked" metal ion such as Cu(II), Ni(II), Zn(II), or Co(II) is added to a solution of a polymer ligand such as poly(acrylic acid), poly(vinylalcohol), poly(ethylenimine), or poly(vinylpyridine), a polymer chelate is rapidly formed, as shown in the first three synthetic routes depicted in Figure 3. Studies on the formation of polymer chelates have been almost exclusively concerned with Cu(II) ion, due in part to the stability of Cu(II) chelates in an aqueous solution which renders them hydrolytically stable under normal experimental conditions. Immediately after a solution of Cu(II) ions has been mixed with a solution of polymer ligand, a polymer-Cu chelate is rapidly formed. For example, stopflow spectroscopic methods have been used to determine that the magnitudes of the formation-rate constant (k_f) and the dissociation-rate constant (k_d) for poly(acrylic acid) with Cu(II) were 10^8 and $10^4 \text{ M}^{-1}\text{sec}^{-1}$, respectively, which are nearly equal to those of the corresponding monomeric dicarboxylic acid, glutaric acid. However, a comprehensive analysis of the overall formation constants of Cu(II) complexes with polymer ligands, in which 4-coordinate Cu(II) is the main species, revealed that the k values are from 10^1 to 10^5 greater than in the monomeric Cu-complex systems, which indicates that the Cu chelate generally forms more readily in the polymer system. This has been interpreted in terms of Cu ions that are occluded in a "cage" of contracted polymer chains, and that while Cu ions are difficult to elute from the polymer domain into the bulk of the solution, labile Cu ions repeatedly attach and detach on ligand units of the polymer. This phenomenon, which is unique to macromolecular polymers, is thought to be general for polymer-chelate systems. It should also be noted that stepwise formation constants increase for poly(vinylpyridine)-Cu(II) and that similar results obtain for Cu ions with poly(vinylamine), poly(n-vinylimidazole), poly(acrylic acid), and poly(vinylalcohol).

The general observation that various organic reactions are catalyzed by metal complexes is particularly relevant to the present problem. The catalytic cycle of a metal complex-catalyzed reaction is usually illustrated as shown below where substrate (S) for ligand (L) substitution is followed by substrate "activation" (S*) and, finally, loss of product (P) with regeneration of the catalyst structure. In most cases the catalytic action of a metal ion depends substantially on the nature of the ligands in the intermediate mixed complex ($L_{n-1}M-S$).



Oxidation reactions of organic compounds with molecular oxygen take place with high efficiency, and details have been published for Cu(II) complex-catalysis involving poly(histidine), poly(4-vinylpyridine), poly(lysine), poly(β -diketones), poly(β -ketoesters), poly(ethyleneimine), and poly(acrylic acid) systems.

Comparatively less data is available for catalytic hydrolysis by polymer-metal complexes; however, in connection with the problem under consideration, the catalytic hydrolysis of oligophosphates by poly(lysine)-Cu(II) complexes has been reported. The hydrolysis of sodium pyrophosphate was effected by using metal complexes of poly(methacrylacetone) as catalysts, with the activity decreasing in the order Zr(IV) > U(VI) > Cr(III) \approx Ce(III) \approx Cu(II). It was found that poly(lysine)Cu(II) complex exerted asymmetrically selective catalysis on the hydrolysis of phenylalanine esters, whereas Cu ions and bis(bipyridyl)Cu had no activity. In addition, a bis(2-carboxypyridine) Ni(II) complex has been attached to cyclohexaamylose, which offers a β -cyclodextrin-type hydrophobic "cavity", and it was found that hydrolysis of *p*-nitrophenyl acetate undergoes hydrolysis 1,000-times faster than the uncatalyzed system.

3.5 Selected Review of Basic Techniques for Chemical Modification of Fiber/Fabric

Conversions of already available textile fibers or co-fibers into derivative fibers with potential ARFGs offers not only the most direct strategy but also one with considerable flexibility, in terms of fiber selection and classes of ARFGs for testing. Before proceeding to the consideration of fabric and ARFGs, it is worthwhile to summarize at this stage the basic techniques that have been developed to modify polymers related to the usual fiber materials applicable for weaving of fabric. Figure 5 outlines such information, with specific examples, and it is apparent that the primary techniques are (1.) direct photochemical modification, (2.) direct chemical modification, (3.) indirect photochemical and/or chemical modification, and (4.) physical deposition and crosslinking of a surface coating. Note that the synthesis of polymer-metal complexes, which were discussed above, may be classified either within the direct chemical modification category or within the indirect chemical modification category. The indirect processes generally involve the random or regioselective functionalization of a relatively unreactive polymer/fiber to give a suitable metastable "intermediate" for final modification or grafting. Thus, for example, polyfunctional cellulosic poly-(amino acids) may be directly attached to "Werner-type" metal complexes, while polyamides, on the other hand, require metal ion coordination. It is further noted that technique (4.) offers the advantage of not having to form specific chemical bonds to the fabric and, as such, is applicable to a wide variety of fabric types.

Additional details concerning this subject and the general area of block and graft copolymers may be found in an excellent report by Ceresa.³²

3.6 Selected Review of Coated Fabrics Technology³³ and Selected Synthetic Hydrophilic Polymers

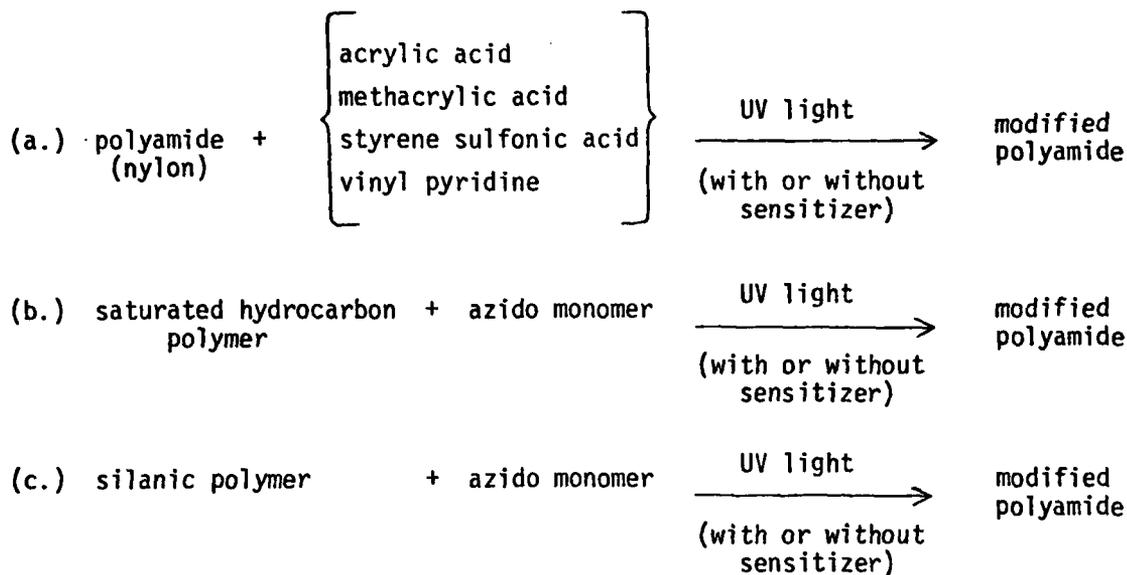
The term "coated fabrics" was originally applied to linseed oil, rubber, or pyroxylin coatings to woven textile support webs; however, recent developments have extended the definition to include plastic coatings on nonwoven textile substrates as well as to laminations with plastic. Further extension of the definition includes woven and

³²Encyclopedia of Polymer Science and Technology. Plastics, Resins, Rubbers, Fibers, Vol. 9, Interscience, New York, NY, pp. 485-528.

³³Ref. 32, Vol. 6, pp. 467-489.

1. Direct Photochemical Modification

Examples:



2. Direct Chemical Modification

Examples:

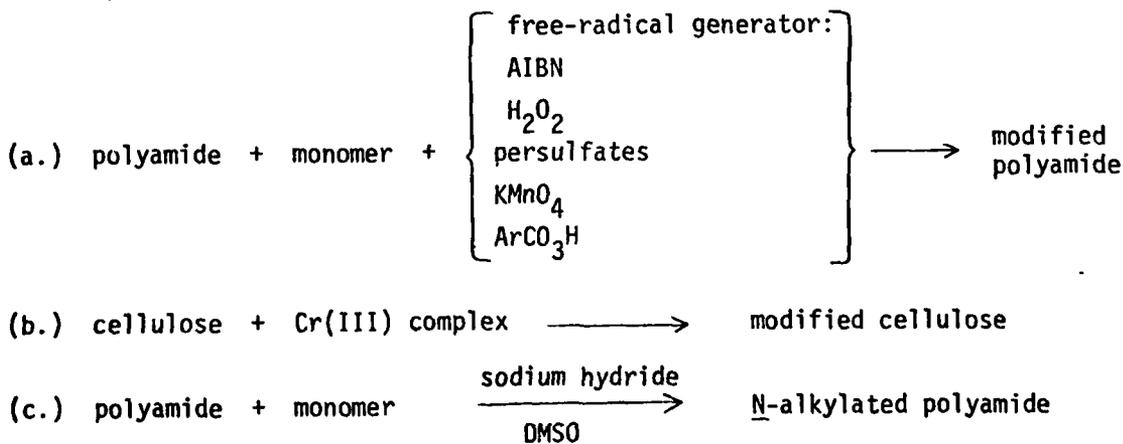
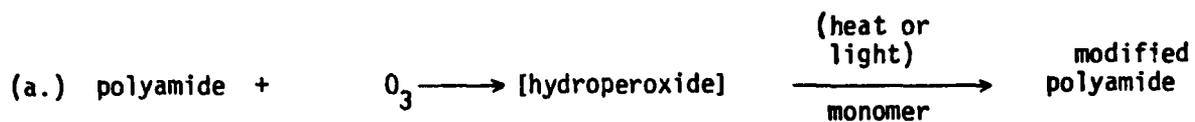


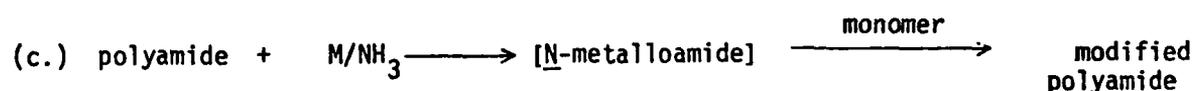
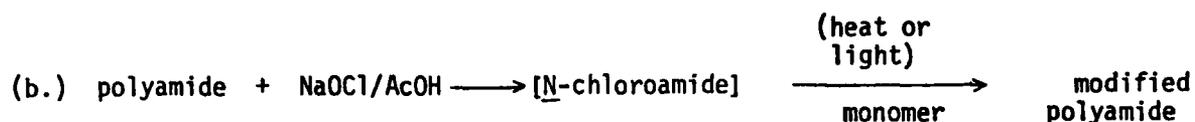
Figure 5. Basic techniques for modification of polymers, fibers, and fabrics.

3. Indirect Photochemical and/or Chemical Modification

Examples:

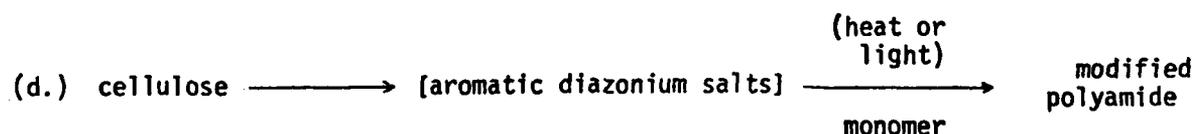


e.g., 2-methyl-4-vinylpyridine
acrylic acid
methyl acrylate



M = Na, K, Li

e.g., ethylene oxide
methyl acrylate



e.g., acrylonitrile
2-methyl-4-vinylpyridine



e.g., CH₂=CHX types

Figure 5. (continued)

(f.) nylon 6,6 + ethylene oxide $\xrightarrow{\text{heat}}$ poly(ethylene glycol)-branched nylon

(g.) "inert" polymer \longrightarrow "activated" polymer or graft co-polymer $\xrightarrow{\text{Cr(III) complex}}$ modified polymers

(h.) cellulose \longrightarrow

Activated Synthons: 6-0-tosylate 2,3-anhydro (epoxide) 3-desoxy-3-amino 3-iododeoxycellulose 5,6-cellulosene (olefin) silyl ethers phosphites
--

 $\xrightarrow{\text{monomer}}$ modified cellulosic polymers

4. Physical Deposition of Insoluble Polymer

fabric + soluble polymer

\downarrow polymer precipitation by
e.g. co-solvent, metal addition, etc.

fabric with polymer coating

\downarrow crosslinking agent

fabric with insoluble crosslinked polymer coating

Figure 5. (continued)

nonwoven textiles with modified properties afforded by surface coating on saturation using thermoset plastic resin compositions. Although cotton fibers are still employed for most applications of coated fabrics, there is a rapidly growing demand for treated textiles of, for example, polyamide fibers for uses requiring maximum tear resistance combined with light weight.

Coating techniques with, for example, vinyl polymers generally involve dispersion of the film-forming (coating) resin in suitable organic solvents followed by introduction of a plasticizer and final fabric treatment by either impregnation or "wet"-coating processes. More recent advances in resin technology have, however, permitted the formation of plastisol coating compositions ordinarily carrying no (or very little) volatile solvents. These compositions are 100% solids dispersions of powdered polymer resin in plasticizer blends which are then used to form a coating paste that is applied to the fabric. Subsequent exposure to a temperature of 350-400°F is usually sufficiently high to permit the resin to form a continuous phase which cools to a coherent "film".

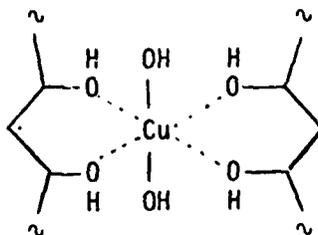
In connection with the particular problem under consideration it should be noted that the use of water-soluble polyesters³⁴ has increased significantly in the area of surface-coatings, partly due to their ease of application. Water-soluble polyesters, which are obtained by incorporating hydrophilic groups in the polymer backbone during polymerization are generally applied in aqueous solution and can be utilized as hydrophilic coatings in treated textile applications. All water-soluble polyesters containing hydroxyl and/or carboxylic acid functionality can be crosslinked to an insoluble state with amino (urea or melamine-formaldehyde), phenolic, epoxy, hydroxyl-containing or isocyanate resins, or with inorganic salts.

Poly(vinyl alcohol)³⁵ or PVA is perhaps of even greater import with regard to formulating design strategies for the ARFGs under consideration. The solubility of PVA in water depends on the degree of hydrolysis of the poly(vinyl acetate) precursor and the molecular weight, with fully hydrolyzed PVAs being soluble only in hot water and partially hydrolyzed PVAs being soluble in water at room temperature. A variety of plasticizers are available for manipulation of PVA coatings, and PVAs are subject to a host of chemical modification reactions characteristic of a secondary hydroxyl group. Notable macromolecular transformations

³⁴Ref. 32, Vol. 10 pp. 383-395.

³⁵Ref. 32, Vol. 14, pp. 149-207.

involve cross linking with many bifunctional compounds and polymer grafting via oxidative coupling. Also of interest is the fact that PVA forms an insoluble copper complex in neutral solution, as pictured below, and also form a molecular compound with sodium hydroxide, which could be thought of as being analogous to crown ether complexes of sodium and other metal ions. This type of interaction may further be related to use of PVA for semipermeable membranes and as a carrier for metal catalysts.³⁶



PVA fiber³⁵ is the most hydrophilic of the synthetic fibers, and when PVA is spun with poly(acrylamide) or acrylic acid-acrylamide copolymers, the resultant hybrid fiber having improved textile qualities is quite resistant to degradation by boiling water, salts, and sea water. The ability to further manipulate composite material containing PVA is also suggested by the fact that PVA filament yarn is moderately stable to diverse reactive chemical agents and can be made to swell on contact with various phenolic-type molecules.

A polyelectrolyte, which is defined as any polymeric substance in which the monomeric units of its constituent macromolecules possess ionizable groups,³⁷ is subcategorized as being either a polyacid, polybase, or polyampholyte, depending upon the nature of its ionization in water solution. The physico-chemical contrasts between such "macroions" and simple electrolytes are striking, with solutions of charged macroions displaying large deviations from thermodynamic ideality, which are in turn very sensitive to the presence of added ions. Polyelectrolyte complexes³⁸ are the result of ionically crosslinking two highly, but oppositely, charged polyelectrolytes. Interestingly, whereas the individual macroions are freely soluble in water, the polyelectrolyte complex undergoes only limited swelling in water and is nevertheless highly permeable to water. The latter phenomenon has been investigated with regard to the development of additives for "increasing moisture breatheability" of plastic sheeting; however, these and related biological applications are in their infancy stage.

³⁶Ref. 32, Vol. 14, p. 180.

³⁷Ref. 32, Vol. 10, pp. 781-861.

³⁸Ref. 32, Vol. 10, pp. 465-780.

Under closely pH-controlled conditions, weak-acid/weak-base polyelectrolytes can be formed, but the most stable polyelectrolyte complexes are made from strong macroions, e.g., poly (sodium styrenesulfonate) and poly(vinylpyridinium chloride). Such complexes rapidly precipitate out of solution and are easily freed of the small ion by-products, e.g., Na^+ and Cl^- . Polyelectrolyte complexes in dry or partially hydrated states are infusible: manipulation into useful forms has therefore been generally accomplished with three-phase solution casting. The minimum water sorbed by a neutral polyelectrolyte complex is ca. ten water molecules per anion/cation pair which implies site-bound hydration.

The extremely high permeability of polyelectrolyte complexes is evident from low-pressure measurements³⁹ which reveal an enhancement factor of ten over reconstituted cellulosic materials and hydroxyethyl methacrylate. Moreover, the ionic charge characteristics, hydrogel structure, and controllable permeabilities to water body fluid solutes have the consequence of imparting polyelectrolyte complexes with excellent biocompatibility toward physiological systems, which in turn has prompted applications investigations in the areas of dialytic membranes, prosthetic materials, and contact lenses.

Although polyamines³⁹ are not usually regarded as representative of a distinct class of compounds, they are, nevertheless, generally formulated as $(-\text{NH}-\text{R}-\text{NH}-\text{R}')_x$ and are described as hydrophilic, polar substances, owing to the multiplicity of nitrogen centers. In acidic or neutral solutions, the nitrogens are charged and under such conditions the polyamines are usually soluble in water. Similar considerations hold for synthetic amide-containing polyamines. A voluminous patent literature exists for polyamines; however, it will only be noted here that polyamines and their N-alkylated derivatives, which are readily synthesized, have been used as bonding agents for cellulosic material and topcoat films, impregnating agents, conductive polymers, and in other situations involving complexation with metal ions.

³⁹Ref. 32, Vol. 10, pp. 616-622.

4. GENERAL STRATEGY CONSIDERATIONS

In summary, our extensive review of the available literature data regarding chemical means of CW agent decontamination and protection has revealed that (a.) molecular fragmentation approaches are unrealistic, (b.) catalytic agent-oxidations may be effective for sulfur mustard but not for G- and V-agents, (c.) organometallic complexes, and especially copper chelates, are hydrolytic catalysts for G-agents in aqueous solution, and (d.) that a variety of organometallic compounds, as impregnates or in organic media, can stoichiometrically "trap" H-, G-, and/or V-agents.

To our knowledge, there is no available information directly related to modifying fibers/fabrics in such a way as to provide them with catalytic reactivity toward the hydrolysis of H-, G-, and/or V-type agents. Hence, the previously stated work objective represents an attempt to provide experimental information that will fill the gap between points (c.) and (d.) noted above.

Within the time and financial constraints of the contract, it was our stated opinion that development of modified fabrics which catalytically hydrolyze agents via ambient fabric-associated water should be the primary objective. Secondary considerations regarding a promising modified fabric, such as mechanistic detail, poisoning of the catalytic effect by sweat and/or hydrolysis by-products, fabric durability, toxicity factors, etc., are obviously important; however, any research along these lines would have required program-scope adjustments.

4.1 Direct Fabric Modification and Catalyst Types

The direct modification of fabric has the desirable advantage of by-passing the need for weaving modified fibers before preliminary testing, and also has practical benefits in the long-run. Given this starting point and the unprecedented nature of the work objective, our fabric modification schemes attempted to build in maximum flexibility with regard to catalyst attachment to fabric and thereby allow for testing a large number of catalyst-fabric combinations. It was reasoned that this approach would provide (at least qualitatively) useful insight regarding catalyst and fabric

structure-activity relationships or "boundary conditions" for this new approach to agent protection. Such an approach avoids situations wherein a given catalyst moiety and fabric combination requires an attachment method that is different from a second catalyst/fabric pair, and so forth, as each combination represents a new set of problems to overcome. To achieve this maximization of scope, we adopted three basic strategies that are utilized in the textile industry, namely, contact or "saturation" modification of fabric, which takes advantage of intermolecular non-bonded attractive forces between fabric and catalyst, fabric grafting with catalyst chelator, which involves covalent bond formation, and physical deposition to produce a catalyst coating.

An additional factor to note here is the assumed dependence of catalyst-promoted agent hydrolysis on fabric-associated water. Textile fabrics have various degrees of "moisture content", dependent primarily on the specific molecular structure(s) involved; however, even the more "hydrophilic" fabrics present only minute quantities of water, relative to aqueous solution situations. We planned to cope with this problem by use of cationic metal reaction sites that can attract and bond both agent and water molecules, as well as induce secondary hydration spheres. Moreover, many of the anticipated catalysts and fabric coatings would involve organic structures having hydrophilic hydroxyl and amino groups, which attract water via H-bonding networks, and can be varied in terms of their proportion to both fiber polymer and metal ion.

4.2 Fabric Selection

After considering a wide structural variety of commercially available textile materials, and especially members of the acrylic, nylon, and polyester classes because of their stability to the planned chemical modifications, it was decided that Nomex (MIL-C-43600B) and a Quarpel-treated nylon-cotton blend (MIL-C3924E) would be worked with.

4.3 Agent-Simulant Selection

Contract specifications dictated that "reactivity evaluations shall be performed using simulants" and that "simulants to be used in the evaluations will be selected by mutual agreement between the Government and the contractor." Consequently, we

initiated an extensive study of this problem regarding agent-simulant selection. It was subsequently recommended and agreed to by the Government that diisopropyl phosphorofluoridate (DFP) was to be used for simulating G-and V-agents, and that 2-chloroethyl methyl sulfide (CMS) was to be used as the simulant for agent H. For unexpected technical reasons, which are discussed in the Methods of Procedure section, CMS was later replaced with the analogous compound 2-chloroethyl isobutyl sulfide (CIS). The rationale for selection of DFP and CMS is given in the following paragraphs.

4.3.1 Theoretical Considerations: The implied purpose of using a simulant within any chemical investigation is to avoid, for whatever reasons, use of the simulated material which is of ultimate interest. In the present contract work concerned with CW agents, simulants are being relied on as a means of by-passing various toxicity problems; consequently, the "best" use of simulants during the development of fabrics having catalytic reactivity toward hydrolysis of H-, G-, and V-agents requires a carefully planned compromise between toxicological factors and hydrolytic reactivity characteristics. Ideally, one would like to use simulants which closely match the agent's hydrolytic behavior but are relatively non-toxic. Our stepwise approach towards deducing such a compromise was as follows.

4.3.2 Survey of Literature Data Directly Related to Potential Simulants for the Agents of Interest: In the 1964-1969 Edgewood Arsenal contract to Grace & Co.,³⁰ which was entitled "Research and Feasibility Studies on Protective Clothing and Decontamination" and which dealt in part with catalytic and non-catalytic reactivity modes toward CW agents, simulants for G- and V-agents included DMMP, DIMP, and TCHP (see Table 1), whereas sulfur mustard (agent H) was studied directly and no other organosulfur compounds were discussed. On the other hand, more recent contract studies⁴⁰ for Edgewood Arsenal by Stanford Research Institute entitled "Oxidation of Sulfur and Amine Model Compounds" utilized dibutyl sulfide (see Table 1) as the simulant for agent H. The journal and textbook⁴¹⁻⁴³ literature (below) were examined.

⁴⁰Contract No. DAAA 15-74-C-0150.

⁴¹T.C. Bruice and S.J. Benkovic in "Bioorganic Mechanisms", Vol. 2, Benjamin, New York, NY, Chapter 6 (1966).

⁴²R.D. O'Brien in "Toxic Phosphorus Esters. Chemistry, Metabolism, and Biological Effects", Academic Press, New York, NY, Chapters 2-4 (1960).

⁴³R.F. Hudson in "Structure and Mechanism in Organo-Phosphorous Chemistry", Academic Press, York, NY (1965).

Table 1. STRUCTURAL COMPARISON OF CW AGENTS AND SIMULANTS REPORTED IN THE LITERATURE

CW Agent	Simulant(s)	Reference(s)
H	$\text{CH}_3(\text{CH}_2)_2\text{S}(\text{CH}_2)_3\text{CH}_3$	40
GB, GD, GA	$(\text{MeO})_2\text{MePO}$, DMMP	30
	$(i\text{-PrO})_2\text{MePO}$, DIMP	30
	$(i\text{-PrO})_2\text{POF}$, DFP	41,42
	$(i\text{-PrO})_2\text{POCl}$, DC1P	41,42
	$(\text{C}_6\text{H}_{11}\text{O})_3\text{PO}$, TCHP	30
VX	(?)	(?)

Information dealing with various aspects of the H-, G-, and V-agents is quite voluminous; however, reports which specifically deal with the selection of simulants for agent hydrolyses were not found by us.

A large number of studies of G- and V-type agent reactivity deal with agent GB (Sarin), and the most frequently encountered agent analog in such work is diisopropyl phosphorofluoridate (DFP, see Table 1). In a comprehensive study of metal chelates as catalysts for hydrolysis of sarin and DFP, it was concluded by Courtney, *et al.*,²⁵ that "the results for these (catalysts), together with the results reported by (other investigators), indicate that generalizations made . . . for the catalytic hydrolysis of sarin also apply to DFP, although the latter compound is more slowly hydrolyzed by all the reagents investigated." This very important conclusion parallels the fact that sarin is inherently more reactive than DFP, as is indicated by the following data⁴⁴ for their base-catalyzed hydrolyses:

$$k_{OH}^{\text{sarin}} / k_{OH}^{\text{DFP}} \approx 30$$

The hydrolysis mechanisms for sulfur mustard and its analogs have been thoroughly investigated and two reports are noteworthy. The first is by Williamson, *et al.*,⁴⁵ (Edgewood Arsenal), and deals with the reaction mechanism of aliphatic sulfur mustard analogs ($\text{RSCH}_2\text{CH}_2\text{X}$). By varying the nature of R and X, mustard analogs were obtained with half-lives between 0.2 sec to >5 hr at pH 7.4 and 37°. It was concluded that inductive/polar effects of R and the leaving group ability of X are controlling factors with regard to hydrolysis, while steric effects are of "minor significance."

The second study by Blandamer, *et al.*,⁴⁶ presents kinetic activation parameters for hydrolysis of 2-chloroethyl methyl sulfide ($\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$). It was deduced⁴⁶ that the transition state involves anchimeric assistance by sulfur in an $\text{S}_{\text{N}}1$ -type mechanism, which is the same rate-limiting mechanistic picture generally assumed for sulfur mustard *per se*. The hydrolytic similarity between $\text{CH}_3\text{SCH}_2\text{CH}_2\text{Cl}$ and sulfur mustard is further revealed by their rate constants for reaction with water: we have compared kinetic data reported by Blandamer, *et al.*,⁴⁶ with that of Bartlett and Swain¹³ and estimate that these two compounds react at essentially the same rate in water at pH 7, 25°.

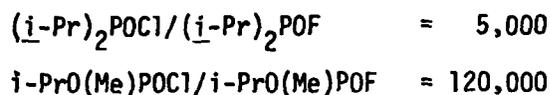
⁴⁴See Table 6-5 in ref. 41.

⁴⁵C.E. Williamson, J.I. Miller, S. Sass, and B. Witten, U.S. Dept. Com., Office Tech. Serv. (AD 611869), Vol. 2, 493 (1966); *Chem Abstr.*, 64, 537 g (1966).

⁴⁶J. Blandamer, H.S. Golinkin, and R. E. Robertson, *J. Am. Chem. Soc.*, 91, 2678 (1969).

4.3.3 Survey of Literature Data Indirectly Related to Potential Simulants for the Agents of Interest: All of the major textbooks devoted either wholly or in large part to organophosphorus chemistry have been reviewed by us from the standpoint of determining those factors which may be of significance with regard to the simulant(s) for G- and V-agents. The following points are noteworthy.

Comparisons of phosphorofluoridate (POF) vs. phosphorochloridate (POCl) reactivity indicate that the chloridate is orders of magnitude more reactive, as shown by the following two representative examples⁴⁷ for such relative rates of hydrolysis:



Steric effects upon the magnitude of second-order rate constants for hydrolysis of both POF and POCl compounds are, in general, less significant than electronic factors. For example, the base-catalyzed hydrolysis of RO(Me)POF decreases by a factor of only ca. 4 in going from R = Me to R = i-Pr.⁴⁴

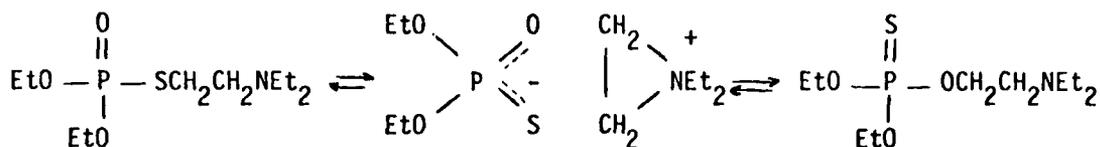
For both POF and POCl systems, the rate of hydrolysis is strongly decelerated upon substituent variation from alkyl, to alkoxy, to dialkylamino^{41,42} and thus serves to explain the above noted slower hydrolysis rate for DFP vs. Srin. These electronic effects are generally dominant and reactivity predictions are usually accurate; however, in this connection, it is interesting that hydrolysis of agent GA (tabun) is considered to be "larger than expected" and is rationalized by "the polarizability of the cyanide group."⁴⁸

Finally, a survey of non-hydrolytic reactions of agent analogs has suggested to us that the following process may be of heretofore unrecognized significance with regard to the details for hydrolysis of agent VX, which has been studied by Epstein and coworkers at Edgewood Arsenal.⁴⁹

⁴⁷See Table 6-4 in ref. 41.

⁴⁸See refs. 59 and 60 cited by Bruice and Benkovic in ref. 41.

⁴⁹J. Epstein, J. J. Callahan, and V. E. Bauer, Phosphorus, 4, 157 (1974).



4.3.4 Simulant Selection and Consideration of Toxicological Safety Factors: Given the fact that relatively safe and easy to handle carboxylic and sulfonic acid chlorides have been previously utilized as agent simulants,⁵⁰ and that hydrolyses of such acid chlorides have been compared⁴¹ to G-agents with regard to steric/electronic effects, it was at first glance a tempting proposition to simply extrapolate these precedents to the present studies. However, in the absence of additional information, we were compelled to reject this approach, as it did not fulfill what we believe to be important criteria for selecting the "best" simulants needed for our best effort. It is our recommendation that the simulants closely match the hydrolytic characteristics of the agents, as opposed to matching of purely physical parameters. The nature of our planned catalytic hydrolyses dictated that steric and (especially) electronic differences between substrates would undoubtedly influence the overall rates of agent reaction and, by the same token, would influence reaction rates with any simulant. From these considerations and an analysis of the information in sections 4.3.2 and 4.3.3 it appeared that it is more reasonable to maintain close structural congruency between simulant and agent rather than strive to achieve an equality of hydrolytic rate constants per se between a simulant and agent of interest. This type of situation has already been noted above in reference to the metal-chelate catalytic hydrolysis studies of Courtney, et al.,²⁵ with sarin and DFP. The fact that DFP is ca. 30-times slower reacting than sarin is a side-issue of little significance. What is more important is the fact that the relative catalyst efficiencies were found to be the same for both compounds. Such parallel (vs. coincident) reactivity patterns imply that what is kinetically true for DFP and a series of catalysts is kinetically true for sarin, except for differences with regard to absolute magnitudes.

DFP is a known cholinesterase inhibitor; however, it is substantially less toxic than sarin, which is in turn regarded as being more potent than either tabun (agent GA) or soman (agent GD).⁵¹ The commercial availability of DFP is also suggestive of its relatively low toxicity. For DFP,⁵¹ LD₅₀ i.v. in monkeys is 0.28 mg/kg.

⁵⁰Dr. Lewis Berkowitz, personal communication.

⁵¹"The Merck Index," 9th Edition, Merck and Co., Rahway, NJ.

The rationale for selecting 2-chloroethyl methyl sulfide (CMS) as a simulant for sulfur mustard is similar to that just discussed; however, in this case the structurally congruous compounds also exhibit nearly identical kinetic behavior. CMS is apparently not considered to be an especially toxic material, and it is commercially available together with a rather wide variety of analogous 2-chloroethyl alkyl/aryl sulfides. At this point one can only speculate as to why these mono 2-chloroethyl-substituted sulfides are less toxic than sulfur mustard (agent H): by recalling the well-known mechanisms for biological alkylations/DNA crosslinking reactions by bis(2-haloethyl) systems, it is obvious that CMS can only function as a mono alkylating agent, and such "one-armed" mustards are generally recognized to be relatively harmless in comparison with their "two-armed" analogs.

5. METHODS OF PROCEDURE

5.1 General

Simulants were commercially obtained as follows: DFP, Aldrich Chemical Co.; CMS, INC/K&K; CIS, Parish Chemical Co. The purity of DFP (95%) and CMS (95%) was established by ¹H NMR and GC. The CIS plurity (97%) was increased (99.7%) by preparative GC before use. GC analysis of the diethyl phthalate to be used for trapping simulant revealed substantial contamination by both low- and high-boiling components. Hence, the following procedure was developed in order to obtain highly purified material that was suitable for GC analyses of the various simulants.

N-(β Aminoethyl-γ -aminopropyltrimethoxysilane [Dow Corning Z-6020] and γ -aminopropyltriethoxysilane [Dow Corning Q1-6011] were purchased through PCR, Inc. Samples of Nomex (MIL-C043600B) and Quarpel treated nylon-cotton blend (MIL-C-3924E) used for fabric modification studies were provided by the Government through the assistance of Dr. Lewis Berkowitz.

Computer-assisted literature searching utilized the on-line "DIALOG" services available from Lockheed Information Systems.

Proton NMR Spectra (60 MHz) were recorded on a Varian EM360-A instrument at ambient probe temperature (25-30°). Normal parameter settings included a 5 ppm (δ) sweep width (continuous-wave), 5 min sweep rate, and minimum filtering. GC analyses were performed with a Varian Model 2100 flame-ionization instrument that was equipped with a Hewlett-Packard 3380 electronic integrator/calculator for automated data processing.

5.2 Preliminary Evaluation of CMS Reactivity by NMR

To gauge the relationships between fabric surface characteristics and the hydrolysis rate of the H-agent simulant (CMS), homogeneous solution studies were carried out by ^1H NMR spectroscopy. The following factors were investigated and clarified (See Table 2):

The effect of "polarity" (dielectric constant). By inspection of the relative ϵ and k values for 30% aqueous acetone, dimethylsulfoxide (DMSO), *N*-methylformamide (NMF), and 50 v/v% DMSO/NMF, it is clear that no simple (obvious) relationship exists between these two physical parameters.

The effect of water content. For experiments with 20-40 v/v% water in DMSO, it was found that the value of k was markedly increased by the addition of water, and that a "leveling-off" of this phenomena is approached, as expected. More importantly, it can be reasonably assumed that the rate acceleration is most pronounced in the low water concentration region that is applicable to fabric surfaces. Note that the rate-enhancement factor of ca. 2 found in 40 versus 30 v/v% aqueous DMSO was also observed in NMF.

The effect of added cationic species. The presence of Na^+ (via NaBPh_4 addition) could be expected by Hard and Soft Acid and Base (HSAB) theory to cause "assisted" chloride ionization and, therefore, a rate acceleration; however, this phenomenon was not substantiated by experiment.

Table 2. HYDROLYSIS DATA FOR H-AGENT SIMULANT, $\text{ClCH}_2\text{CH}_2\text{SCH}_3$ (CMS), at $32 \pm 1^\circ\text{C}$ AS DETERMINED BY ^1H NMR AT 60 MHZ

Solvent ^a	Dielectric Constant, E	v/v% D_2O	Additive	k , min^{-1}
Acetone	21	—	—	—
		0	—	0.0036
DMSO	46	—	—	—
		20	—	"slow"
		20	0.50 eq CuBipy	"slow"
		30	—	0.0347
		30	0.04 eq NaBPh ₄	0.0216 ^b
		40	—	0.0805
NMF	182	—	—	—
		30	—	0.0140
		30	—	0.0135
		40	—	0.0283
DMSO : MNF	?	30	—	0.040 ^c

^aDMSO = dimethylsulfoxide; NMF = N-methylformamide. ^bData point deviations allow for $k = 0.0327$. ^cDue to peak overlap and other complicating factors, data point deviations allow for $k = 0.030$ and $k = 0.062$.

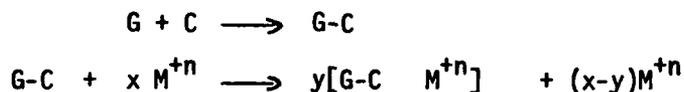
The effect of added CuL₂ species. The presence of a relatively large amount of copper (II)bipyridyl, CuBipy, had no significant influence upon the reaction rate for CMS, even though CuBipy has been reported to be an effective hydrolytic catalyst for DFP and sarin. NMR line-broadening data suggests that CuBipy and CMS undergo sulfur-metal coordination which therefore provides a rationalization for the different reactivity of CMS and DFP toward CuBipy.

The effect of absolute CMS concentration upon its hydrolysis mechanism. At relatively high concentrations of CMS the postulated thiiranium ion intermediate undergoes competitive reactions with water and CMS. Future investigations with regard to mechanistic detail, kinetics, and/or determination of hydrolysis product identity must anticipate complications due to these pathways.

The salient implication of these findings is the critical need to achieve relatively high-levels of fabric moisture content in order to achieve reasonable rates of CMS hydrolysis.

5.3 Development of Quantitative Assay Procedures for Determination of Metal Ion Loading onto Chelating Fabrics

A major goal of this project was to attach certain chelating agents to fabric and thereby provide a means of obtaining novel materials which have metal ion catalysts bonded to their surface. The overall concept may be represented by the following equations, wherein G is an unspecified functional group on the fabric surface, C is the chelating moiety, and M⁺ⁿ is a metal ion of interest.



The prototype chelating agent selected for developng this general type of modification was N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane [Dow Corning Z-6020], (MeO)₃Si(CH₂)₃NHCH₂CH₂NH₂, and the metal ions of initial concern were Cu⁺² and Fe⁺³.

5.3.1 Method A for Cu⁺²: Quantitative analysis of the extent of Cu⁺² chelation obtained for a given fabric treatment procedure utilized an indirect method wherein a specific amount of treated fabric G-C was allowed to come into contact with a known amount of copper ion, x, and the residual amount of free copper ion, x-y, was then determined by UV-visible spectroscopic analysis. Preliminary experiments with CuSO₄ solutions over the range of 700-850 nm revealed that the extinction coefficient for aquated Cu⁺² was too low to allow for reliable measurements in the concentration range of interest. To overcome this problem, aliquots of a solution which contained free Cu⁺² were treated with an excess of bipyridyl (Bipy) in order to form the (Bipy)₂Cu⁺² complex, which exhibits a more intense and blue-shifted absorption relative to Cu⁺² alone. In this manner it was established that Cu⁺² concentrations as low as ca. 1 x 10⁻⁴M gave significant absorbance readings ($A \approx 0.010 \pm 0.002$).

The general analytical methodology used to measure Cu⁺² chelating capacity of a treated fabric was as follows:

1. A 9 in x 9 in square of treated fabric was cut into nine 1 in x 1 in squares, which were then placed in a 50-ml Erlenmeyer flask equipped with a 1/2 in magnetic stirring bar.
2. A 50-ml portion of de-ionized water was volumetrically added and the fabric pieces were allowed time to "wet", as determined by visual inspection.
3. A 1-ml aliquot of 0.04 M CuSO₄ solution was added and, after ca. 5 min of stirring time to allow for chelation, a 1-ml aliquot of the resultant solution was removed and was added to a 1-cm cuvette.
4. 2-ml of ca. 0.01 M Bipy was added to the cuvette and, after thorough mixing, the absorbance value (A) was read in triplicate at 675 nm.
5. In the absence of a chelating agent, the Cu⁺² concentration was 0.27 mM and the corresponding absorbance reading (A₀) is 0.022 ± 0.002; hence, the extent of chelation for a given test fabric with absorbance A may be represented by the equation shown below.

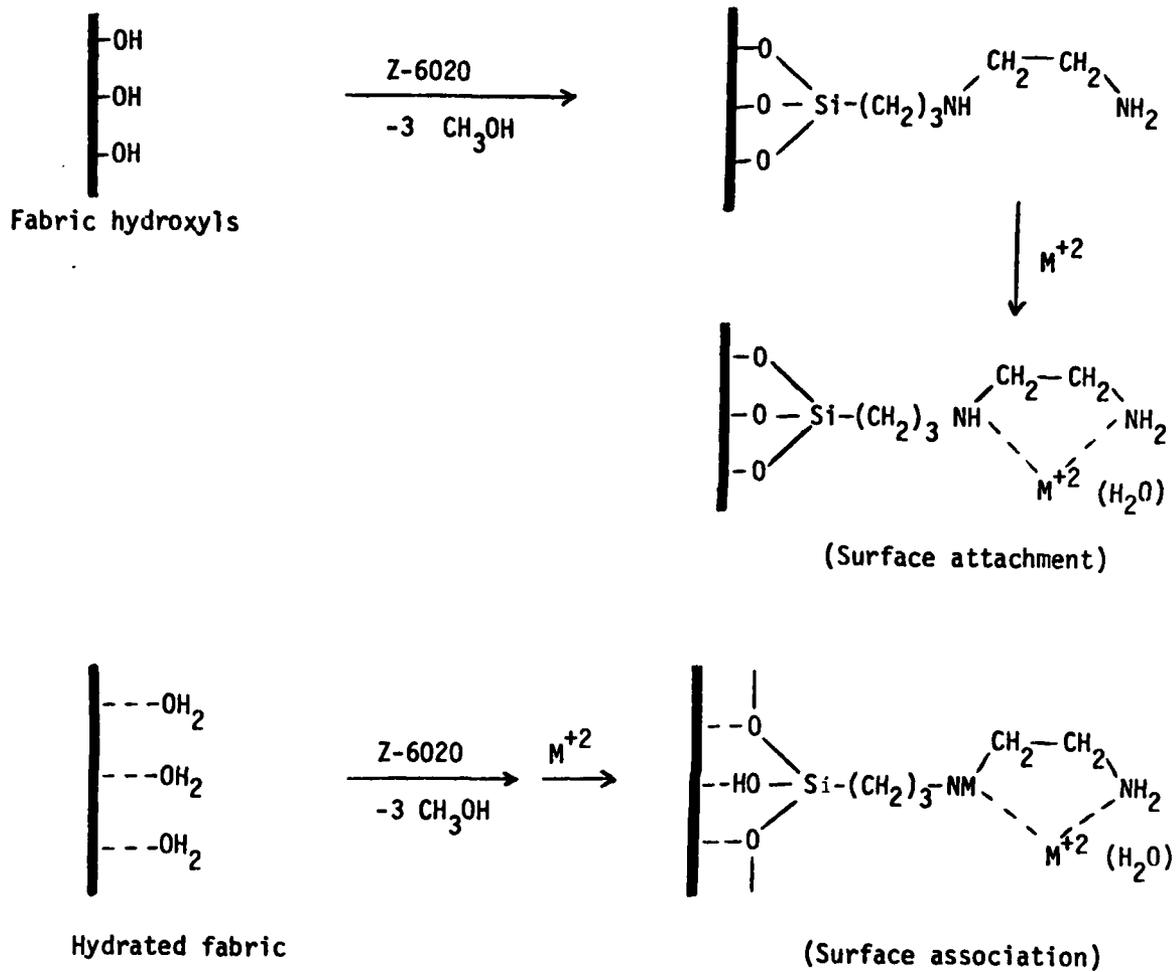


Figure 6. Schematic illustration of Z-6020 bonding to fabric surfaces by either covalent attachment and/or non-covalent associative interactions.

In addition to the development of suitable analytical techniques for measurement of bound metal ions such as Cu^{+2} and Fe^{+3} (see Section 5.3), it was necessary to explore a variety of procedures for attachment/association of this new chelating silane that has not, to our knowledge, been previously bonded to fabrics.

The results of initial investigations with the Quarpel-treated nylon-cotton blend suggested that Z-6020 bonding to surface hydroxyl groups of cotton was not easily accomplished using Z-6020 solutions. For example, the following procedures when applied to 9 in x 9 in fabric samples did not afford Cu^{+2} loading levels significantly different from untreated fabric itself (0.02 mmol $\text{Cu}^{+2}/81 \text{ in}^2$).

Procedure 1: Compressed-air spray application of a solution of 0.5 ml of Z-6020 in 50 ml of MeOH; 24 hr curing at 80° ; de-ionized water wash (twice); 4 hr drying at 80° .

Procedure 2: Stirring of fabric in 500 ml of water (de-ionized) containing 1.0 g (1.08 ml) of Z-6020 at room temperature for 20 hr; water wash (twice).

Procedure 3: Stirring of fabric in 500 ml of water containing 4 g of Z-6020 at 60° for 4 hr; water wash (twice) with manual scrubbing to remove surface-associated polymer.

Procedure 4: Same as Procedure 3 except for a 40 hr heating period.

To possibly overcome this problem "activation" of the fabric surface by either acid, base, or oxidation was studied by carrying out the following experiments which also included an attempt to use hydrolyzed protein as a novel "coupling" agent.

Procedure 5: 9 in x 9 in cotton blend, 1 hr in 1 N NaOH at 25° , H_2O wash, 40 hr in 25° solution of Z-6020 (5 ml) in H_2O (500 ml). The standard Cu^{+2} Bipy chelation test with a 3 in x 3 in air-dried test piece indicated no increase in Cu^{+2} uptake.

Procedure 6: 9 in x 9 in cotton blend, 10 min in conc HCl at 25° , H_2O wash. Evidence for extensive polymer degradation with excessive loss of fabric quality; Z-6020 treatment not pursued with this sample.

Procedure 7: 9 in x 9 in cotton blend, 18 hr at 80° with slurry of hydrolyzed protein (5 g) in H₂O (50 ml). The resultant brittle coating mitigated against Z-6020 adhesion.

Procedure 8: 9 in x 9 in Nomex, 15 hr at 25° with Fenton oxidizing mixture consisting of 1 mmol FeSO₄, 2 mmol EDTA · 2Na, and 6 mmol H₂O₂ in H₂O (750 ml). Wash with H₂O, air-dry, saturate with neat Z-6020 fluid, air-dry, "cure" at 60° for 72 hr. Cu⁺² Bipy chelation test of a 3 in x 3 in piece of this sample, after 18 hr H₂O wash, indicated metal ion uptake. To confirm this finding, another 3 in x 3 in portion of this treated material was stirred in 200 ml of 0.05 M CuSO₄ and after 1.5 hr the initially green fabric had turned deep blue in color, which persisted after two washings in H₂O. This was the first observation of the chelation of Cu⁺² by a surface-attached chelating agent.

Following this successful modification of "oxidatively activated" Nomex with neat Z-6020 (as opposed to solutions of Z-6020), a continued search was made using the undiluted Z-6020 fluid as well as the undiluted Q2-6011 analog, (EtO)₃Si(CH₂NHCH₂CH₂N₂). In general, a 9 in x 9 in piece of regular or "pre-treated" fabric was saturated with the silane fluid and then allowed to air dry for 12-15 hr before "curing" at 60° for 72 hr. The material was thoroughly washed with water (de-ionized) for 12 hr, soaked in 0.05 M Cu⁺² solutions for 1 hr, and finally washed to remove excess (non-chelated) copper ion. The following conclusions were drawn from the results summarized in Table 3.

(a.) Untreated cotton blend and untreated Nomex can be directly modified by bonding with Z-6020 through available functional groups and/or water on the fabric surface; however, the Nomex material affords ca. 14% lower loading than cotton (0.63 vs. 0.54 mmol Cu⁺²/g fabric, respectively).

(b.) "Clorox" (5% aqueous NaOCl) causes "activation" of Nomex fabric, as a ca. 22% increase in Z-6020/Cu⁺² chelation is achieved, relative to untreated Nomex (0.66 vs. 0.54 mmol Cu⁺²/g fabric).

Table 3. SELECTED LISTING OF FABRIC MODIFICATIONS WITH Z-6020
AND Q1-6011 SILANE CHELATING FLUIDS

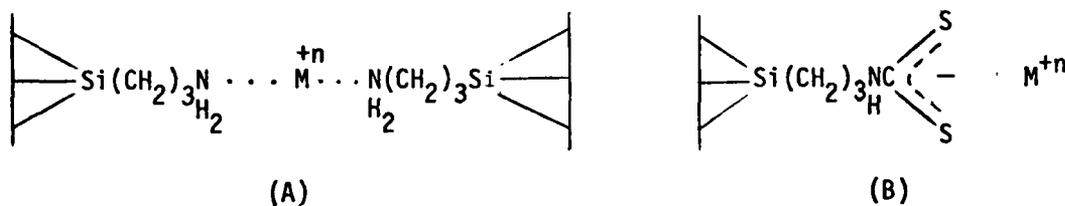
ARC ID No.	Treatment Summary ^a	Analytical Results for Cu ⁺² Uptake ^b
GZ-79-41	Nomex/Z-6020/CuSO ₄	0.54 mmol Cu ⁺² /g fabric
GZ-79-45Cu	Cotton/Z-6020/CuSO ₄	0.63 mmol Cu ⁺² /g fabric
GZ-79-41A	Nomex/Fenton Oxidation/ Z-6020/CuSO ₄	1.71 mmol Cu ⁺² /g fabric
GZ-79-43-NCu	Nomex/Clorox Oxidation/ Z-6020/CuSO ₄	0.66 mmol Cu ⁺² /g fabric
GZ-79-45XCu	Cotton/MeOH Extraction/ Z-6020/CuSO ₄	0.75 mmol Cu ⁺² /g fabric
GZ-79-41	Nomex/Z-6020/CuSO ₄	0.54 mmol Cu ⁺² /g fabric
GZ-79-45Cu	Cotton/Z-6020/CuSO ₄	0.63 mmol Cu ⁺² /g fabric
GZ-79-41A	Nomex/Fenton Oxidation/ Z-6020/CuSO ₄	1.71 mmol Cu ⁺² /g fabric
GZ-79-43-NCu	Nomex/Clorox Oxidation/	0.66 mmol Cu ⁺² / fabric
GZ-79-45XCu	Cotton/MeOH Extraction/	0.75 mmol Cu ⁺² / fabric

^aSee text discussion for more detailed procedure. ^bBipy chelation method.

(c.) Methanol extraction of cotton blend (removal of Quarpel finishing) also "activates" the fabric, relative to untreated material, as a ca. 19% increase in Z-6020 loading was measured (0.75 vs. 0.63 mmol Cu⁺²/g fabric).

(d.) Treatment of Nomex with a Fenton's oxidation mixture of FeSO₄, H₂O₂, and EDTA provided the greatest degree of fabric "activation", as evidence by a ca. 220% increase in Cu⁺² uptake relative to untreated Nomex (1.71 vs. 0.54 mmol CU⁺²/g fabric).

(e.) In principle, γ -aminopropyltriethoxysilane (Q1-6011) can serve as either an interstrand cross-linking agent (A) or an entry, via CS₂, to dithiocarbamates (B) for bidentate chelation with a wide variety of metal ions. However, coupling conditions which hold for the analogous Z-6020 fluid were found to be ineffective with Q1-6011.



This somewhat unexpected difference in reactivity may be tentatively ascribed to greater steric "bulk" about silicon in (EtO)₃Si vs. (MeO)₃Si, which hinders attachment by nucleophilic groups from the fabric surface and/or water. Acid or base catalysis suggests itself as a logical approach to by-passing this problem.

At this stage of development regarding fabric treatment with Z-6020, two important observations were noted: (a.) the Z-6020 silane was not incorporated onto fabric when a solvent was used, and (b.) while direct application of Z-6020 to fabric was successful, there was some question as to the bonding mode, i.e. were there fabric/Z-6020 covalent bonds and/or interpenetration of polymerized Z-6020 and fabric polymer. A series of experiments were subsequently undertaken to determine whether the Z-6020 could be applied in reasonable quantity using a solvent system (thereby favoring the stronger mode of covalent attachment to fabric), and secondly whether exposure to moisture had a significant effect upon the extent of Z-6020 attachment.

In each experiment a 4.5 in x 4.5 in square of cotton-blend which had been thoroughly extracted with methanol using a Soxhlet apparatus, was treated with Z-6020 fluid in the quantity and manner specified in Table 4. An additional sample (ES-79A-31A) was prepared by mounting the fabric on a holder-frame, wetting with 80% aqueous ethanol, and then coating with Z-6020 fluid. A 2 in x 2 in square of each fabric was eventually exposed to CuSO_4 solution for 24 hr and was then thoroughly washed in water (de-ionized), air-dried, and finally analyzed for Cu^{+2} content.

The collective data in Table 4 support the conclusions that (a.) metal-ion incorporation into Z-6020 modified fabric is maximized by modification of dry fabric with the Z-6020 fluid, and that (b.) the presence of water during any stage of the fabric modification with Z-6020 leads to increased Cu^{+2} uptake.

The aforementioned discovery that $\text{FeSO}_4\text{-H}_2\text{O}_2$ (Fenton Reagent) treatment of fabrics leads to increased Z-6020 attachment and subsequent Cu^{+2} uptake deserved further investigation. The procedure outlined for GZ-79-41A (see Table 3) was applied to 9 in x 9 in squares of Nomex and cotton blend, and a second set of material was treated with twice the amount of oxidizing reagents to determine if increased metal ion uptake would result. It was also of interest to check if the 12 hr water wash before metal ion uptake could be eliminated to save time and possibly result in greater metal ion loading.

Finally, Z-6020 metal ion modification of bulk cotton having greater surface area was of interest with regard to multi-layer fabric strategies.

From the results summarized in Table 5, the following conclusions were inferred:

(a.) Increasing the relative molar amount of Fenton oxidizing reagents by a factor of 2.0 increased the extent of Cu^{+2} uptake by cotton blend by a factor of 1.6, which is consistent with that expected from the introduction of increased numbers of functional groups. However, the extent of Fe^{+3} pick-up was unchanged which implicates a dependence of metal ion loading upon the ion's formal oxidation state. In view of the somewhat rigid nature of the fabric-attached chelation matrix, and geometrical considerations for ligand coordination to Cu^{+2} vs. Fe^{+3} , these findings seem reasonable.

Table 4. PROCEDURES FOR OPTIMIZATION OF FABRIC MODIFICATION WITH Z-6020 CHELATING FLUID

ARC ID No.	Z-6020 (ml)	Solvent (ml)	Reaction Temperature	Time (hr)	Cu ⁺² w/w%	Content ^a mmol/g
ES-79A-20A ^b	10	pyr (200)	reflux	1	0.39	0.06
ES-79A-29B ^b	10	pyr (200) H ₂ O (2)	reflux	1	1.00	0.16
ES-79-29C ^c	10	DMF (100)	25°C	24	0.84	0.13
ES-79-29D ^c	10	<u>n</u> -BuQH (100)	reflux	1	0.78	0.12
ES-79-29E ^d	10	DMF (100) Et ₃ N (10)	25°C	18	1.70	0.26
ES-79-31B ^c	10	DMF (100) Et ₃ N (10)	25°C	48	0.80	0.12
ES-79-31A	----- (see text) -----				1.00	0.16

^aDetermined by the EDTA method. ^bDried under vacuum (1 torr) for 30 min at 60°.

^cDried in air for 2 hr at 70°. ^dDried 1 hr in air at 100% relative humidity and then as in footnote c.

Table 5. SELECTED LISTING OF FABRIC MODIFICATIONS WITH Z-6020 SILANE CHELATING FLUID

ARC ID No.	Treatment Summary	M ⁺ⁿ Uptake ^a	
GZ-79-41A	Nomex/Fenton Oxidation/ Z-6020/wash/ML _n	1.71 mmol Cu ⁺² /g	—
VLB-79-32A	Nomex/Fenton Oxidation/ Z-6020/wash/ML _n	0.85 mmol Cu ⁺² /g	0.096 mmol Fe ⁺³ /g
VLB-79-32A'	Nomex/Fenton Oxidation/ Z-6020/ <u>no</u> wash/ML _n	0.81 mmol Cu ⁺² /g	0.286 mmol Fe ⁺³ /g
VLB-79-32B	Nomex/2-fold Fenton Oxidation/Z-6020/wash/ ML _n	0.54 mmol Cu ⁺² /g	0.028 mmol Fe ⁺³ /g
VBL-79-32B'	Nomex/2-fold Fenton Oxidation/Z-6020/ <u>no</u> wash/ ML _n	1.52 mmol Cu ⁺² /g	0.300 mmol Fe ⁺³ /g
VLB-79-32C	Cotton blend/Fenton Oxidation/Z-6020/ wash/ML _n	0.52 mmol Cu ⁺² /g	0.105 mmol Fe ⁺³ /g
VBL-79-32D	Cotton blend/2-fold Fenton Oxidation/ Z-6020/wash/ML _n	0.83 mmol Cu ⁺² /g	0.091 mmol Fe ⁺³ /g

Table 5. (continued)

GZ-79-41A	Nomex/Fenton Oxidation/ Z-6020/wash/ML _n	1.71 mmol Cu ⁺² /g	—
VLB-79-32A	Nomex/Fenton Oxidation/ Z-6020/wash/ML _n	0.85 mmol Cu ⁺² /g	0.096 mmol Fe ⁺³ /g
VLB-79-32A'	Nomex/Fenton Oxidation/ Z-6020/ <u>no</u> wash/ML _n	0.81 mmol Cu ⁺² /g	0.286 mmol Fe ⁺³ /g
VLB-79-32B	Nomex/2-fold Fenton Oxidation/Z-6020/wash/ ML _n	0.54 mmol Cu ⁺² /g	0.028 mmol Fe ⁺³ /g
VLB-79-32B'	Nomex/2-fold Fenton Oxidation/Z-6020/ <u>no</u> wash/ ML _n	1.52 mmol Cu ⁺² /g	0.300 mmol Fe ⁺³ /g
VLB-79-C	Cotton blend/Fenton Oxidation/Z-6020/ wash/ML _n	0.52 mmol Cu ⁺² /g	0.105 mmol Fe ⁺³ /g
VLB-79-32D	Cotton blend/2-fold Fenton Oxidation/ Z-6020/wash/ML _n	0.83 mmol Cu ⁺² /g	0.091 mmol Fe ⁺³ /g
GZ-79-45 Cu	Cotton blend/Z-6020/ wash/ML _n	0.63 mmol Cu ⁺² /g	—
VBL	Bulk cotton/Z-6020/ wash/ML _n	0.19 mmol Cu ⁺² /g	0.017 mmol Fe ⁺³ /g
VLB	Bulk cotton/Z-6020/ <u>no</u> wash/ML _n	0.19 mmol Cu ⁺² /g	0.528 mmol Fe ⁺³ /g

^aDetermined by the EDTA (for Cu⁺²) and o-phenanthroline (for Fe⁺³) Analytical methods.

(b.) The Nomex fabric does not respond in the manner outlined in point (a.), as the extent of either Cu^{+2} or Fe^{+3} uptake actually decreased. This may be due to fabric degradation ("over oxidation"); however, more work is needed to substantiate this hypothesis.

(c.) Reproducibility between individual experiments is not good, as evidenced by "identically" prepared fabrics GZ-79-41A and VLB-79-32A which gave 1.71 vs. 0.85 mmol Cu^{+2} /g fabric, respectively.

(d.) In the majority of cases (3 of 4), omitting the water wash between Z-6020 coating and metal ion treatment resulted in significantly increased metal ion loading capacities, viz.. 300-1000% improvement.

(e.) Somewhat suprisingly, on a normalized weight basis, Z-6020 treatment of cotton blend fabric was more effective than treatment of bulk cotton: 0.63 vs. 0.19 mmol Cu^{+2} /g sample. We offer no explanation for this result, which nevertheless militates against further research with the later material.

As a final refinement to the attachment of silane chelating agents to fabric, the incorporation of 2-cyanoethyltriethoxysilane, $\text{Et}_3\text{OSiCH}_2\text{CH}_2\text{CN}$, was studied from the viewpoint of increased hydrophilicity. An abbreviated procedure for silane treatment is as follows.

Solutions of Z-6020 and, where applicable, 2-cyanoethyltriethoxysilane, were prepared in DMF. This mixture is applied to methanol-extracted cotton-blend; excess solution was blotted off the fabric and the material was hung to "cure" in a -100% relative humidity atmosphere at room temperature for 24 hr. The fabric was then dried in an oven at 60° for 3 to 6 hr. Portions of each fabric sample were treated with CuSO_4 solution (saturated 10% aqueous ethanol) and after thorough rinsing, the samples were dried at room temperature before Cu^{+2} analysis by the o-phenanthroline method.

$$\% \text{ chelation} = \frac{A_0 - A}{A_0} \times 100 = \frac{0.022 - A}{0.022} \times 100$$

5.3.2 Method B for Cu⁺²: While the aforementioned method for Cu⁺² determination was satisfactory, modifications were sought to provide improvements. A procedure utilizing the disodium salt of ethylenediaminetetracetic acid (EDTA) was subsequently devised. Thus, the copper-containing fabric sample was treated with 10 ml of 0.1 M EDTA disodium salt for 1 hr in an ultrasonic cleaner, and the absorbance of the resultant blue solution was then measured at 720 nm. Comparison of this A-value with a Beer's Law plot obtained with solutions of known Cu⁺² concentration allowed for determination of the concentration of Cu⁺² in the sample of interest. The standard solutions which were prepared from CuCl₂ · 2H₂O exhibited a linear Beer's Law plot over the range of 1.0 to 10.0 mM Cu⁺².

5.3.3 Determination of Fe⁺³: Iron content in tested fabric was spectrophotometrically established by complexation (as Fe⁺²) with o-phenanthroline according to the procedure of Fortune and Mellon.⁵³

5.4 Preparation of Chemically Modified Fabrics

5.4.1 Modification with Silane Compounds

As pictured in Figure 5, reaction of a fabric with Z-6020 can produce either a surface-attached bidentate chelating functionality for subsequent attachment of transition metal ions, as potential agent-catalysts, or it can produce a surface-associated polymer network of this chelating ethylenediamine derivative. The versatility of this strategy, which allows for evaluation of numerous metal ions and quaternization for anionic catalyst bonding, led to a considerable amount of work aimed at obtaining such fabric-attached/associated catalysts.

⁵³ Fortune and Mellon Industrial and Engineering Chemicals, 10, 60 (1938).

Unlike fabrics prepared by coating with the neat Z-6020 silane, which had rough, hard, and stringy surfaces, these mixed-silane fabrics are generally smooth and only slightly more stiff than the untreated material. In the one case (ES-79A-41A) where a second coat was applied, the rough surface was obtained. A summary of the pertinent data regarding these fabrics is given in Table 6, and samples 55A, 55A-Cu, 55B, and 55B-Cu were transmitted to Dr. Lewis Berkowitz on 19 April 1979 for preliminary testing. Results of these tests are not available at this time.

The final studies of this mixed-silane fabric treatment were concerned with refinements in both silane composition and analytical methodology for measurement of the extent of Z-6020 attachment. Solutions of Z-6020 and various amounts of $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CN}$ in DMF were liberally applied to methanol-extracted cotton-blend, and excess solution was removed by blotting. The fabrics were air dried at 100% relative humidity at room temperature for 24 hr and were then cured at 60° for 3 hr. Sections of the resultant modified fabric were suspended in 0.5 N sodium chloride solution and were then titrated with 0.102 N HCl to a pH of 2 and then back-titrated with 0.0988 N NaOH. The titration curves displayed a small hysteresis, giving a slightly higher value of functionality calculated from the back titration than for the acid titration. Data for preparation and analysis of these fabrics is given in Table 7 and capacities achieved are graphically shown in Figure 7. From Figure 7 it is apparent that relatively high-levels of amino group incorporation may be achieved with neat Z-6020 (ca. 1.6 meq/g) and that the extent of this functionalization decreases smoothly as the relative proportion of $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CN}$ is increased. It is interesting to note that extrapolation of the curve in Figure 7 indicates ca. 0.2 meq/g of amino functionality at 0% Z-6020. Since one would have expected this extrapolation to pass through the origin (i.e., 0 meq/g at 0% Z-6020), our findings suggest that either the cyano silane treatment affords some reduced functionality, such as $\text{SiCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$, or that titratable moieties in the fabric itself are measured together with the amino groups, from the Z-6020.

5.4.2 Modification with Quaternary Ammonium Groups

Attachment of quaternary ammonium functionalities onto fabric surface was desired in order to bind anionic transition metal oxides, which have been reported to be agent hydrolysis catalysts. In addition, these charged groups could also provide for

Table 6. SELECTED LISTING OF MIXED-SILANE TREATED COTTON FABRIC

ARC ID No.	Size	DMF(ml)	Z-6020(ml)	(EtO) ₃ SiCH ₂ CH ₂ CN(ml)	Cu ⁺² Analysis ^a (mole/g)
ES-79A-41A (2 coatings)	4" x 4"	10	3	10	8.93 x 10 ⁻⁴
ES-79A-41B	4" x 4"	10	3	10	3.10 x 10 ⁻⁴
ES-79A-55A	9" x 9"	10	3	10	4.27 x 10 ⁻⁴
ES-79A-55B	9" x 9"	10	10	—	6.64 x 10 ⁻⁴

^aDetermined by the O-phenanthroline analytical method.

Table 7. DATA FOR AMINO GROUP INCORPORATION ONTO METHANOL-EXTRACTED COTTON-BLEND USING MIXTURES OF Z-6020 AND 2-CYANOETHYLTRIE-THOXSILANE

Reactants ^a (ml)			Capacity ^b (meq/g)		
A	B	%A	Acid	Base	Avg
10	0	100	1.55	1.67	1.61
5	5	50	0.66	0.75	0.70
3	7	30	0.49	0.55	0.52
2	8	20	0.35	0.43	0.39
1	9	10	0.22	0.39	0.30

^aA = Z-6020, $[H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3]$; B = 2-cyanoethyltriethoxysilane, $(EtO)_3SiCH_2CH_2CN$. ^bAmine content of fabric; "Acid" indicates values obtained by titration with HCl, whereas "Base" indicates values obtained by titration of the acidified fabric with NaOH.

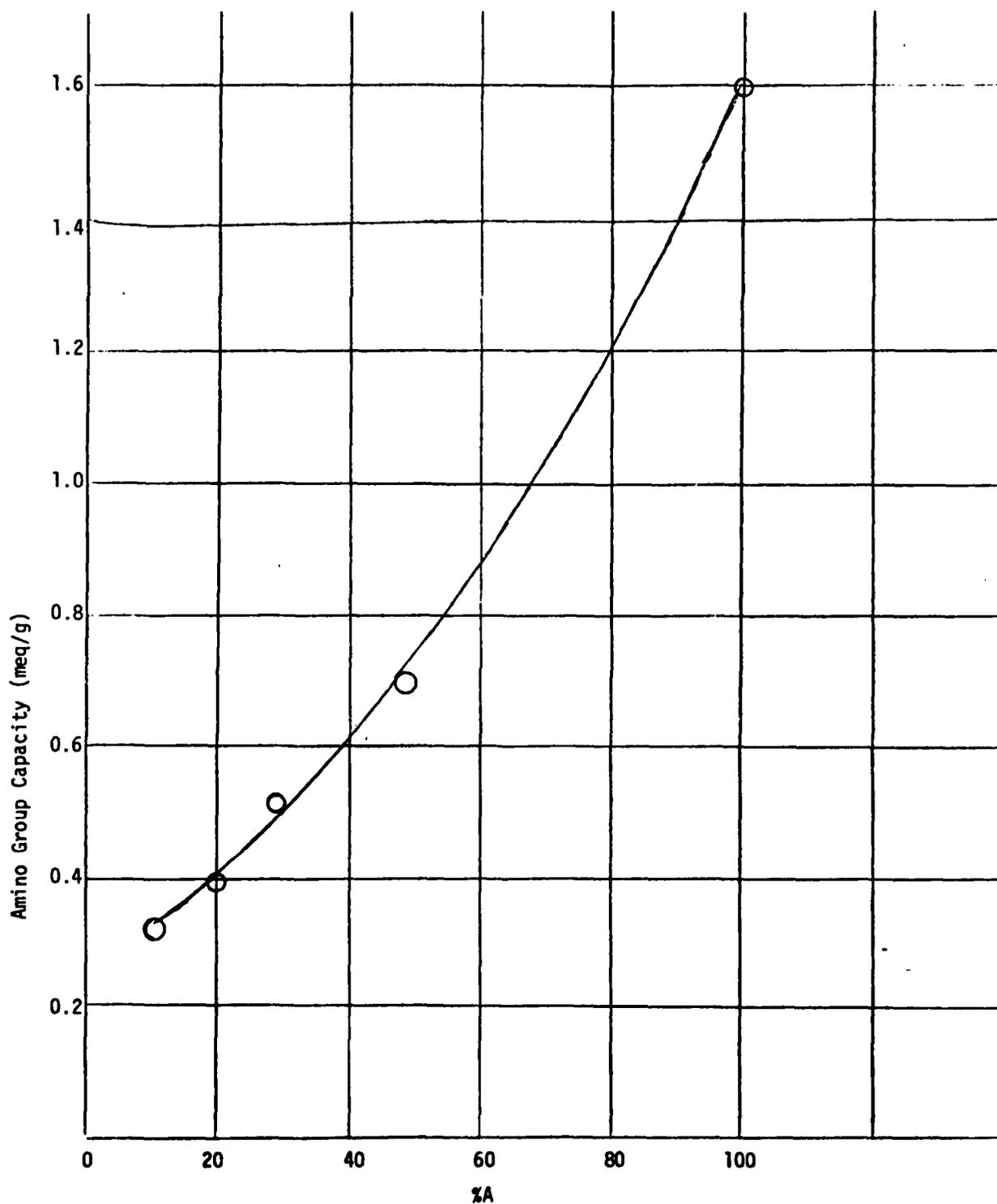


Figure 7. Plot of amino group capacity (meq/g) achieved by treatment of methanol-extracted cotton-blend with mixtures of Z-6020 (A) and $(\text{EtO})_3\text{SiCH}_2\text{CH}_2\text{CN}$ (B)

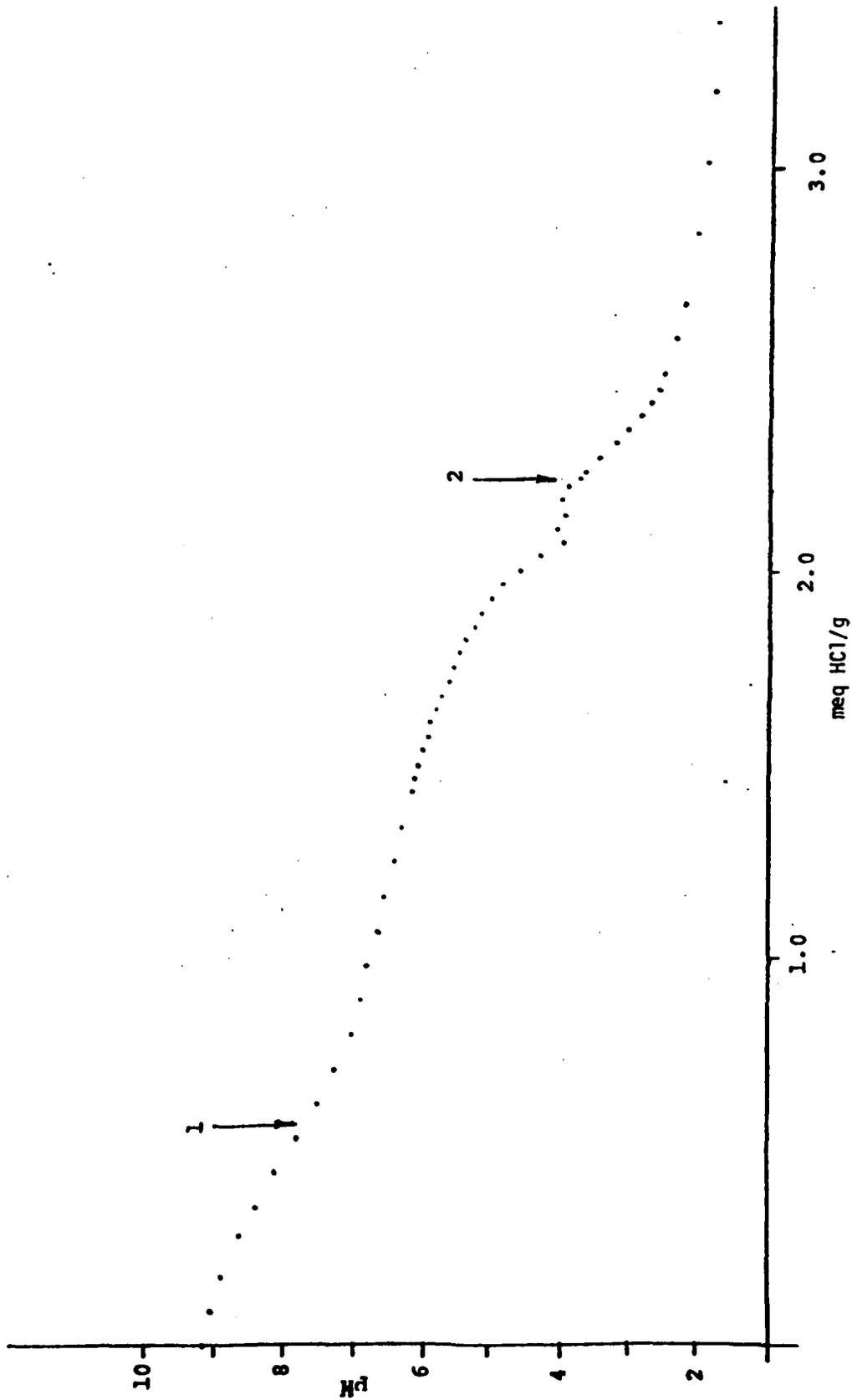


Figure 8. Titration curve for quaternized fabric sample ES-79A-51B using 0.1 N HCl.

Fabric ES-79A-89: Two 9 in x 9 in sections of the cotton blend fabric were stirred in 20% aqueous NaOH for 1 hr. A solution of 2-chloroethyldiethylamine (40 g, 0.23 mol) in 100 ml of water was prepared and one-third of the solution was added to the fabric at 0° and the mixture was then heated to 80°. The remainder of the amine hydrochloride solution was then added in approximately equal portions at 15 min intervals and the fabric was maintained at 80° for a total of 2 hr. Workup utilized sequential 2 M NaOH, 1 M NaOH, and water washes followed by air drying.

Fabric ES-79A-96: Two 9 in x 9 in sections of cotton-blend were dried under vacuum at 80° for 24 hr. These samples were then introduced into a solution of 0.15 mol potassium t-butoxide (prepared from 6 g of potassium metal) in 500 ml of t-butanol, and the mixture was maintained at room temperature under N₂ atmosphere for 3 hr. A solution of 2-chloroethyldiethylamine (0.17 mol) in ether (100 ml) was added and the mixture stood for 24 hr with occasional stirring. A white precipitate formed and there was no evidence of amine odor. The fabric was washed with water and was then air dried.

Fabric ES-79A-106A: A 4 in x 4 in section of cotton-blend fabric was repeatedly coated with an aqueous solution of AgBF₄ (2.0 g) until the solution was expended, and the fabric was then dried under vacuum at 40° for 3 hr. The material was then saturated with a solution of 2-chloroethyldiethylamine (0.058 mole) in 50 ml of ether. The solution was allowed to air-evaporate and the fabric was repeatedly treated in this manner until the solution was expended. The final fabric was allowed to stand for 24 hr and was thoroughly washed with 5% aqueous sodium thiosulfate and water before air drying.

Fabric ES-79A-106B: A 9 in x 9 in section of cotton-blend fabric was coated with an aqueous solution of silver nitrate (10 g) and was then dried as in the case of sample ES-79A-106A. The fabric was further treated with an ether solution containing 2-chloroethyldiethylamine (0.08 mole) and was allowed to stand for 24 hr before washing with 5% aqueous sodium thiosulfate, water, and final air drying.

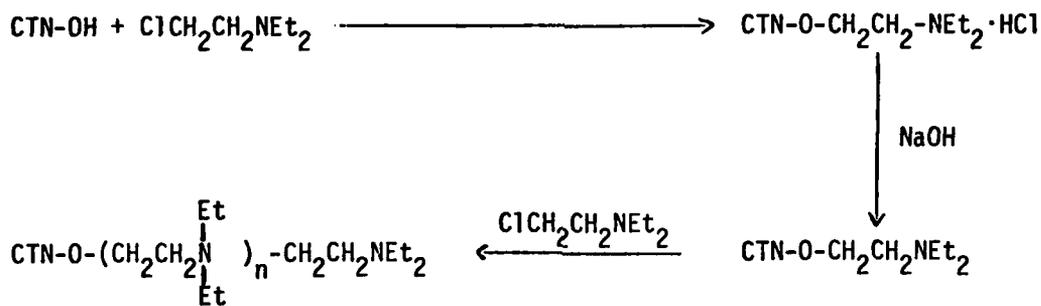
Results: Sections of each DEAE-modified fabric were titrated with 0.102 N HCl and then back titrated with 0.0988 N NaOH. Surprisingly, only fabric sample ES-79A-79 showed significant base capacity. The titration curves for this sample

displayed a substantial hysteresis, with acid titration indicating 0.2 meg/g and base titration indicating 0.4 meg/g. While this loading is comparable to that obtained from either cotton or cellulose,⁵⁴ we had hoped that the level would be appreciably greater (1-5 meg/g). Failure of the procedure employing aqueous DMSO (ES-79A-1) was particularly perplexing since the presence of DMSO greatly improved the solubility of 2-chloroethyldiethylamine in the reaction mixture. Likewise, the reaction in *t*-butyl alcohol (ES-79A-96) proceeded quite smoothly with potassium chloride precipitate forming slowly over a period of several hours. No amine odor was present at the apparent conclusion of this reaction and the fate of the amine is uncertain. In the reactions which employed silver salts, the amine may have formed a stable complex with the silver cation thus preventing the formation of silver chloride and generation of the desired high concentration of aziridinium ion intermediates within the limited confines of the fabric.

In order to improve upon the aforementioned DEAE incorporation technique, further experimentation was carried out with the result being that DEAE-functionalized fabric can now be produced according to a simple method which leads to much higher levels of amino group. The fabric is first treated with 10-25% aqueous NaOH at 0° to - 10° for 1 hr and is then removed, pressed dry, and treated with a 40% aqueous solution of 2-diethylaminochloroethane hydrochloride. The resultant fabric is covered with plastic to prevent evaporation of reagents and water, and is maintained at room temperature for 18-24 hr. Loading may be increased by repetition of the treatment. The best results seem to occur when a very large quantity of amine hydrochloride is used. This probably arises from the hydrochloride neutralizing all of the hydroxide present, thus eliminating this powerful anionic nucleophile from competition for the transient N, N-diethylaziridinium ion intermediate.

While there seems to be no obvious reason why loading could not be increased to higher levels, a noticeable deterioration in the physical properties of the fabric has been noted when loading of about 1.0 to 1.5 meg/g have been achieved. In particular, the fabric shrinks substantially and has a definite tendency to roll-up along the edges when wet. The treatment might best be applied to unwoven yarn and thus avoid some of these problems.

Fabric loadings were again evaluated by 0.1 N HCl titration of hydroxide-equilibrated fabrics and then back-titration with 0.1 N NaOH. The general shape of the titration curve for fabrics with apparent loadings above 1.0 meq/g is that of carbonate-bicarbonate base systems. Presumably, this behavior arises from CO₂ neutralization of the bound hydroxide, and evidence suggests that the fabric is capable of anion exchange. The presumed sequence of reactions leading to the ion exchange capability is outlined below.



Differential DEAE Loading: A 9 in x 9 in section of DMF-extracted cotton blend was treated with 20% aqueous NaOH at 0° for 1 hr. The fabric was removed, blotted dry, and sprayed with 40% aqueous 2-diethylaminochloroethane hydrochloride (17 g). The fabric stood covered and undisturbed for 20 hr at room temperature. (Sample ES-79A-110A)

The treatment sequence was repeated using 20 g (Sample ES-79A-110B) and then 40 g (Sample ES-79A-110C) of 40% aqueous 2-diethylaminochloroethane hydrochloride.

A section of fabric was removed after each treatment and was thoroughly washed with 1.0 N NaOH, water, and then air dried. The weighed section was placed in 0.5 N KCl, boiled, cooled overnight, and then titrated with 0.1 N HCl followed by back titration with 0.1 N NaOH. The average of the acid and base titration end-points for the three differentially treated fabrics were: 0.26 meq/g, 0.6 meq/g, and 1.35 meq/g, respectively. Figure 9 is the titration curve for (sample ES-79A-110C, and the similarity of this curve to that for acid titration of carbonate is rather obvious.

Ion Exchange Bonding of Oxy-Anion Catalysts to DEAE-Functionalized Fabric. Six 9 in x 9 in sections of DMF-extracted cotton-blend was subjected to five cycles of treatment as described for ES-79A-110. The quantity of 2diethylaminochloroethane

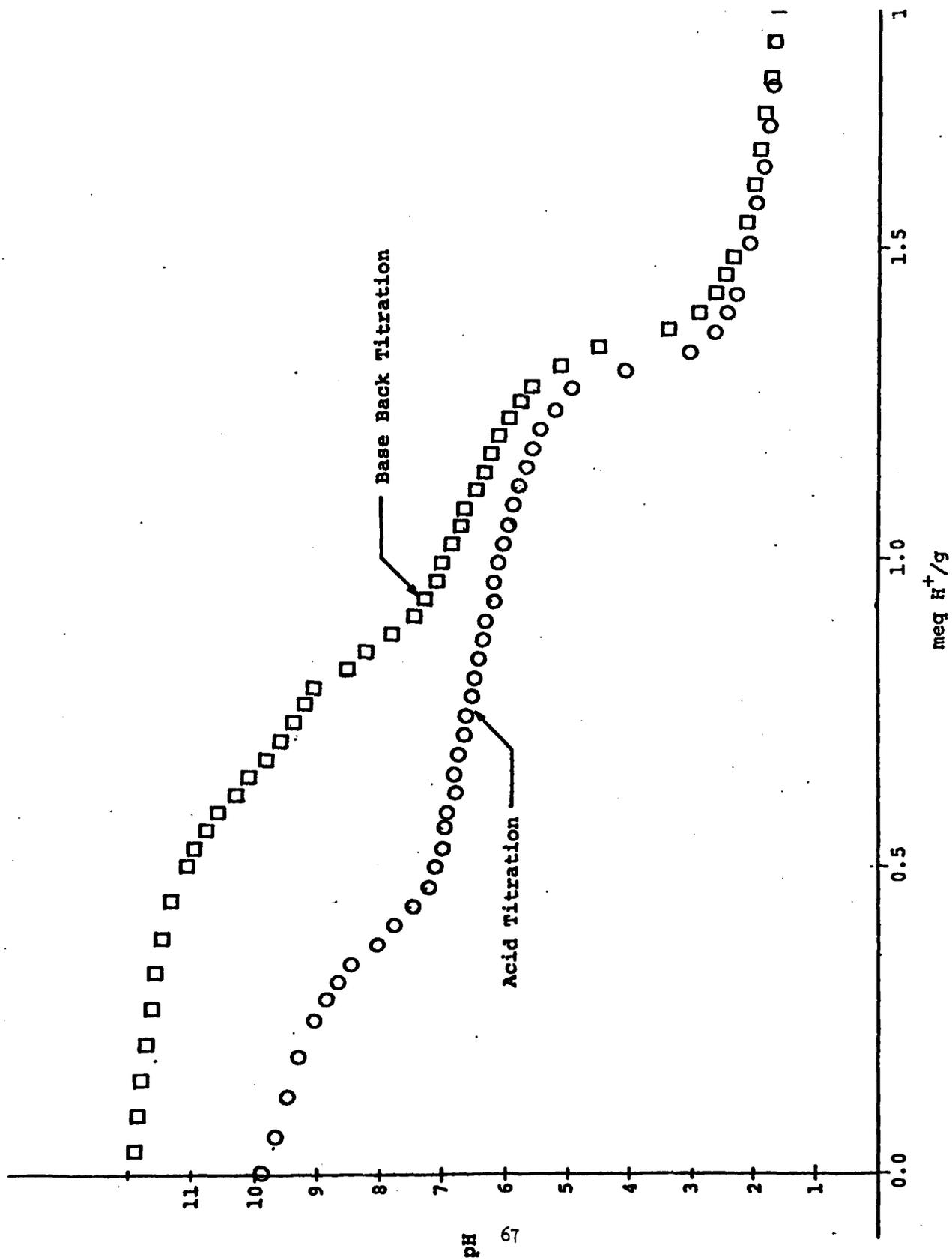


Figure 9. Titration curves for DEAE-functionalized nylon-cotton blend fabric (sample ES-79A-110C).

hydrochloride bonded to each fabric during each cycle was not measured. After preparation, each of the fabrics was sequentially soaked in 1 N NaOH for 24 hr, washed with water, soaked in 0.1 N HCl for 1 hr, washed with water, and then soaked in 1 N NaOH for 24 hr. At this point, a representative sample for analysis was cut from one section and the remainder of the fabrics was subjected to two cycles of soaking in 1 N KCl for 24 hr. Five of the resultant Cl⁻-loaded fabrics were then treated with solutions of the various oxy-anion catalysts as follows:

<u>ARC ID No.</u>	<u>Source of Oxy-Anion Catalysts</u>
ES-79A-127A	3.97 g Na ₂ MoO ₄ ·2H ₂ O in 400 ml H ₂ O
ES-79A-127B	6.03 g Na ₂ WO ₄ ·2H ₂ O in 400 ml H ₂ O
ES-79A-127C	2.27 g NaVO ₃ in 400 ml H ₂ O
ES-79A-127D	5.14 g Na ₃ PO ₄ in 400 ml H ₂ O
ES-79A-127E	1.22 g K ₂ MnO ₄ in 400 ml H ₂ O
ES-79A-127F	Untreated after KCl

All samples were equilibrated for at least 24 hr and then dried.

<u>ARC ID No.</u>	<u>Initial Silane</u>	<u>Initial Fabric ID</u>
ES-79A-51A	H ₂ N(CH ₂) ₃ Si(OEt) ₃	GZ-47
ES-79A-51B	H ₂ NCH ₂ CH ₂ NH(CH ₂) ₃ Si(OMe) ₃	ES-79A-31

The final fabric products were titrated with 0.1 N HCl. The aminopropylsilane fabric (ES-79A-51A) showed no base capacity, whereas the diamine treated fabric showed some base capacity with a distinct break at 2.4 meq/g and a somewhat less distinct inflection point at about 0.3-0.5 meq/g (see Figure 8).

5.4.2.2 Diethylaminoethyl-Functionalized Nylon-Cotton Blend.

A significant amount of effort was directed toward the production of 2-(diethylamine)ethyl-(DEAE) functionalized cotton (CTN) fabric: CTN-NHCH₂CH₂NEt₂. The rationale for preparing this material is that the tertiary amine could then be

converted to a quaternary ammonium salt by treatment with methyl iodide or it could be further elaborated into a quaternary ammonium polymer by reaction with 2-chloroethyldiethylamine.

The procedure initially employed was similar to that used for preparation of DEAE cellulose and sepharose⁵⁴ and has been successfully applied to cotton cloth.⁵⁵ In all cases the cotton-blend fabric was thoroughly extracted with DMF and was then washed with 20% aqueous sodium hydroxide to remove base soluble materials.

Fabric ES-79A-79: A 9 in x 9 in square of fabric (9.5 g) was placed in 25% aqueous sodium hydroxide (300 ml) at 0° for 1 hr. An aqueous solution of 2-chloroethyldiethylamine hydrochloride (60 g, 0.35 mol in 100 ml) was added and the entire mixture was quickly heated to 80° and maintained at this temperature for 90 min. The resultant fabric was thoroughly washed with 2 M NaCl, 1 M NaOH, and water before air drying.

Fabric ES-79A-81: A 9 in x 9 in section of cotton was treated with 2-chloroethyldiethylamine hydrochloride (30 g, 0.18 mol) and anhydrous K₂CO₃ (48 g) in 700 ml of DMF at 70° for 24 hr. Water (250 ml) was then added and the mixture was again heated for 24 hr. The resultant fabric was thoroughly washed in 1 M NaOH and then water before air drying.

5.4.3 Polymer-Coated Fabrics

5.4.3.1 Poly(ethyleneimine): An aliquot (75 ml) of a dilute solution (0.75 w/v%) of poly(ethyleneimine), (-CH₂CH₂NH-)_n, was sprayed on a 9 in x 9 in piece of fabric. When the fabric became wet, spraying was ceased and the fabric was allowed to air dry. Spraying was then continued in this manner until all of the solution was used. This procedure gives ca. 1.0 g of poly(ethyleneimine)/ft² (Sample ID Nos. ES-78-95-A for Nomex and Es-78-95-B for cotton blend).

5.4.3.2 Poly(acrylamide): A 2.5 w/v% solution of poly(acrylamide) in water was prepared. A 10.41 g piece of Nomex was dipped into this solution and was then allowed to drain while drying. The process was repeated four times. After drying overnight, the fabric weighed 11.26 g (8.3% weight gain).

⁵⁴H. A. Sober and E. A. Peterson, J. Am. Chem. Soc., 76, 1711 (1954).

⁵⁵J. A. Todhunter, personal communication.

5. Poly(acrylamide)-Poly(vinylalcohol) Co-Polymer: About one-third of fabric sample ES-78-107-A (see above) was sprayed with a solution of 1.0 g of poly(vinylalcohol) in 100 ml of 50% aqueous ethanol.

Moisture-Uptake Measurements: The aforementioned polymer-coated fabrics were intended as hydrophilic surfaces. To gauge the extent of water absorption which is achieved, a "% gain" factor was measured as follows:

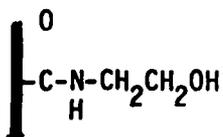
Poly(acrylamide) [ES-78-107-A]:

Dried <u>in vacuo</u> , 80°, 1 hr - - - - -	0.2158 g	} 4% gain
Air at 32°/90% RH, 1 hr - - - - -	0.2248 g	

Poly(acrylamide)-Poly(vinylalcohol) [ES-78-107-B]:

Dried <u>in vacuo</u> , 80°, 1 hr - - - - -	0.2554 g	} 5.5% gain
Air at 32°/90% RH, 1 hr - - - - -	0.2695 g	

5.4.3.3 Poly N-(2-hydroxyethyl)methacrylamide : One of our primary objectives in coating fabrics with polymers was to evaluate the propensity of the polymer matrix to absorb both the simulant and water molecules. The need for the absorption of the simulant is obvious, and the greater the water content of the polymer matrix, the faster the hydrolysis rate, regardless of the specific mechanism of the nature of the catalyst. We therefore studied the preparation of poly N(2-hydroxyethyl)methacrylamide from reaction of poly(methyl methacrylate) with 2-aminoethanol, as a polymer analog of N-methylformamide that was earlier shown by us to be a good reaction medium for sulfur mustard simulant, CMS.



Incorporation of aminoethanol into the polymer has been achieved (ES-79-129-1); however, the extent of incorporation was ca. 50% of the theoretical amount. This

synthetic polymer and other commercially available polymers were used in coating fabric samples according to the specifications listed below.

ES-79-139-A: Cotton-blend (2.459 g) treated with an aqueous solution of poly(acrylamide) (1.0 g) and poly(ethylene oxide) (1.0 g); final weight = 3.587 g.

ES-79-149-A: Cotton-blend (2.478 g) treated with an aqueous solution of poly(acrylamide) (0.256 g), poly(ethylene oxide) (0.117 g), and poly(ethyleneimine) (0.512 g); final weight = 10.54 g.

ES-79-133-A: Cotton-blend (9.51 g) coated with poly N-(2-hydroxyethyl)methacrylamide) (1.03 g of ES-79-129-1); final weight = 10.54 g.

ES-79-137-A: Methanol-extracted.⁵⁶ As already noted, it was possible for us to remove the Quarpel coating from the nylon-cotton blend by extraction and thereby increase the loading of, for example, Z-6020 chelating agent. To quantify the effect of continuous extraction, a 10.387 g piece of cotton-blend was extracted with MeOH in a Soxhlet apparatus for 2 hr. The dried extract afforded a curd-like, waxy, yellow precipitate that weighed 0.255 g and represented 2.5 w/w% cotton-blend (2.25 g) coated with poly[N-(2-hydroxyethyl)methacrylamide] (1.00 g of ES-79-129-1); final weight = 2.71 g.

ES-79-139-A: Methanol-extracted cotton blend (2.46 g) coated with poly(acrylamide) (1.00 g) and poly(ethylene oxide) (1.00 g); final weight = 3.59 g; very stiff and waxy coating.

ES-79-149-A: Methanol-extracted cotton blend (2.48 g) coated with poly(acrylamide) (0.256 g), poly(ethylene oxide) (0.117 g), and poly(ethyleneimine) (0.512 g); final weight = 3.675 g. A weight gain of 0.312 g over the theoretical value may represent enhanced water uptake (ca. 10%).

5.4.4 Mercerization and Swelling of Cotton Blend Fabric to Facilitate Chemical Modification and/or Provide an Improved Agent-Reaction Surface.

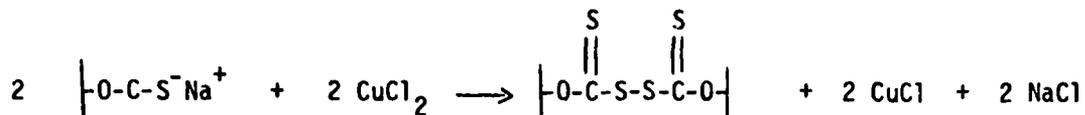
A 9 in x 9 in square of cotton-blend fabric was stirred in boiling 15% NaOH for 2 hr and was then thoroughly washed with water. This "mercerization" procedure is generally assumed to increase the fabric's equilibrium water content relative to that of untreated cotton. When applied to normal cotton-blend material, the NaOH solution becomes dark brown in color whereas the methanol-extracted cotton-blend affords a pale yellow NaOH solution. In any event, no obvious physical difference between these fabrics can be detected, and both appear to be "bulkier" than their respective progenitor materials.

After water washing, the mercerized fabric was sequentially rinsed with methanol and then toluene, which presumably afforded "anhydrous" fabric with the same degree of porosity as in the wet state.

5.4.5 Introduction of Xanthate Functionalities onto Cotton-Blend.

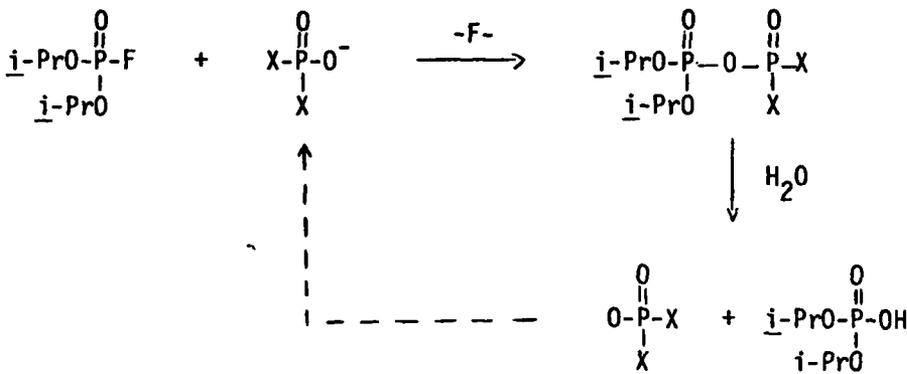
The addition of xanthate moieties ($-CS_2^-$) to a fabric surface was desirable in that such functionalities have been recently shown to chelate with a wide variety of metal ions. Consequently, we explored methods to achieve this fabric modification, and the findings are summarized as follows.

A 9 in x 9 in square of methanol-extracted cotton-blend fabric was treated with 10 ml of CS_2 in 0.2 M NaOH for 24 hr at 25^o; however, the resultant material (ES-79-147-A) showed no visible sign of modification. Repetition with boiling 15% NaOH for 1 hr followed by soaking in CS_2 and final water wash gave similar negative results (ES-79A-5-A). In a third reaction, the boiling in 15% NaOH (1 hr) was followed by treatment with CS_2 (11 ml) in an ultrasonic cleaner for 1 hr, and final soaking for 18 hr under normal conditions. The resultant fabric (ES-79A-5-B), which was moderately stiff and "bulkier" in appearance, caused a solution of $CuCl_2$ to produce a white precipitate that was taken as evidence for the reaction shown below.

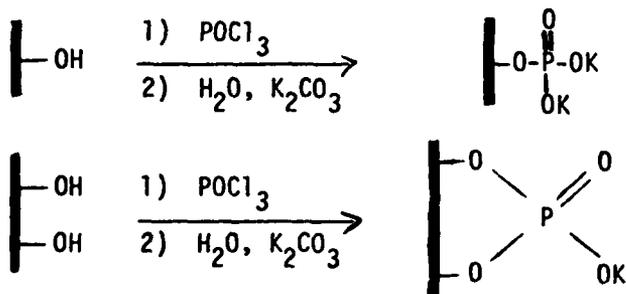


5.4.6 Investigation of "Phosphorylated Fabric"

Consideration of organic reaction theory predicts that the self-propagating reaction cycle involving a generalized phosphate anion could function in a catalytic manner to cause relatively facile hydrolysis of V- and G-type agents akin to DFP, as is pictured below. More persuasively, it has been experimentally determined



that phosphate causes the catalytic hydrolysis of DFP; however, detailed information regarding the generality of this phenomenon has yet to be established. Our approach to the attachment of phosphate groups to a fabric surface was based on standard organophosphorus synthetic transformations.



Several samples of chemically treated cotton-blend fabric were thus prepared under a variety of conditions as a means of obtaining "phosphorylated fabric".

ES-79A-21A: A 9 in x 9 in square of methanol-extracted cotton-blend was subjected to solvent exchange with toluene, and was then treated with a mixture of pyridine (200 ml) and POCl₃ (50 ml) in toluene (300 ml) solvent for 18 hr at 25°. The sequential workup involved washing with 50% aqueous THF, water, aqueous K₂CO₃, water (3-times), and final drying.

ES-79A-21B: Same procedure as with ES-79A-21A except for the use of "mercerized cotton fabric.

ES-79A-21C: Same procedure as with ES-79A-21B except for the use of a 2 hr reflux time. The resultant material was noticeably fragile.

ES-79A-25A: A 4.5 in x 4.5 in square of methanol-extracted cotton-blend was treated with POCl₃ (50 ml) in Et₃N (150 ml) for 1 hr at 25°, and was then sequentially washed with water, 5% aqueous K₂CO₃, and more water (3-times) before air drying.

KES-79A-25B: Same procedure as with ES-79A-25A except for the use of a 1 hr reflux time.

ES-79A-27A: A 4.5 in x 4.5 in square of methanol-extracted cotton-blend was treated with POCl₃ (30 ml) in pyridine for 2 hr at 5°. The usual water/K₂CO₃/water wash sequence was finally followed by vacuum drying.

ES-79A-27B: Same procedure as with ES-79A-27A except for use of 30 min reflux time. Red-brown colored fabric.

ES-79A-27C: Same procedure as with ES-79A-27A except for use of 10 min reflux time. Red-brown colored fabric.

5.4.7 Investigation of Fabric "Activation" by Cyanogen Bromide

The cyanogen bromide (CNBr) "activation" of chromatographic stationary phases for subsequent covalent attachment of coupling agents is well-known and it was of interest to determine if such methodology could be applied to the fabrics and objective of the present project.

Procedure A: A 9 in x 9 in square of methanol-extracted cotton-blend was treated with cyanogen bromide (1.5 g in 4 portions) in aqueous solution maintained at pH 10-12 for 10 minutes. Quarter sections of the "activated" fabric were then individually treated with either 4,4'-di(hydroxamidosulfo)diphenylether, cyclodextrin, poly(ethyleneimine), or histidine using, in each case, a 1% aqueous solution of the intended catalyst. Titration of the later two fabrics with acid and base (0.1 N) revealed little, if any, uptake of poly(ethyleneimine) and histidine, respectively.

Procedure B: A 9 in x 9 in square of DMF-extracted cotton-blend was treated with 3 g of cyanogen bromide in an aqueous solution maintained at pH 10 by addition of NaOH. The fabric was divided into four sections; each section was placed in 0.1 M phosphate buffer (pH 6.0 and 0°) containing 1% solutions of either diethylamine, poly(ethyleneimine), 4,4'-di(hydroxamidosulfo)diphenylether, or histidine. After 1 hr the solutions were allowed to come to room temperature. Very little acid or base capacity was found by titration, and alkaline hydrolysis of the diethylamine treated fabric did not release diethylamine, based on GC analysis of the reaction mixture.

5.4.8 Lanthanide Hydroxide-Coated Fabrics

There are several reports of the lanthanide group hydroxides being active catalysts for the hydrolysis of phosphate esters and DFP. It was appropriate, therefore, to investigate the possibility that a dispersion of these hydroxides within a suitable matrix might provide effective catalysis for hydrolysis of G- and V-type agents. The majority of effort centered on obtaining a workable formulation and technique for coating the fabric employing mainly $\text{La}(\text{OH})_3$, as it is prototypal of this group of elements and is also relatively inexpensive.

Initially, a sample of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ was titrated with 0.1 N NaOH. The titration gives a normal base titration curve with an average buffering pH of 8.5. The formation of $\text{La}(\text{OH})_3$ is essentially complete at pH 9.5 and this was chosen as the end point for further work. As described below, several procedures were utilized for application of $\text{La}(\text{OH})_3$.

Fabric ES-79A-123A: A solution of poly(acrylamide) (1.0 g), poly(ethylene oxide) (1.0 g) and poly(vinylalcohol) and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ was prepared in 250 ml of water. The pH was adjusted to 9.5 with 1.0 N NaOH, Globules of a white material appeared and could not be dispersed. A second attempt was made using the same polymer components and a slurry of $\text{La}(\text{OH})_3$ obtained from $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ (5.0 g). Upon addition of $\text{La}(\text{OH})_3$ to the polymer mixture a tractable dispersion was obtained. This was then applied to a 9 in x 9 in square of Nomex, unfortunately, over the course of the coating process, the dispersion separated and led to an unsatisfactory final product.

Fabrics ES-79A-126A, B, and ES-79A-133A, B: Solutions of either LaCl_3 or GdCl_3 were prepared and the pH was brought to 9.5 The resulting hydroxide slurries were each applied to the fabric until the slurry was expended. The fabric was then coated on each side with poly(ethylene oxide) (1 g/100 ml H_2O), which resulted in a fabric coating that was reasonable homogeneous but has some tendency to become detached.

<u>ARC ID No.</u>	<u>Initial Fabric</u>	<u>Initial Chloride</u>
ES-79A-126A	Nomex	5.4 g $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$
ES-79A-126B	Cotton-Blend	5.1 g $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$
ES-79A-133A	Nomex	5.1 g $\text{GdCl}_3 \cdot n\text{H}_2\text{O}$
ES-79A-133B	Cotton-Blend	5.0 g $\text{GdCl}_3 \cdot n\text{H}_2\text{O}$

Fabric ES-79A-132A: A section of DMF-extracted cotton-blend was treated with aqueous lanthanum chloride (5.0 g in 40 ml water) and then with 20 ml of 5 N NaOH. The resultant fabric was coated three times on each side with polyethylene oxide (1.0 g/100 ml water).

Fabrics ES-79A-130 A, B: A section of fabric was coated with a solution of lanthanum chloride and polyethylene oxide. After drying, this material was treated with 60 ml of 1 N NaOH to produce a matrix dispersed $\text{La}(\text{OH})_3$. This resulted in an uneven distribution of $\text{La}(\text{OH})_3$. Evidently the original coating has a tendency to flow when rewet or was uneven to start with.

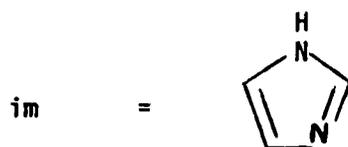
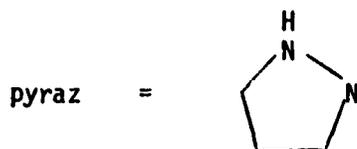
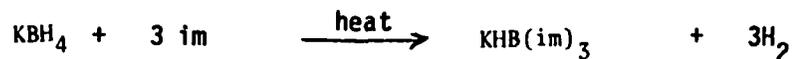
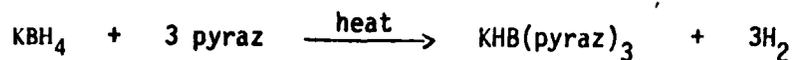
<u>ARC ID No.</u>	<u>Initial Fabric</u>	<u>Initial Chloride</u>
ES-79A-130A	Cotton Blend	5.3 g $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$
ES-79A-130B	Nomex	5.1 g $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$

Fabrics ES-79A-134A, B: A solution of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ in 50 ml of water was added to a stirred solution of poly(ethyleneimine) (20 g of 30% solution in a total volume of 50 ml). A white slurry formed and remained homogeneous over a 2-day period. Solutions prepared in this manner were spread on Nomex (ES-79A-134A) and cotton-blend (ES-79A-134B). The resultant material was somewhat stiffer than original, and had a rather "rubbery" texture.

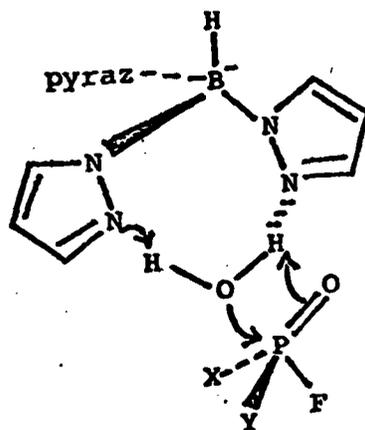
5.4.9 Synthesis and Characterization of a Novel Borate Salt as a Potential Catalyst for DFP Hydrolysis

Borate salts of general structure $\text{M}^+ [\text{HBL}_3]^-$ with heterocyclic ligands (L) were of interest to us in cases where such L groups can either (a.) react with DFP and/or CIS, (b.) chelate with some transition metal, (c.) function in "push-pull" hydrolyses of DFP and CIS, or (d.) lead to formation of polymeric networks via intermolecular transition metal-ion bridging. Trofimenko⁵⁷ has prepared potassium hydro(tris-pyrazolyl)borate $[\text{DHB}(\text{pyraz})_3]$ as shown below, and we have extended this procedure to prepare the isomeric tris-imidazole salt $[\text{KHB}(\text{im})_3]$, mp 260°C (dec).

⁵⁷S. Trofimenko, J. Am. Chem. Soc., 89, 3170 (1969).



These and similar complexes provide a fascinating array of possible materials modification and modes of hydrolytic catalysis since the "push-pull" pathway illustrated below has precedent in enzymatic systems and is therefore highly reasonable.



The 60 MHz ^1H NMR spectrum of KHB(im)_3 in DMSO-d_6 showed two peaks in the aromatic region at δ 7.28 (1 H) and δ 6.85 (2 H), which are thus isochronous with peaks from imidazole under identical conditions: δ 7.70 (1 H) and δ 7.00 (2 H). In acetone- d_6 the three non-equivalent imidazolyl hydrogens can be seen as three distinct signals of equal integrated intensity at δ 7.32, 6.92, and 6.85. While the hydrido proton was not seen in the NMR spectra, due to extreme broadness, the presence of a B-H bond was evidenced by an IR absorbance at 2435 cm^{-1} .

5.5 NMR Investigations of DFP Hydrolysis and Evaluation of Hydrolytic Catalysts

5.5.1 Safety Considerations: Technical information⁵⁸ concerning DFP provides physical properties, toxicity data, and general handling precautions. Our guidelines for manipulating DFP involved the use of the "buddy system" and the use of a well-ventilated fume hood restricted for work with this simulant. For operations requiring a high degree of manual dexterity, two pairs of standard examination gloves are worn, while other work is performed with heavy-duty, cotton-lined, "Platex" gloves. Use of dilute solutions of DFP outside the hood, which is dictated by various laboratory instrument requirements, requires extreme caution.

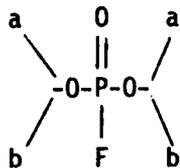
5.5.2 Analytical Characterization of DFP and Its Hydrolysis Product, Diisopropylphosphoric Acid: Gas chromatography and ¹H NMR were the analytical methods selected for establishing the purity of DFP and for eventual monitoring of its concentration during model hydrolytic kinetic runs and fabric testing. Using the GC conditions specified below, the DFP was found to contain ca. 95% DFP, as the major volatile component ($t_{\text{air}} = 2.5$ min), and ca. 5% diisopropylphosphoric acid (DPA), (i-PrO)₂-P(O)OH as the only other volatile component ($t_{\text{air}} = 12$ min) present in a concentration which was detectable by flame-ionization.

Column:	1/8 in x 6 ft 2% OV 101 on Chrom G/HP
Column temp.:	80°
Injector temp.:	170°
Detector temp.:	300°
Flow:	30 ml/min N ₂

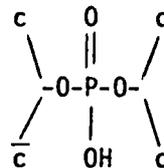
These GC identifications were initially supported by ¹H NMR spectra (Figure 10) in acetone-d₆ : D₂O (1:5, 1% TSP) which showed diastereotopic i-Pr methyl groups (a and b) as a closely-spaced ($\Delta\nu_{ab} = \text{ca. } 1$ Hz) pair of doublets ($^3J_{\text{HH}} = 6$ Hz) centered at $\delta 1.54$, while the enantioto i-Pr methyl groups (c and c) of DPA were seen as a partially overlapped doublet ($^3J_{\text{HH}} = 6$ HZ) centered at $\delta 1.44$. Unambiguous evidence for these assignments was obtained by subsequent addition of ca. 2 equiv of NaOD/D₂O,

⁵⁸Aldrich Chemical Co. Technical Information sheet for product no. D 12,600-1 (1972).

which caused complete conversion (within 5 min) of DFP signals into those assigned to DPA. No significant differences in these spectral parameters were seen in either CDCl_3 (1% TMS), DMSO-d_6 (1% TMS), or $\text{DMSO-d}_6 : \text{D}_2\text{O}$ (1:5, 1% TSP).



DFP (S_1 point group)



DPA (C_{2v} point group)

5.5.3 Preliminary DFP Hydrolysis Studies: Before fabric testing by the GC method, it was highly desirable to directly evaluate the behavior of DFP and DPA in aqueous solutions by ^1H NMR. In this manner, it would be possible to easily monitor the rate of DFP hydrolysis to DPA under relatively well-defined conditions (pH, water content, etc.) using various samples of the potential catalysts as either homogeneous solution components or as heterogeneous (surface-attached) components. Such data would then provide a reasonable indicator of relative reactivity toward DFP, and thus provide "benchmarks" for the more complex conditions associated with final GC methods. The NMR analysis would also allow for accurate monitoring of material balance and thereby reveal, e.g., precipitation of reaction components or the existence of transient intermediates.

Five categories of experiments were initially carried out: (1.) controls with regard to "base-line" hydrolytic rates, (2.) examination of metal ion-containing treated fabrics, (3.) tests of reported Cu^{+2} catalysts for DFP (and sarin) hydrolysis, (4.) examination of imidazole and phosphate as novel types of general and/or specific base catalysts for hydrolysis, and (5.) tests of reported N-hydroxylamide catalysts for DFP hydrolysis.

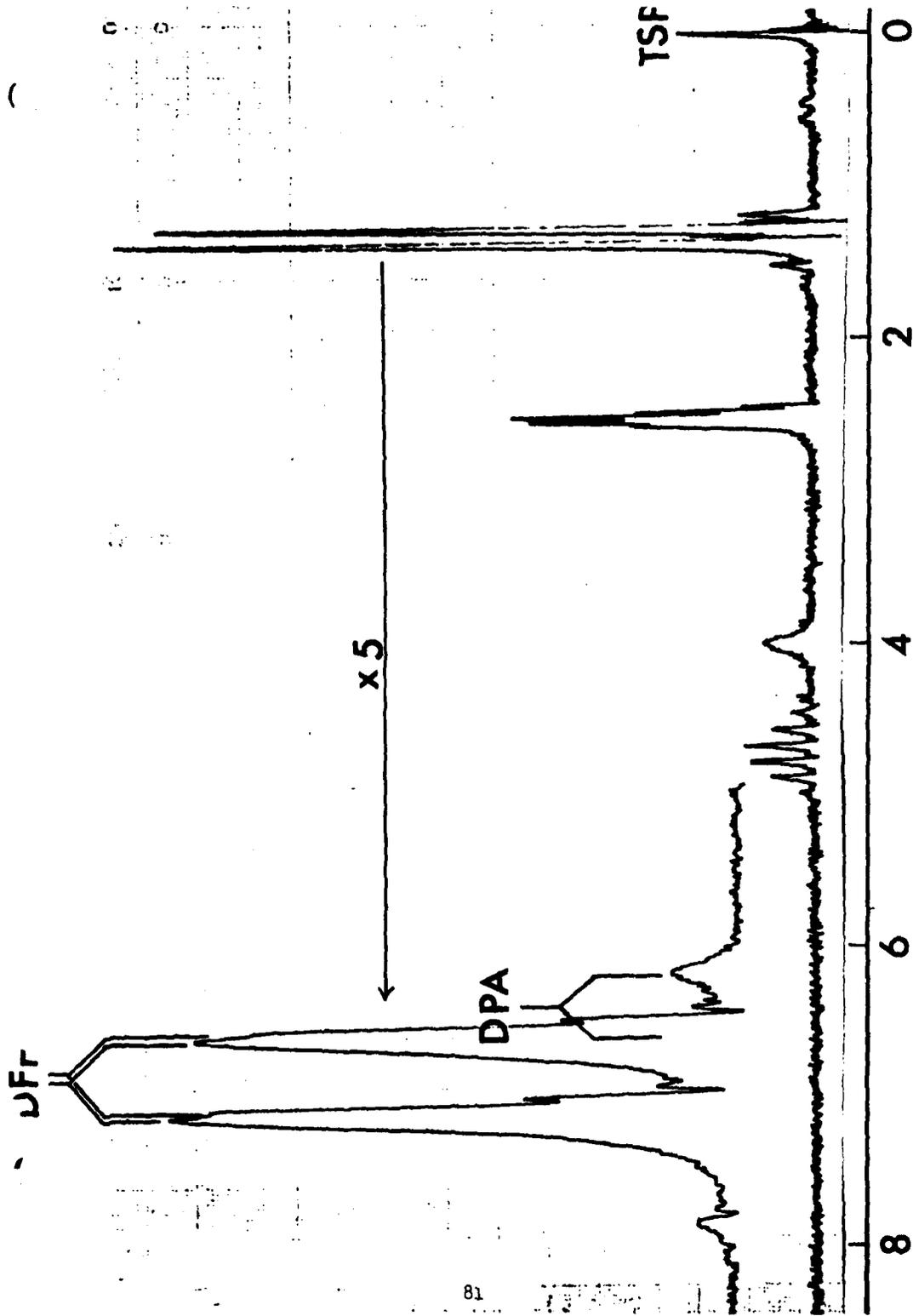


Figure 10. ^1H NMR spectrum (60MHz) of DFP in acetone- d_6 : D_2O (1:5) containing 1% TSP as an internal chemical shift ref.

General Procedure: Standard quantities per NMR sample tube, prepared either individually or as stock solution, were as follows:

10 μ l (0.057 mmol) DFP
4 μ l N-methylformamide internal reference (δ_{CH_3} 2.91)
0.2 ml acetone- d_6
1.0 ml D_2O

All untreated and treated fabrics were 2 cm^2 specimens that were used in the form of eight 25 mm^2 pieces (5 x 5 mm). A standard 3-dram glass vial with screw-cap was used as the reaction vessel. Initial ("zero-time") spectra were recorded as soon as possible after mixing, and the solutions were then returned to the reaction vessels until an NMR spectrum was again taken. Integration of the N-methylformamide and i-Pr methyl absorptions can be used to accurately measure DFP and DPA concentrations; however, for the present purposes the "% Hydrolysis" was simply computed from the relative peak heights illustrated in Figure 11 for the indicated spectral absorptions.

$$\begin{aligned} \% \text{ Hydrolysis} &= \frac{[\text{DPA}]}{[\text{DFP}] + [\text{DPA}]} \times 100 \\ &= \frac{\text{Peak height C}}{\text{Peak height A} + \text{Peak height C}} \times 100 \end{aligned}$$

From data summarized in Table 8 the following conclusions were drawn:

(1.) Untreated cotton blend and untreated Nomex had no significant effect on the spontaneous rate of DFP hydrolysis in an unbuffered medium; however, this "non-effect" may be due to an initial DFP concentration which is much greater than the hydrolytic capacity of these fabrics (vide infra). Consequently, the diminution in DFP concentration would have been too small to detect by NMR.

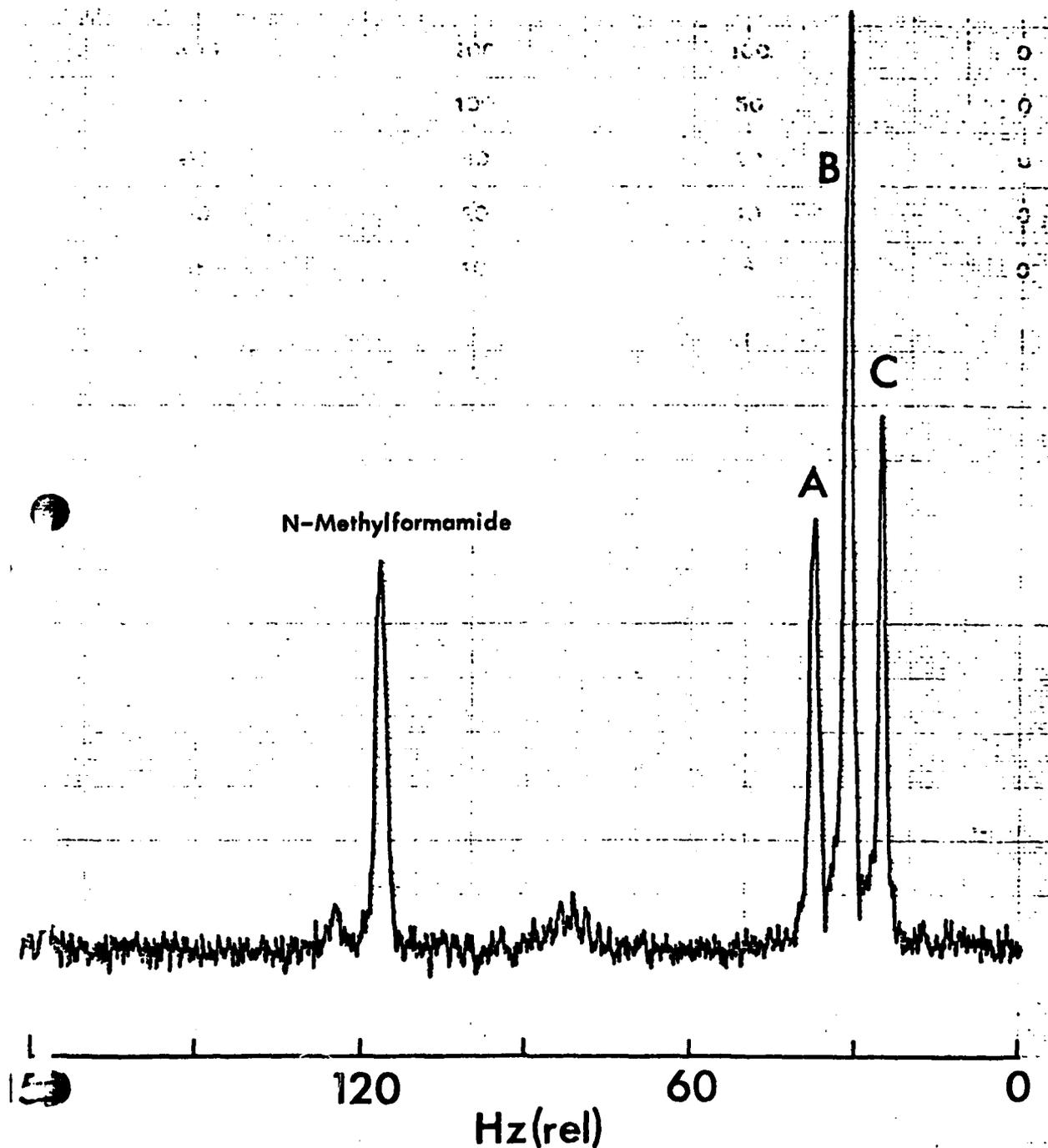


Figure 11. Partial ^1H NMR spectrum (60MHz) of a partially hydrolyzed solution of DFP in acetone- d_6 : D_2O (1:5) containing N-methylformamide as an internal reference.

Table 8. ^1H NMR HYDROLYSIS DATA FOR DFP (0.05 M) IN ACETONE- d_6 : D_2O (1:5) AT 25°

Test Catalyst	Amount	% Hydrolysis			Remarks
		"Zero-Time"	24 hr	64 hr	
None	—	14	51	91	—
Cotton Blend	2 cm^2	14	46	88	—
Nomex	2 cm^2	14	55	92	—
Cotton Blend/ Ag^+	2 cm^2	8	11	18	H/D exchange into acetone
Nomex/ Cu^{+2}	2 cm^2	10	90	100	Blue color @ 24 hr.
Nomex/ Fe^{+3}	2 cm^2	7	10	16	Yellow color @ 65 hr.
TMEDA· Cu^{+2}	1 mole %	9	33	77	—
Bipy· Cu^{+2}	1 mole %	9	37	80	—
Imidazole	500 mole %	10	94	ND	—
Na_3PO_4	200 mole %	"fast" (1/2 = <u>ca.</u> 10 min.)			—
$\text{PhC(O)N(C}_2\text{H}_5)_2$	50 mole %	10	50	ND	—
$\text{PhS(O}_2\text{)N(OH)H}$	50 mole %	10	54	ND	—

(5.) The N-hydroxybenzamide [PhC(O)N(OH)H] and N-hydroxybenzenesulfonamide [$\text{PhS(O}_2\text{)N(OH)H}$] compounds showed no evidence of a catalytic effect under the reaction conditions studied, which is in direct conflict with earlier literature reports. As concluded in point (3.), this apparent difference in behavior may be due to pH effects (vide infra).

5.5.4 Investigation of pH and Buffer Effects: As already noted, careful evaluation of hydrolytic rate data for DFP hydrolysis by various catalysts requires the consideration pH and, moreover, maintenance of essentially constant pH. Theoretical consideration and general literature data suggests that the hydrolysis of DFP and analogous compounds should be facilitated by increasing pH (i.e. increasing hydroxide ion concentration), and that acid-catalyzed hydrolysis would be significant only at relatively low values of pH (i.e. relatively high proton concentration). Since the nature of the pH-rate profile for DFP hydrolysis is a critical factor with regard to the design and/or employment of fabric-attached catalysts, we have evaluated this reactivity feature for comparison with available literature data.

Preliminary NMR experiments with a 25 mM concentration of DFP in TRIS and phosphate (KH_2PO_4) buffers established that relatively high buffer concentrations (ca. 1 M) are needed to minimize pH change (ca. 0.2 unit) during the course of generating 1 equiv HF and 1 equiv DPA from 1 equiv of DFP.

Table 9 summarizes the various pseudo first-order rate constants (k) that were obtained for DFP hydrolysis under well-defined homogeneous conditions, and the salient features of this data are as follows:

(a.) Phosphate (KH_2PO_4) exerts a rate-accelerating effect on DFP hydrolysis, relative to TRIS. At pH 7.3, 7.8, and 8.3, the rate accelerations are 70, 2, and 90%, respectively; however, the reason for the apparently diminished enhancement factor at pH 7.8 is not known at this time.

Table 9. ^1H NMR HYDROLYSIS DATA FOR DFP (25 mM) IN ACETONE- d_6 : D_2O (1:5)
AT 25°C IN TRIS AND KH_2PO_4 BUFFERS (1 M)

Buffer	pH	k, min^{-1} ($\times 10^3$)	Correlation Coefficient
TRIS	7.3	2.33	0.99
TRIS	7.8	5.00	0.99
TRIS	8.3	2.50	0.92
KH_2PO_4	7.3	3.96	0.99
KH_2PO_4	7.8	5.10	0.99
KH_2PO_4	8.3	4.75	0.99

(b.) The hydrolysis rate for DFP increases by a factor of 210% upon pH increase from 7.3 to 7.8 in TRIS buffer. While less dramatic results obtain for KH_2PO_4 buffer (30% increase), and rate decelerations apparently hold for pH 8.3, these data nevertheless suggest the need for maintaining a "moderate" level of alkalinity during the course of reaction.

5.5.5 Investiation of Metal Chelating Fabrics for Catalytic Hydrolysis of DFP at a Constant Ph of 7.8: In an earlier section of this report, data were presented for DFP hydrolysis in the presence of fabric which had been chemically modified with Z-6020 fluid so as to have chelated transition metal ions. Since pH was not controlled in these preliminary studies, the experiments were repeatd with pH control at a value of 7.8 using phosphate buffer. "One point" kinetic measurements according to the standard ^1H NMR technique are summarized as follows:

<u>ARC ID No.</u>	<u>Metal Ion</u>	<u>Reaction Time (min)</u>	<u>% DFP Hydrolysis</u>
GZ-79-49	Cu^{+2}	91	62.7
GZ-48-N	Fe^{+3}	60	63.7
GZ-45X	Ag^{+}	64	69.9
GZ-45	Zn^{+2}	70	73.6
Control	None	74	65.9

Consideration of these data reveals that little, if any, catalysis was measured, as the extent of hydrolysis in the presence of test fabrics was essentially the same as that obtained for the control sample which lacked metal ion. While these findings might at first glance suggest the failure of the strategy behind design of these chelating fabrics, it must be noted that 1M TRIS buffer was used to maintain pH. It is possible that the NH_2 functionality of the large excess of TRIS molecules serves to "tie up" metal coordination sites that would normally be acessible to the PO functionality of DFP during the catalytic process.

5.5.6 Investigation of "phosphorylated Fabric" as a Catalyst for DFP Hydrolysis: It was already noted that "Phosphorylated fabrics" represent a potentially active class of agent-reactive materials. The following "one point" kinetic data for DFP hydrolysis were obtained by the NMR method using phosphate buffer at pH 7.8:

<u>ARC ID No.</u>	<u>Reaction Time (min)</u>	<u>% DFP Hydrolysis</u>
ES-79A-27A	75	73.2
ES-79A-27B	110	55.5
ES-79A-27C	79	65.3

Under the homogeneous reaction conditions employed and with pH control by 1M KH_2PO_4 , no major rate acceleration was in evidence, relative to the control reaction sample. Here again it is unfortunate that the "masking" effect(s) of buffer cannot be evaluated with the limited amount of available data.

5.5.7 Investigation of Miscellaneous Candidate Catalysts: The $\text{KHB}(\text{im})_3$ catalyst discussed above was examined together with β -cyclodextrin, which has the potential for "guest-host" complexation with DFP and subsequent catalytic hydrolysis. Using the NMR method, phosphate buffer at pH 7.8, and linear least-squares analysis of data points, the following data were obtained:

<u>Sample</u>	<u>$k \times 10^3 \text{ (min}^{-1}\text{)}$</u>	<u>Correction Coefficient</u>
β -cyclodextrin (20 mole %)	6.5	0.97
$\text{KHB}(\text{im})_3$ (50 mole %)	7.5	0.98
Control	5.1	0.99

These results have demonstrated the operation of modestly-sized hydrolysis rate acceleration factors for both the $\text{KHB}(\text{im})_3$ (47% increase) and β -cyclodextrin (28% increase).

Investigation of Hydroxamic Acids and Cognate Systems as Catalysts for DFP

Hydrolysis: Based on various literature reports and, primarily, our own mechanistic reasoning, we explore a wide and interesting variety of potential DFP hydrolysis catalysts using the NMR kinetic method. The test catalysts are pictured in Table 10, which also gives specific details for comparative studies that attempted to establish the relative catalytic properties toward DFP. From these "one point" kinetic data it appeared that benzohydroxamic acid (BHA), $C_6H_5CONH(OH)$, was the most promising candidate, as the extent of DFP hydrolysis over the standard reaction period (70 5 min) was the greatest. Additional kinetic measurements with BHA were therefore carried out and involved variation of BHA concentration, relative to DFP. From the slopes of the pseudo first-order hydrolysis plots shown in Figure 12 it is apparent that while the hydrolysis rate increases with initial BHA concentration, at low conversion, there is a "leveling off" effect as the reaction proceeds. In the absence of further kinetic data, we tentatively suggest that two DFP hydrolysis pathways are operative, as shown below, and that the route involving DFP reaction with BHT may provide an intermediate that decomposes into DPA, with regeneration of BHT, relatively slowly.

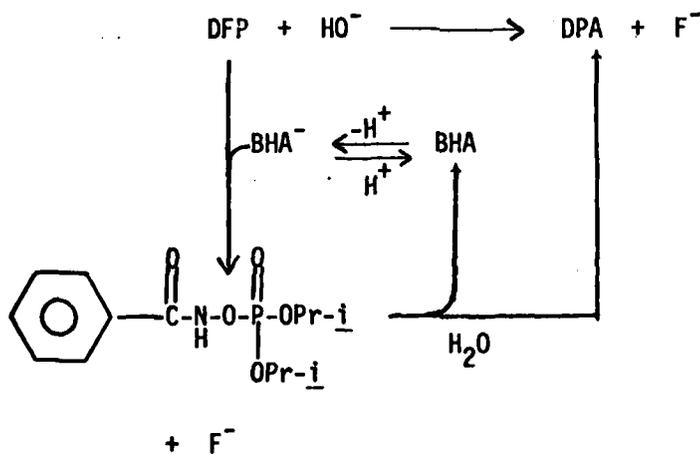
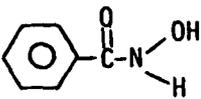
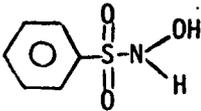
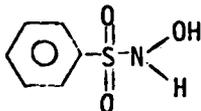
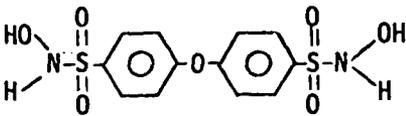
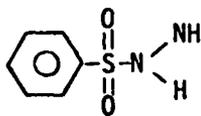
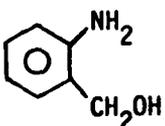


Table 10. COMPARISON OF VARIOUS COMPOUNDS AS POTENTIAL CATALYSTS
FOR THE HYDROLYSIS OF DFP AT pH 7.8 IN PHOSPHATE BUFFER (1M)

Compound ^a	% DFP Reacted ^b	Reaction Time (min)
	29.3	76
	53.6	76
	55.6	82
	44.2	78
	66.7	78
	58.2	69

^aAll reactions utilized compound concentrations which were one-half the concentration of DFP (see general NMR kinetic procedure discussed in the text).

^bDetermined from DFP vs. DPA relative NMR peak areas.

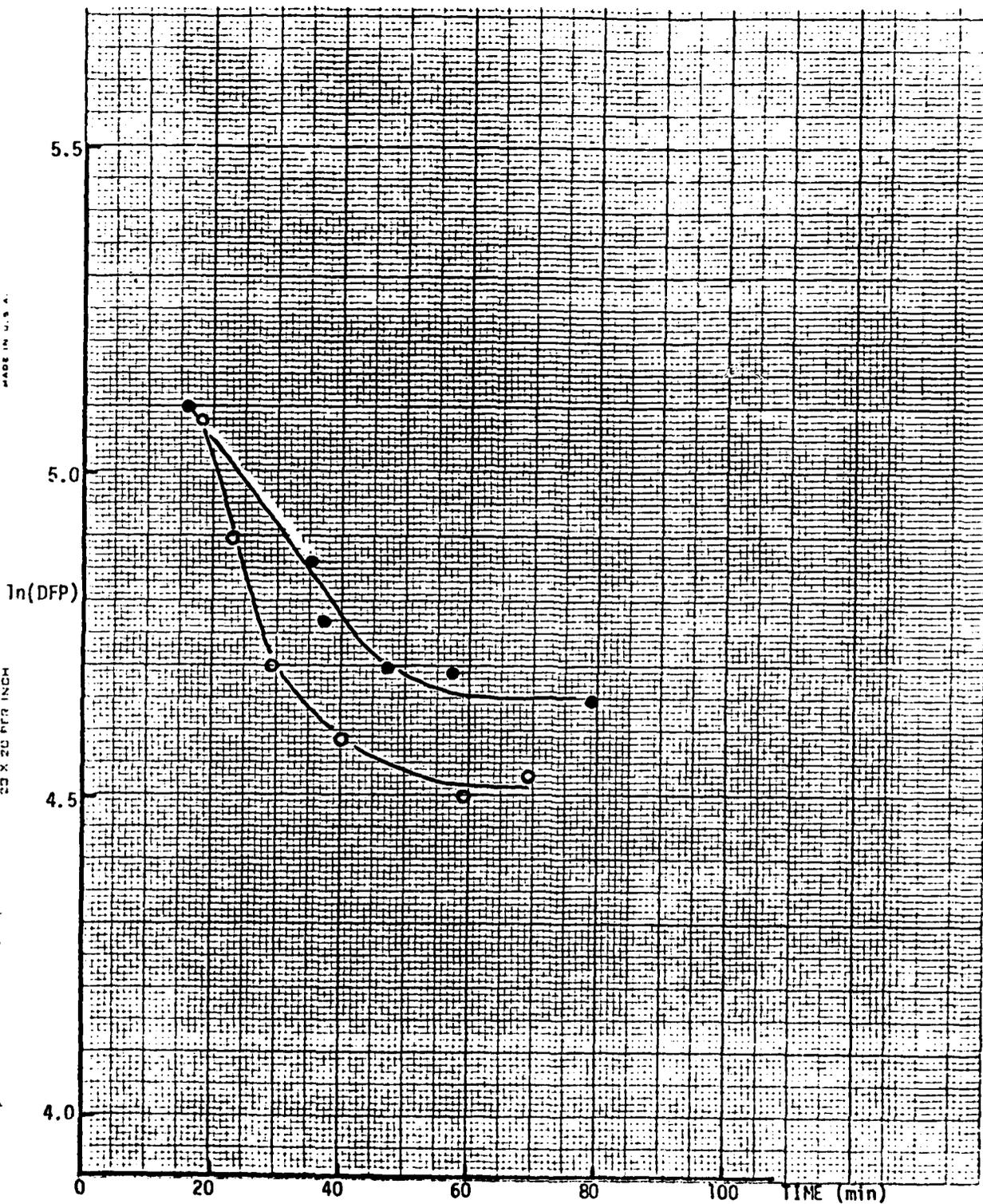


Figure 12. Pseudo first-order plots for the hydrolysis of DFP in the presence of 20 mol % (solid circles) and 50 mol % (open circles) BHA; pH = 7.8.

5.6 Design, Construction, and Studies with the Fabric Testing Apparatus

5.6.1 General

The fabric test system which is described in the following sections was designed to closely reproduce the essential aspects of the Dawson cup apparatus. Humidified air at a constant flow rate is passed over the surfaces of a fabric sample and the entrained vapors are absorbed in a high boiling and specially purified organic solvent (diethyl phthalate). Unlike the Dawson cup apparatus, the present system operated at a positive pressure; additionally, the air flow over the fabric surface was not vigorously laminar, and the flow rate was generally 50 ml/min on each side of the fabric.

5.6.2 Fabric Test System

As shown in Figure 13, compressed air was regulated (200 k Pa) and the line was split into two streams. Each line passed through a cut off valve (C), which allowed air flow to be stopped without changing flow settings, and then through a needle valve, which allowed the desired flow rate to be set. Copper tubing was used through the end of the valve system and tygon tubing was used in the remaining parts.

The stream to be used for the fabric side of the test apparatus was passed through a water gas wash (H) thermostated at 30° while the stream to be used for the penetration side remained dry. The gas wash at 30° provides air at 90% relative humidity at 32° (90°F). It was necessary to run the humidified stream through a warmed conduit (I) in order to prevent condensation in the air line. The controlled air entered the test chamber which was maintained at 32° and contained the test apparatus and vapor traps. The exhausted air (K) was vented to a hood.

5.6.3 Fabric Test Chamber

The fabric test chamber detailed in Figure 14 provided a controlled (32°) temperature environment for the test apparatus, and was constructed as a 2' x 2' x 1' box. Double-opening doors on one 2' x 2' side provided for ready access, while supporting structures, and air lines were used as indicated. Heat was provided by two 100 watt lamps (K) whose operation was controlled by a thermowatch R apparatus (H,I).

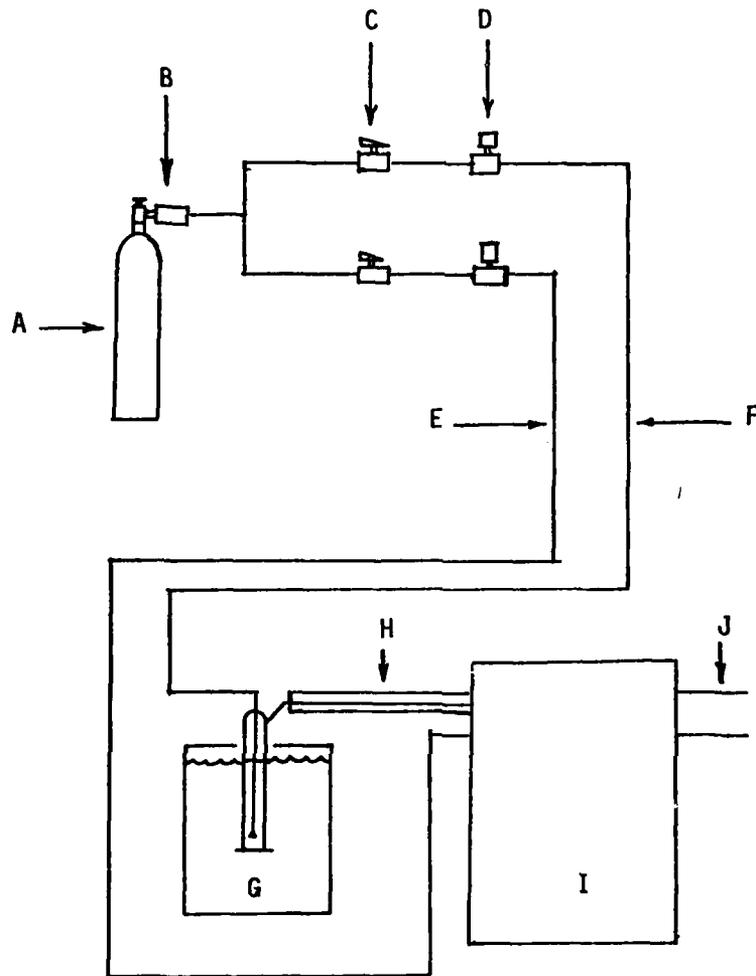


Figure 13. Schematic diagram of the fabric test system: A = air tank, B = pressure regulator, C = gas cock, D = needle valve, E = air line to penetration side of the test apparatus, F = air line to simulant side of the test apparatus, G = thermostated gas wash, H = heated conduit, I = test chamber (see Figure 14 for details), and J = exhaust line.

5.6.4 Fabric Test Apparatus

The fabric test apparatus shown in Figure 15 was constructed around a 30-mm o-ring joint (B). A section of fabric is cut to fit just inside the o-ring (about 28mm diameter) and it is then placed on top of a sheet of polyethylene wrap, which extends beyond the o-ring, provides added support for the fabric, and also functions as an air-flow barrier. The presence of the plastic film over the o-ring did not cause significant leakage.

Both sections of the apparatus are held together securely with a Size No. 50 ball-joint clamp, and the simulants are introduced directly onto the fabric sample through the T 29/26 joint. Air enters through a short glass duct (A) and is deflected over the fabric surface by a baffle (E) and proceeds to the traps through a short duct and joint (H).

5.6.5 Vapor Traps

As depicted in Figure 16, air containing the simulant vapors enters the trap through a 5-mm o-ring joint attached to a 90° bent tube. This tube is secured to a 9 in Pasteur pipet inserted through and sealed to a cork stopper, which is in turn inserted into an 18-mm x 150-mm sidearm test tube containing 10.0 ml of diethyl phthalate. Air exits through the sidearm and proceeds through a short piece of Tygon tubing to a quick-disconnect fitting joined to the exhaust line.

5.6.6 Fabric Test Procedure

A section of fabric for testing against the simulant was placed in the test apparatus, and the apparatus was then reassembled and placed with the test chamber. Airflows were set and temperatures of the chamber and gas wash were checked. The fabric was equilibrated with 90% relative humidity air at 32° (90° F) for 1 hr.

The desired number of traps were filled with purified diethyl phthalate and were reassembled; each trap contained 10.0 ml of diethyl phthalate stock solution of the internal standard used for GC analysis. The weight of a single 10.0-ml sample of the stock solution was determined for each run.

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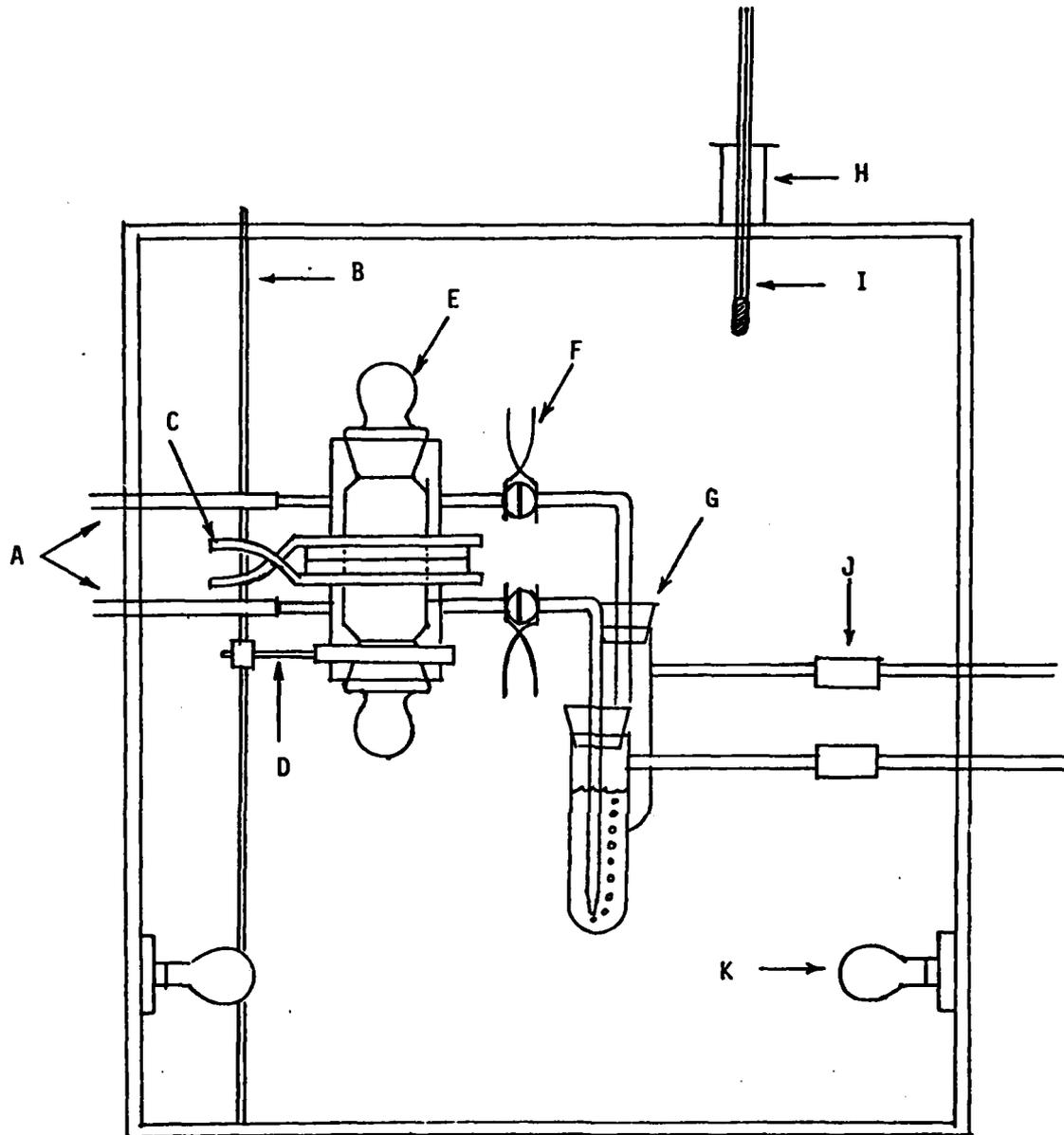


Figure 14. Schematic illustration of the fabric test chamber: A = entering air lines, B = support rod, C = Size No. 50 ball joint clamp, D = three finger clamp, E = test apparatus (see Figure 15 for details), F = Size No. 18 ball joint clamp (two per line), G = traps (see Figure 16 for details), H = Thermowatch R sensing head, I = thermometer, J = quick-disconnect hose coupling, K = 100 watt incandescent light bulb.

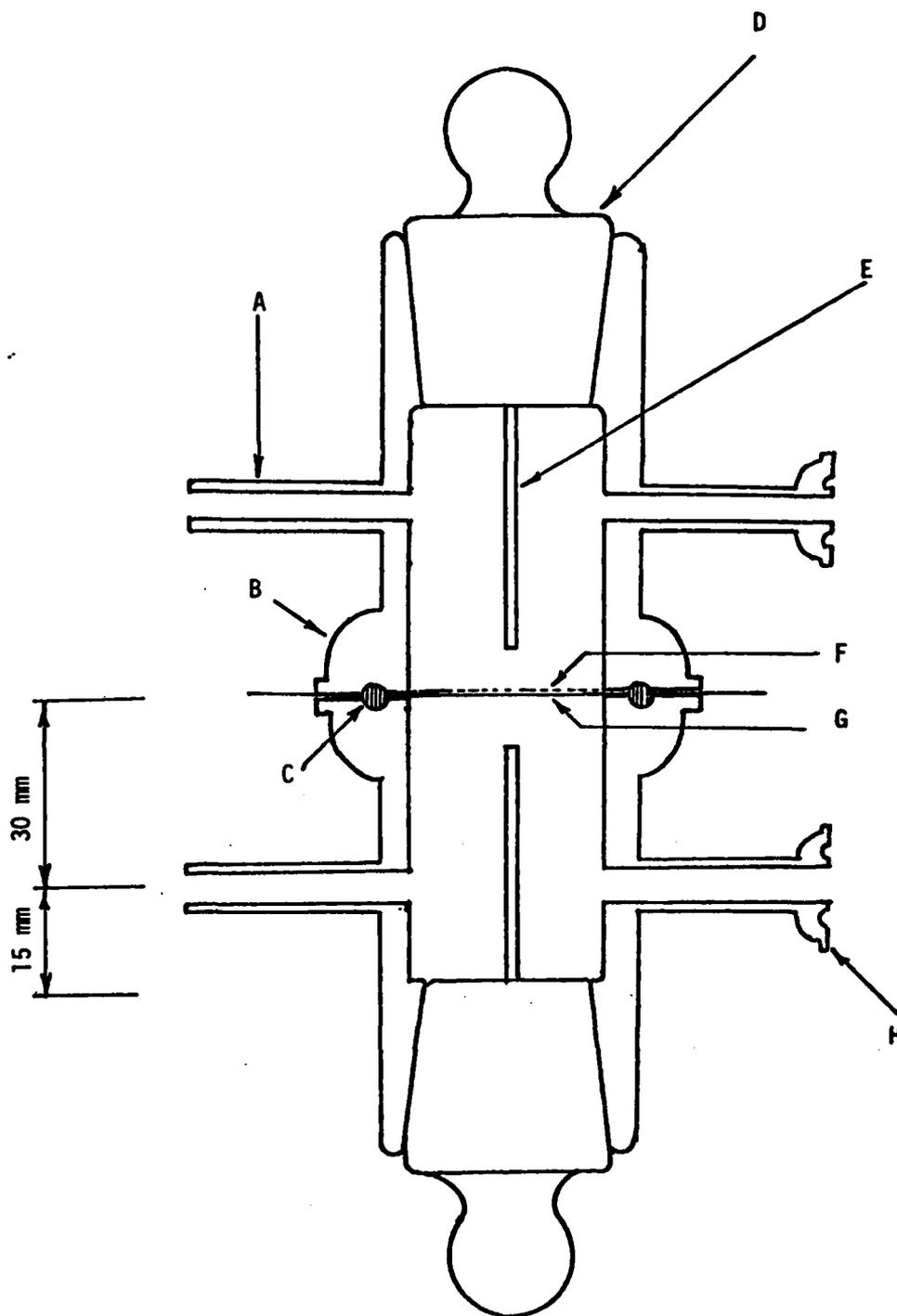


Figure 15. Schematic diagram of the fabric test apparatus: A = air inlet tube, B = 30 mm O-ring joint, C = O-ring, D = 29/26 outer joint and stopper, E = Baffle, F = fabric sample, G = plastic film, H = 5 mm O-ring joint.

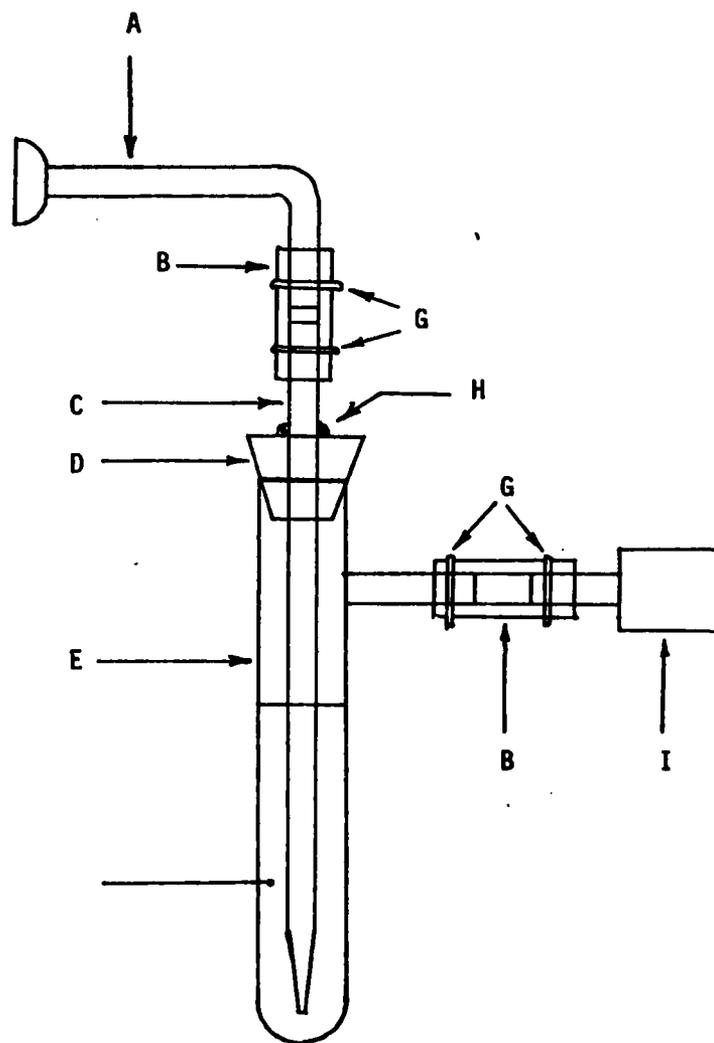


Figure 16. Schematic diagram of the vapor traps: A = 5 mm O-ring joint with 90° bent tube, B = Tygon tubing, C = 9 in micropipet, D = cork stopper, E = 150 mm x 18 mm side-arm test tube, F = diethyl phthalate, G = wire, H = glue bead, I = quick-disconnect hose fitting.

The simulant was introduced onto the fabric as three 20 ul-drops with the air flow interrupted. The initial traps were then attached and air flow was resumed. Traps were changed at predetermined intervals, and during these changes the air flow was interrupted.

5.6.7 Data Analyses

All trap samples were analyzed by GC. The measured parameter was the area ratio of the simulant to an internal standard. Comparison with known concentration standards gave the absolute concentration of simulant in the trap and, hence, the calculated total quantity of trapped simulant.

Due to large differences in retention time between simulants and diethyl phthalate, several trapping samples could be analyzed prior to elution of the diethylphthalate from the first injection. Some increase in retention time occurred as a result of the effective increase in liquid phase loading on the column stationary phase, but no alteration in sensitivity of the analysis was noted.

Several tests were undertaken to determine the adequacy of the overall procedure. There was initially some concern that the internal standard might be lost from the diethyl phthalate-standard mixtures placed in the simulant traps. However, in one 4 hr run with 50 ml/min of air flow through each trap, less than 2% loss of bromobenzene (1 part per trillion) from the diethyl phthalate was found. This loss was within the limit of error of the measurement and is thus negligible. Total retention of the simulant was shown in an experiment with 2-chloroethyl methyl sulfide (CMS) wherein two consecutive traps were used, and the second trap was found to contain only a trace of simulant. In the absence of a fabric sample, >95% of the simulant could be accounted for in the single trap.

5.6.8 Gas Chromatography

Two instruments were used at various periods during the research period, Varian model 940 and Varian model 2100 flame ionization systems, which were both equipped for on-column injection. A Hewlett-Packard Model 3380 digital integrator was used

with both instruments. The 940 used 1/8" x 10' stainless steel columns while the 2100 used 2 mm x 6' glass columns. Nominal injection size was 1.0 ml of diethyl phthalate for both instruments.

Specific analysis conditions for each simulant are summarized as follows.

2-Chloroethyl Methyl Sulfide (CMS)

Instrument: Varian 940

Column: 10' x 1/8" OD, 5% OV-101 on Chromosorb G-HP

Carrier: 15 ml/min N₂ or He

Temperatures: injector: 200°
column: 130°
detector: 300°

Internal Standard: bromobenzene.

2-Chloroethyl Isobutyl Sulfide (CIS)

Instrument: Varian 2100

Column: 6' x 2 mm ID, 2% OV-101 on Chromosorb G-HP

Carrier: 30 ml/min N₂

Temperatures: injector: 200°
column: 90°
detector: 300°

Internal Standard: bromobenzene

Column: 6' x 2 mm, 5% Carbowax 20 m on Chromosorb W/AQDMCS

Carrier: 30 ml/min N₂

Temperatures: injector: 200°
column: 110°
detector: 300°

Internal Standard: o-dichlorobenzene

Diisopropylfluorophosphate (DFP)

Instrument: Varian 2100

Column: 6' x 2 mm , 5% Carbowax 20M on Chromosorb W/AWDMCS

Carrier: 30 ml/min N₂

Temperatures: injector: 200°

column: 110°

detector: 300°

Internal Standard: *o*-dichlorobenzene

5.6.9 Special Notes Regarding the Fabric Testing Procedure and Test Results

The use of a positive pressure system can lead to leaks which cause loss of simulant. The only place where this actually caused a problem was at the trap-test apparatus joint, where the weight of the trap was supported through the joint. The problem was solved by using two clamps on each joint.

DFP does not penetrate either polyethylene or polyvinylchloride film sufficiently well to allow their use as an air flow partition in the test apparatus.

All simulants had a very low residence time in the test apparatus. About 90% loss occurred within 30 minutes. We are uncertain of the cause; however, it could be either the non-laminar air flow within the apparatus or the inherent volatility of the simulants.

Initial test fabric analyses with CMS have already been summarized in Monthly Technical Report No. 7, and at that time it was decided to continue testing with CIS. After performing more than 20 fabric analyses with CIS, it was determined that the extent of separation between CIS and its hydrolysis product is relatively small on the 1/8 in x 6 ft OV-101 GC column, and that co-injection of both compounds can sometimes give rise to only "one" peak. Hence, the CIS analyses under such conditions unreliable. Use of a 1/8 in x 6 ft 5% OV-17 column can be used to by-pass this separation problem, however, time for these additional studies was not available to us.

As a final note, it should be emphasized that the purity of the diethyl phthalate trapping medium is a crucial factor in the aforementioned GC analyses. To achieve the level of purity dictated by the analytical procedure utilized (i.e., trace analysis), all non-volatile material had to be removed and materials less volatile than diethyl phthalate had to be reduced to less than part per million levels. Accomplishing this task required a significant amount of work which is worthwhile to summarize.

Diethyl phthalate was purchased from Mallinckrodt, Baker, and Aldrich Chemical Companies. The stated purity was ca. 98%, and GC analyses revealed the presence of 15 to 30 detectable components more volatile than diethyl phthalate and 5 to 10 components which were less volatile. The "crude" diethyl phthalate was distilled through a 30 cm x 25 mm insulated fractionating column, and about 95% of the distillate was collected. The distillate was then placed in Flask B shown in Figure 17, and heat applied to the column and pot (B) was sufficient to allow the diethyl phthalate to slowly reflux at the top of the column (E).

Reflux under vacuum was maintained for 3 hr. A moderate quantity of material (50-100 ml) collected on the cold finger in the Dewar trap. Upon cooling to room temperature, vacuum was broken between the pot and the column and the contents of the pot were analyzed by GC. The procedure removes all components which directly interfere with analysis of CMS, CIS, and DFP simulants and generally leaves significant quantities of only one or two components more volatile than diethyl phthalate.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary of Important Findings

6.1.1 Z-6020 has been used to impart Nomex and cotton-blend fabrics with metal ion-chelation properties, which thus provides potential hydrolysis catalysts bonded to

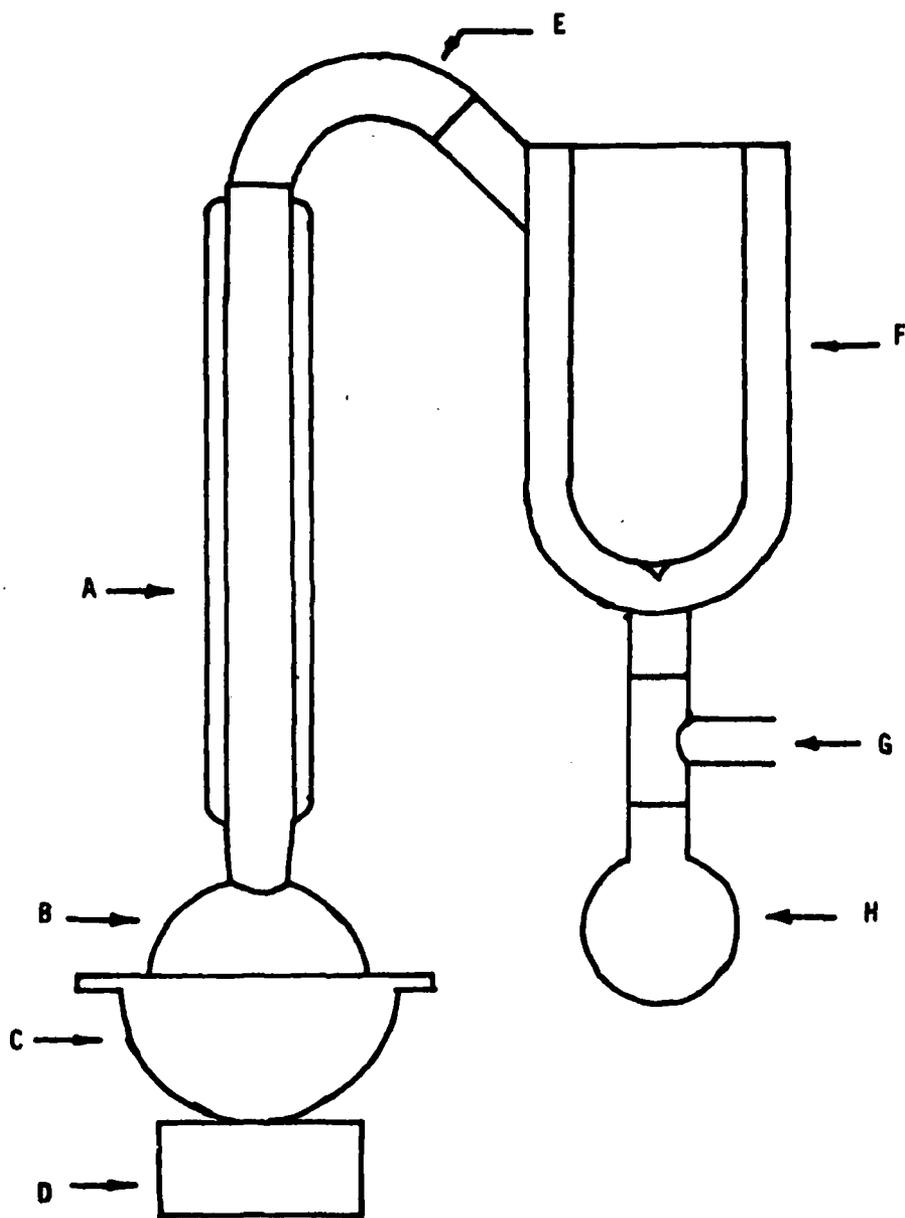


Figure 17. Schematic diagram of the vacuum fractionating apparatus for removal of low boiling components from diethyl phthalate: A = jacketed and heated fractionation column packed with glass helices, B = 2 l round bottom flask (pot), C = heating mantle, D = magnetic stirrer, E = 120° bent adapter, F = Dewar trap with CO₂ acetone (-79°) coolant, G = T-shaped adapter to vacuum, H = catch flask.

fabric surface. In this connection, the uptake of Cu^{+2} by Z-6020-modified Nomex was significantly enhanced by initial fabric "activation" by a Fenton's oxidation mixture of FeSO_4 , H_2O_2 , and EDTA. It was also found that fabric CO-treatments with Z-6020 and a cyano-silane led to more homogeneous modifications.

6.1.2 Diethylaminoethylated (DEAE) fabric was prepared with anion-loading capacities of 1.0-1.5 meq/g, which thus allowed for electrostatic bondings of potential polyoxy anionic hydrolysis catalysts such as molybdate, tungstate, vanadate, and phosphate.

6.1.3 Polymer-coated fabrics were prepared and were found to give fabrics with enhanced water uptake (ca 10%). The polymer-coating procedure was also used in conjunction with the bonding of various lanthanide hydroxide gels $\text{La}(\text{OH})_3$, $\text{Nd}(\text{OH})_3$, $\text{Y}(\text{OH})_3$, and $\text{Gd}(\text{OH})_3$ as potential hydrolysis catalysts.

6.1.4 A modified version of the Dawson cup apparatus was designed and constructed for modified fabric tests against the selected simulants, viz. CMS, CIS, and DFP. While the general functions of the system were highly successful, it was found that difficulties arose in the GC analyses and in the selective permeability of simulants through the test-cell's polymer-film partition membrane.

6.1.5 A mechanistic study of the sulfur mustard simulant has clearly demonstrated the need to achieve relatively high-levels of fabric moisture content in order to achieve reasonable rates of CMS hydrolysis.

6.1.6 The mechanism of DFP hydrolysis was studied by ^1H NMR model system for the sarin-type agents. In this manner, a wide variety of reported and candidate catalysts (free and fabric-bound) were evaluated. It was found that close pH control is necessary for meaningful comparisons, and that increased alkalinity leads to increased rates of DFP hydrolysis. The most promising catalysts were phosphate and N-hydroxyamides.

6.2 Selection and Prioritization of Modified Fabric Samples

We have delivered 28 modified fabric samples for testing as protective fabrics against toxic chemical agents. Each sample was provided in a separate envelope, with the Andrusis Research Corporation sample ID number.

The priority for testing, rationale behind that priority, and general description of the fabrics are given below.

6.2.1 Testing Priority 1, Lanthanide Hydroxide/Poly(ethyleneimine) Coated Fabrics.

The gross similarity of poly(ethyleneimine) to triamines and tetraamines, which are known to readily react with toxic chemical agents, indicates that this material alone might well be an effective fabric additive. The lanthanide hydroxide gels and certain soluble basic lanthanide complexes are known to catalyze the hydrolysis of a variety of phosphate derivatives. One section was prepared using magnesium and may therefore be used for evaluation as a non-lanthanide metal hydroxide. Coupled together, the hydroxide gels and polyamines offer reasonable promise for providing a protective system.

As prepared, the two-component fabric coating is water soluble. This should not interfere with initial testing; however, we realize that in a truly workable system, some form of bonding of the poly(ethyleneimine) to the fabric would be needed. Such bonding is certainly possible and can be pursued if warranted.

A list of fabrics in this category is given in Table 11.

6.2.2 Testing Priority 2, Anion Exchange Fabrics. If any conclusions are to be drawn from the literature and our own work, they should definitely include the assumption that the only reliable means of destroying the various organophosphorus agents is reaction with an active nucleophile. This generally means a rather strongly basic anion.

Repetitive treatment of cotton blend with strong base followed by treatment with 2-(diethylamino)ethyl chloride hydrochloride produces a modified fabric with moderate base-exchange capacity, which we believe to consist of short chains of poly(N,N-diethylethyleneimine) grafted onto the cotton. Fabrics containing phosphate, molybdate, tungstate, vanadate, and chloride counterions are included. One fabric section, which was an attempt to incorporate permanganate, seems to have decomposed to manganese dioxide; this later fabric is therefore of questionable composition but is included for completeness. All other fabrics except the chloride have anions which we expect to show reasonable reactivity with the agents.

Table 11. PRIORITY 1 FABRICS: METAL HYDROXIDE-POLY(ETHYLENEIMINE)
COATED FABRICS

<u>ARC ID No.</u> ^a	<u>Fabric</u>	<u>Wt. Metal Chloride</u>
ES-79A-134A	NOMEX	5.0 g $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-134B	COTTON	5.0 g $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-136A	NOMEX	4.3 g $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-136B	COTTON	4.0 g $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-136C	NOMEX	4.0 g $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-136D	COTTON	4.1 g $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-138A	NOMEX	4.2 g $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-138B	COTTON	4.1 g $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-138C	COTTON	5.0 g $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$

^aPrepared by coating a mixture of the metal chloride with 20 g of 30% poly(ethyleneimine) in 100 ml H_2O onto the fabric.

A list of these fabrics is given in Table 12.

6.2.3 Testing Priority 3, Silane Treated Fabrics. Several fabrics treated with mixtures of 3-(2-aminoethylamino)propyltrimethoxysilane (Z-6020) and 2-cyanoethyltriethoxysilane are included in this group. The amine functionality should provide a reactive site while the cyanoethyl moiety may provide a "holding" medium for the agent. Moderate loadings of amine functionality (about 1.5 meg/g of modified fabric) were achieved for the fabrics treated with Z-6020 alone. It is doubtful that this can be significantly increased without further research of the coupling chemistry.

A list of these fabrics is given in Table 13.

6.2.4 Testing Priority 4, Lanthanide Hydroxide Treated Fabrics. As noted in Section 5.2.1, the lanthanide hydroxides show some promise in the catalysis of several organophosphorus compounds. The fabrics were impregnated with the hydroxides by several procedures, and were then coated with poly(ethylene oxide) as a binder and holding agent. Their homogeneity and appearance need improvement, and they have some tendency to shed the hydroxide as a powder and should be handled carefully.

A list of these fabrics is given in Table 14.

Table 12. PRIORITY 2 FABRICS: ANION EXCHANGE FABRICS

<u>ARC ID No.</u>	<u>Anion</u>
ES-79A-127A	MO_4^{2-}
ES-79A-127B	WO_4^{2-}
ES-79A-127C	VO_3^-
ES-79A-127D	PO_3^{3-}
ES-79A-127E ^a	MnO_4^{2-}
ES-79A-127F	Cl^-

^aThis fabric decomposed; the most likely composition now includes MnO_2 .

Table 13. PRIORITY 3 FABRICS: SILANE TREATED FABRICS

<u>ARC ID No.</u>	<u>Ratio of $H_2NCH_2CH_2NHCH_2CH_2CH_2Si(OMe)_3$ To $NCCH_2CH_2Si(OEt)_3$</u>
VLB-79-77A	10:0
VLB-79-77B	5:5
VLB-79-77C	3:7
VLB-79-77D	3:10
VLB-79-77E	2:8
VLB-79-77F	1:9

Table 14. PRIORITY 4 FABRICS: LANTHANIDE HYDROXIDE IMPREGNATED FABRICS

<u>ARC ID No.</u>	<u>Fabric</u>	<u>Preparation</u>
ES-79A-126A	NOMEX	5.4 g of $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ plus 1 N KOH to pH 9.5 Slurry coated onto fabric then coated with aqueous polyethylene oxide
ES-79A-126B	COTTON	As - 126A using 5.1 g $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-130A	COTTON	1.0 g polyethylene oxide aqueous solution with 5.3 g $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$. Applied to fabric and then treated with 1 N KOH to precipitate $\text{La}(\text{OH})_3$
ES-79A-130B	NOMEX	As -130A using 5.1 g of $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-132	COTTON	5.0 g $\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous solution. Applied to fabric and then precipitated with 5 N NaOH
ES-79A-133	NOMEX	As -126A using 5.1 g $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$
ES-79A-133B	COTTON	As -126A using 5.0 g $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$

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Commander Naval Facilities Engineering Command Attn: Code 03 200 Stovall Street Alexandria, VA 22332	1	NORAD Combat Operations Center/DBN Cheyenne Mtn Complex, CO 80914	1
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Commander Nuclear Weapons Training Group, Atlantic Naval Air Station Attn: Code 21 Norfolk, VA 23511	1	OUTSIDE AGENCIES Battelle, Columbus Laboratories Attn: TACTEC 505 King Avenue Columbus, OH 43201	1
Chief, Bureau of Medicine & Surgery Department of the Navy Washington, DC 20372	1	Director of Toxicology National Research Council 2101 Constitution Ave, NW Washington, DC 20418	1
Commander Naval Weapons Center Attn: Code 3171 China Lake, CA 93555	1	ADDITIONAL ADDRESSEES Commander USEUCOM Attn: ECJ5-O/LTC James H. Alley APO, NY 09128	1