

UNCLASSIFIED

AD NUMBER
ADB022386
NEW LIMITATION CHANGE
TO Approved for public release, distribution unlimited
FROM Distribution authorized to U.S. Gov't. agencies only; Proprietary Information; OCT 1977. Other requests shall be referred to Chemical Systems Lab., DRDAR-CLJ-R, Aberdeen Proving Ground, MD 21070.
AUTHORITY
USAARDC ltr, 9 Mar 1979

THIS PAGE IS UNCLASSIFIED

THIS REPORT HAS BEEN DELIMITED
AND CLEARED FOR PUBLIC RELEASE
UNDER DOD DIRECTIVE 5200.20 AND
NO RESTRICTIONS ARE IMPOSED UPON
ITS USE AND DISCLOSURE.

DISTRIBUTION STATEMENT A

APPROVED FOR PUBLIC RELEASE,
DISTRIBUTION UNLIMITED.

ADB022386

AD

CONTRACTOR REPORT ARCSL-CR-77056

STUDY OF REACTIVE MATERIALS FOR DEVELOPMENT
OF NEW PROTECTIVE CLOTHING CONCEPTS

THIRD QUARTERLY PROGRESS REPORT

by

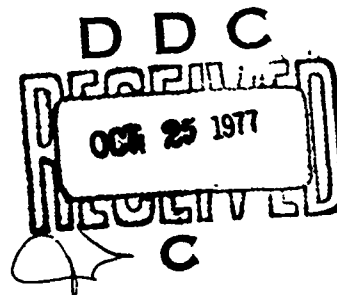
Donald R. Cowsar
Danny H. Lewis
Gary W. Whitehead

October 1977

Southern Research Institute
2000 Ninth Avenue South
Birmingham, Alabama 35205

Contract DAAAL5-77-C-0015

This document contains
proprietary information on
pp. 6 to 18 inclusive



US ARMY ARMAMENT RESEARCH AND DEVELOPMENT COMMAND
Chemical Systems Laboratory
Aberdeen Proving Ground, Maryland 21010

DDC FILE COPY

Distribution limited to U.S. Government agencies only
because of proprietary information; October, 1977.
Other requests for this document must be referred to
Director, Chemical Systems Laboratory, Attn: DRDAR-CLJ-R,
Aberdeen Proving Ground, Maryland 21010.

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Disposition

Destroy this report when no longer needed. Do not return it to the originator.

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

19 REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARCSI-CR-77056	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER (9)
4. TITLE (and Subtitle) STUDY OF REACTIVE MATERIALS FOR DEVELOPMENT OF NEW PROTECTIVE CLOTHING CONCEPTS		5. TYPE OF REPORT & PERIOD COVERED Third Quarterly Report Mar 1977 - Aug 1977
6. AUTHOR(s) Donald R. Cowsar, Danny H. Lewis Gary W. Whitehead		7. PERFORMING ORG. REPORT NUMBER SORT-3808-I
8. PERFORMING ORGANIZATION NAME AND ADDRESS Southern Research Institute 2000 9th Avenue South Birmingham, Alabama 35205		9. CONTRACT OR GRANT NUMBER(s) DAAA15-77-C-0015
10. CONTROLLING OFFICE NAME AND ADDRESS Director, Chemical Systems Laboratory Attn: DRDAR-CLJ-R Aberdeen Proving Ground, MD 21010		11. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Task 1L762710A09506
12. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) Director, Chemical Systems Laboratory Attn: DRDAR-CLW-P Aberdeen Proving Ground, MD 21010 (CPO - Sheldon Day 671-2801)		13. REPORT DATE Oct 1977
14. DISTRIBUTION STATEMENT (of this Report) Distribution limited to U.S. Government agencies only because of proprietary information; October, 1977. Other requests for this document must be referred to Director, Chemical Systems Laboratory, Attn: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010.		15. NUMBER OF PAGES 18
15. SECURITY CLASS. (of this report) UNCLASSIFIED		16. DECLASSIFICATION/DOWNGRADING SCHEDULE NA
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Chemical warfare agents Microencapsulation Protective clothing Polyamides Decontamination Ethyl cellulose Interfacial polymerization Simulants		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This report describes investigations of reactive materials suitable for incorporation in or on fabrics for protection from percutaneous chemical warfare agents. Microencapsulated forms of alkali metal hydroxides and aliphatic amines were prepared and are currently being evaluated as reactive materials for the deactivation of chemical agents. Preliminary results indicate that agent simulants can be effectively neutralized by the encapsulated materials.		

DD FORM 1 JAN 73 1473

NOV 65 IS OBSOLETE

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

328 100

mt

PREFACE

The research described in this report was authorized under Task 1L762710A09506, Body Protection Investigations. The work was conducted from May 20, 1977, through August 22, 1977. The experimental data are contained in Notebooks 8573 and 8699.

The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Director, Chemical Systems Laboratory, Attn: DRDAR-CLJ-R, Aberdeen Proving Ground, Maryland 21010; however, Defense Documentation Center is authorized to reproduce the document for United States Government purposes.

The information in this document has not been cleared for release to the general public.

ACKNOWLEDGMENT

Mr. Charles T. Riddle, Assistant Chemist, made significant contributions to the work described in this report.

ACCESS to or	
NTIS	White Section <input type="checkbox"/>
DDC	Grey Section <input checked="" type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	SPECIAL
B	

SUMMARY

The objective of this work is to investigate reactive materials suitable for incorporation in or on fabrics for protection from percutaneous chemical warfare (CW) agents. These can be in the form of materials applied to the fabric or by modification of the fabric itself. Such sites must show reactivity for H, G, and V agents and must not unduly change the fabric permeability.

Microencapsulation, the technique of encasing extremely small droplets or particles of active materials in protective or functional coatings, is being investigated in the development of new protective clothing concepts. We are preparing and evaluating decontaminating microcapsules that contain strong-base alkali-metal hydroxides, sym-bis(N-chloro-2,4,6-trichlorophenyl) urea, and various amines as the core phase. We are now identifying and developing microcapsule wall materials that will be stable to the highly basic core agents and contain them effectively and yet will be permeable to CW agents. The microcapsules will be applied with resin binders to fabric substrates.

We have used the interfacial polymerization and phase separation methods to microencapsulate both aqueous and nonaqueous materials, including aqueous sodium hydroxide, monoethanolamine, ethylenediamine, N,N-dichlorodimethylhydantoin, sym-bis(N-chloro-2,4,6-trichlorophenyl)urea, and sodium hypochlorite in polyamide and ethyl cellulose walls.

We continued to use batch screening methods for determining the potential reactivity of the candidate microcapsules with agents. We developed gas chromatography techniques to evaluate the reactivity of microcapsules with mustard, HD. The results of our evaluations suggest that unencapsulated and microencapsulated alkali-metal hydroxides and aliphatic amines deactivate mustard very slowly. We found that microcapsules comprising ethyl cellulose as the wall material and XXCC3 as the core material would deactivate neat mustard rapidly. We are now assessing the stability of the ethyl cellulose microcapsules.

CONTENTS

	<u>Page</u>
I. STATEMENT OF THE PROBLEM	5
II. BACKGROUND	5
III. APPROACH TO THE PROBLEM	6
IV. RESULTS.	6
A. Candidate Microcapsules	8
B. Development of Microcapsule Screening Procedures . . .	11
C. Reactivity Studies	12
V. DISCUSSION OF RESULTS	14
A. Screening Procedures	15
B. Reactivity of Candidate Microcapsules	15
VI. CONCLUSIONS	16
VII. FUTURE WORK	16
DISTRIBUTION LIST	19

STUDY OF REACTIVE MATERIALS FOR DEVELOPMENT OF NEW PROTECTIVE CLOTHING CONCEPTS

I. STATEMENT OF THE PROBLEM

The objective of this work is to investigate reactive materials suitable for incorporation in or on fabrics for protection from percutaneous chemical warfare (CW) agents. These can be in the form of materials applied to the fabric or by modification of the fabric itself. Such sites must show reactivity for H, G, and V agents and must not unduly change the fabric permeability.

II. BACKGROUND

There are two mechanisms by which a textile material may now afford protection against CW agents. One of these is sorption, which is provided by carbon-treated foams and non-woven fabrics; the other is chemical deactivation, which is provided by chloroamide-treated clothing items. Since the protective clothing must be effective against all types of CW agents, sorption might, at first consideration, appear to have a considerable advantage in this respect. However, because the activated charcoal in current protective garments does not neutralize CW agents but merely sorbs them, subsequent desorption is a potential problem. Desorption is particularly troublesome when contaminated garments are worn into protective enclosures or when they are discarded for replacement.

Chloroamides of various types have been impregnated in clothing materials for CW-agent protection. These compounds readily liberate hypochlorite in the presence of moisture. Chloroamides attack mustards such as H to form sulfoxides by oxidation and attack phosphorylating agents such as GB and VX to induce hydrolysis. However, clothing treated with chloroamides gradually loses its effectiveness and requires periodic retreatments. Moreover, chloroamides cause severe skin irritation in some individuals.

Many bulk reagents are effective neutralizers and decontaminants for CW agents. Current storable formulations are based on strong-base reagent combinations such as lithium hydroxide in monoethanolamine (MEA) and sodium hydroxide and diethylenetriamine in methyl cellosolve. Unstable formulations such as sodium and calcium hypochlorite (Chlorox and HTH) are also effective. Hydroxamic acids, oximes, phenols, and metal-ion complexes are all effective in promoting the deactivation of chemical agents in aqueous solutions. However, none of the

bulk chemicals has been suitably formulated for application to fabrics to provide protective clothing.

III. APPROACH TO THE PROBLEM

Microencapsulation, the technique of encasing extremely small droplets or particles of active materials in protective or functional coatings, should prove useful in the development of new protective clothing concepts. Stable microcapsules containing colorless but reactive dyes have been applied to nonwoven substrates, such as paper, to produce carbonless copy paper, e.g., NCR's "no-carbon-required" business papers. Microcapsules containing fragrances have been applied to books and advertisements to produce "scratch-and-smell" articles. In numerous other applications microcapsules are being used to separate active ingredients, to control odor, to mask taste, to control volatility and flammability, to moderate chemical reactivity, to provide slow release of contents, and to protect the environment. Microcapsules containing methyl parathion within walls of semi-permeable nylon are currently being marketed as a controlled-release pesticide formulation.

Microcapsules have been used as sorbing and deactivating agents. Microcapsules of sodium hydroxide have been used to remove phenols and other organic acids from refinery waste water, and microcapsules containing organic solvent have been used to remove MEA from aqueous solutions.

With the microcapsule approach to protective clothing, we are preparing and investigating decontamination microcapsules that contain strong-base alkali metal hydroxides and various primary and secondary amines as the core phase. We are identifying and developing polymeric wall materials that will be stable to the highly basic core reagents and contain them effectively and yet will be permeable to CW agents. Since the microcapsule walls are very thin, i.e., 1 to 10 micrometers (μm), we anticipate that agent-permeation rates can be maximized. The program comprises the microencapsulation of standard decontamination materials which have known reactivity with H, G, and V agents, and the evaluation of microcapsules applied to fabric substrates.

IV. RESULTS

In the early stages of the project, most of our effort was directed toward the development of laboratory procedures for microencapsulating agent-reactive decontamination materials in semipermeable polymeric films. We have successfully adapted the interfacial polymerization method of micro-

encapsulating liquid microdroplets in condensation polymers formed in situ for this application. We have used the method to microencapsulate both aqueous and nonaqueous core materials, including sodium hydroxide, monoethanolamine, ethylenediamine, diethyltriethylamine, and poly(ethyleneimine), in polyamide (nylon) walls.

The second reporting period was largely directed toward development of procedures for the screening of candidate microcapsule systems for agent reactivity. Two reagents, diphenyl chlorophosphate and methanesulfonyl chloride, were evaluated as potential simulants for chemical-warfare agents. Most of our earlier evaluations were based on the DB-3 method which utilizes the colorimetric reagent δ -(4-nitrobenzyl)pyridine. Although the DB-3 method is sensitive, it is laborious and requires the development of optimum conditions for individual simulants. Even with the best conditions, however, we experienced variability in the technique due to deterioration of reagents or to unknown causes. Our experiments indicated that solutions of monoethanolamine and sodium hydroxide will not significantly decontaminate diphenyl chlorophosphate under the conditions employed in our tests. The reaction of methanesulfonyl chloride with those

agents does not appear to be exceptionally fast either, although methanesulfonyl chloride reacts considerably faster than diphenyl chlorophosphate. In addition, our preliminary results indicated that microcapsules decontaminate dilute solutions of simulants at much slower rates than they decontaminate neat simulants.

During the current reporting period, we developed procedures designed to evaluate the reactivity of candidate microcapsules with HD. In most of our screening procedures, we contaminated microcapsules with neat agent rather than with dilute solutions. After appropriate equilibration periods, unreacted mustard was washed from the microcapsules with hexane and analyzed by standard gas chromatography techniques. The results of our evaluations of alkali-metal hydroxides and aliphatic amines as potential core materials suggest that the rates of decontamination of HD are slower than expected. When we contaminated 0.03 gram (g) of a typical core solution containing 90% of monoethanolamine, 5% of sodium hydroxide, and 5% of water with 0.02 g of neat HD, we found 20% deactivation after 4 hours and 65% deactivation after 24 hours. In addition, we found that freshly prepared polyamide microcapsules containing these same core materials deactivated 19 and 35% of the HD during 4 and 24 hr, respectively. After the microcapsules were aged in closed containers for several weeks, no change in decontaminating ability was noticed.

In view of the low reactivities observed for polyamide microcapsules containing monoethanolamine and sodium hydroxide cores, considerable effort was expended in developing new candidate

microcapsule systems. We were successful in preparing organic-core polyamide microcapsules containing saturated solutions of RH-195, and sym-bis(N-chloro-2,4,6-trichlorophenyl)urea(CC2). When we screened these microcapsules for mustard reactivity, we found decontamination rates similar to those observed for microcapsules containing monoethanolamine and sodium hydroxide.

We recently developed a phase-separation technique for encapsulating XXCC3* in ethyl cellulose. When we screened these microcapsules for mustard reactivity, we observed rapid rates of decontamination. We found that 0.30 g of ethyl cellulose microcapsules which contain 75% of XXCC3 will deactivate 87% of neat mustard (0.02 g) in less than 1 hour.

A. Candidate Microcapsules

Our first evaluations with simulants of microcapsules containing cores of alkali-metal hydroxides and aliphatic amines suggested that the deactivation potential of those microcapsules gradually decreased as the microcapsules were aged. Accordingly, much of the current reporting period was devoted to the preparation and evaluation of new microcapsule systems. The core reagents and wall materials we have utilized in recent batches of microcapsules are shown in Table 1.

Microcapsules from Batches 8699-72, -94, and -125 were prepared by the method described in our First Quarterly Report. As indicated, the core in Batch 8699-94 contains 1% of 4-(N,N-dimethylamino)pyridine, a hypernucleophilic acylating agent. This reagent has been used by numerous workers as a powerful catalyst in acyl transfer reactions, and in this use it is superior to pyridine and other tertiary amines. We reasoned that this amine should catalyze the hydrolysis of HD and the phosphate esters, such as GD and GA, and make the kinetics of decontamination in the core material much faster.

During this period, we were successful in preparing organic-core polyamide microcapsules containing saturated solutions of N,N-dichlorodimethylhydantoin (RH-195) and sym-bis(N-chloro-2,4,6-trichlorophenyl)urea (CC2). The microcapsules were prepared by modification of the interfacial polymerization described in our First Quarterly Report. Although the modification was simple in concept, a number of trials were required to optimize the process for specific core materials and wall-forming polymers. The following are the experimental details of the method we developed for preparing polyamide microcapsules containing primarily a saturated solution of RH-195 in a mixture of tetrachloroethylene and epichlorohydrin. The core composition of these microcapsules was chosen because of its known decontaminating ability.

* XXCC3 is 90% by weight sym-bis(N-chloro-2,4,6-trichlorophenyl)urea (CC2) and 10% by weight ZnO.

Table 1. Core Reagents and Wall Materials
of Candidate Microcapsules

Batch	Core Reagents	Wall Material
8699-71	HTH	ethyl cellulose
8699-72	95% MEA 5% NaOH	polyamide
8699-82	XXCC3	ethyl cellulose
8699-92	67% tetrachlorethylene 29% epichlorohydrin 4% RH-195	polyamide
8699-94	89% MEA 5% H ₂ O 5% NaOH 1% 4-(N,N-dimethyl)- aminopyridine	polyamide
8699-105	XXCC3	ethyl cellulose
8699-120	92% CCl ₄ 8% XXCC3	polyamide
8699-125	90% MEA 5% NaOH 5% H ₂ O	polyamide
8699-126	96% CHCl ₃ 4% CC2	polyamide

Microencapsulation Procedure (Batch 8699-92):

We prepared an aqueous dispersing medium by dissolving 1.4 g of poly(vinyl alcohol) (Vinol 205, Air Products) in 55 g of hot (80°C) deionized water. After cooling the mixture to room temperature, we added 1.6 g of hexanediamine, 0.2 g of ethylenediamine, and 5 g of concentrated hydrochloric acid. We prepared an organic phase by dissolving 0.45 g of RH-195 in 3 g of epichlorohydrin and 7 g of tetrachlorethylene. An emulsion was formed by our adding the organic phase to the dispersing medium and stirring at 700 rpm. After 1 minute the stir rate was reduced to 400 rpm, and 8.75 g of 4 N sodium hydroxide was added to neutralize the amine hydrochloride salts. At this point a polyamide wall formed rapidly around the core microdroplets. The microcapsules were stirred at 400 rpm for 1 hour to ensure complete wall formation. The microcapsules were isolated by dilution with 100 milliliters of water, filtration on a Büchner funnel, and repeated water washes. The dry microcapsules weighed 1.25 g and ranged in size from 25 to 75 μ m in diameter. Microcapsules from Batch 8699-126 were prepared by the method described above with one exception. The core material was comprised of 96% of CHCl₃ and 4% of CC2. The CC2 used in this preparation was isolated from XXCC3 by extraction into CHCl₃ and removal of ZnO by gravity filtration.

Microcapsule Batches 8699-71, -82, and -105 were prepared with ethyl cellulose as the wall material because of the known high permeability of HD through cellulose polymers. We were successful in preparing ethyl cellulose microcapsules containing the solid decontaminants sodium hypochlorite (HTH) and stabilized XXCC3, but we were unsuccessful in preparing stable ethyl cellulose microcapsules containing RH-195. These ethyl cellulose microcapsules were prepared by a phase separation technique which utilizes the solubility difference of the polymer in hot and cold cyclohexane. In each case, the ethyl cellulose was dissolved in hot (refluxing) cyclohexane, the insoluble core material was added, and phase separation (precipitation) was induced by cooling. Again, a number of trials were required to optimize the stir rates and cooling times in order to obtain microcapsules of the proper size. The following are the experimental details we developed for the encapsulation of XXCC3 in ethyl cellulose.

Microencapsulation Procedure (Batch 8699-82):

We prepared a nearly saturated solution of ethyl cellulose (Dow Ethocel, Type 20) by adding 4 g of

polymer to 98 g of refluxing cyclohexane. The solution was heated and stirred with a 4-blade impeller at 800 rpm until the ethyl cellulose had dissolved. The stir rate was then increased to 1500 rpm, 4 g of XXCC3 was added, and the heat source was removed. As the solution was stirred and allowed to cool, the polymer separated from solution and encapsulated the dispersed XXCC3. After 2 hours the microcapsules were isolated by filtration and washed with cold cyclohexane. Residual solvent was removed by the application of vacuum, and the yield of microcapsules was 3.9 g. The microcapsules ranged in size from 50-250 micrometers.

B. Development of Microcapsule Screening Procedures

In general, our earlier evaluations of candidate microcapsules systems were hindered by the use of unsatisfactory simulants, by the variability of the DB-3 method, and by the use of methanol as a solvent for decontamination studies. In addition, we found the rates of decontamination of simulants in solution to be much slower than the rates with neat reagents.

Accordingly, we abandoned the use of simulants and developed screening procedures based on agents, and more specifically the mustard HD. In most cases, we contaminated microcapsules with neat HD rather than with dilute solutions. After appropriate equilibration periods, unreacted HD was washed from the microcapsules with an aprotic solvent and analyzed by standard gas chromatographic techniques. When we followed the disappearance of HD by the peak-height technique, we found some discrepancies in the data after the microcapsules remained in contact with mustard for more than eight hours. In some cases, we observed almost linear decreases in the concentration of mustard for the first eight hours and then slight increases after that time. We reasoned that small changes in the chromatographic conditions were responsible for the observed changes in the peak heights of the standards. To minimize errors of this type, our later evaluations were based on the use of 0-dichlorobenzene as an internal standard. The concentrations of HD were calculated from a ratio of peak heights between those of the internal standards and those of mustard. Our procedures were further optimized by changing the chromatographic conditions, and the best evaluations were based on a linear temperature program rather than isothermal conditions.

Our initial studies based on the peak heights of mustard without an internal standard were carried out as follows: Several 0.03-g samples of a given microcapsule batch were weighed

into one-dram vials. The vials were then charged with 15 microliters (μl) of mustard HD, and after appropriate periods the samples were quenched with 1 ml of hexane. These sample weights were chosen to allow for at least a 3:1 excess of active decontaminating agent over HD. These excesses would minimize slow reaction rates due to low concentrations of deactivating agent. Appropriate volumes (5 μl) of the hexane washes were injected into a Tracor 560 gas chromatograph equipped with a 1 meter x 3 millimeter outside-diameter column loaded with 10% of Apiezon L on acid-washed Chromosorb Q. The retention time of the HD was four minutes at a column temperature of 150°C. The concentration of HD was determined by comparison of the peak heights with that of calibration standards.

Although the procedure is reasonably accurate ($\pm 5\%$), the method is hindered by our inability to disperse the liquid HD evenly over the sample of microcapsules. A small clump of microcapsules retain most of the HD, and care must be taken to deliver the agent directly onto the microcapsules. In future studies, we plan to contaminate the microcapsules with dilute solutions of HD in a volatile solvent like diethyl ether, and remove the solvent rapidly by application of a light vacuum. Nevertheless, the data reported in the following section allow us to make a number of conclusions concerning the reactivity of various batches of microcapsules.

C. Reactivity Studies

Our earlier evaluations of microcapsules containing cores of alkali-metal hydroxides and aliphatic amines suggested that the deactivation potential of these microcapsules gradually decreases as the microcapsules are aged. We also found that the reactivity of the simulant, diphenyl chlorophosphate, was very low. The reaction of methanesulfonyl chloride with those reagents does not appear to be exceptionally fast either, although methanesulfonyl chloride reacts considerably faster than diphenyl chlorophosphate. Our recent results indicate that monoethanolamine and sodium hydroxide also react slowly with HD.

As shown in Table II, we found the deactivation of HD by a solution comprising 90% of monoethanolamine, 5% of sodium hydroxide, and 5% of water to be very slow. This solution is equivalent to that expected in the core of microcapsules from Batch 8699-72. Approximately 50% of the HD was decontaminated by these reagents over a period of eight hours. In addition, microcapsules prepared with these same reagents in the core

Table II. Deactivation of HD by Polyamide Microcapsules
Containing Primary Monoethanolamine and
Sodium Hydroxide

Sample	Core Reagents	Agent remaining		
		1 hr	4 hr	8 hr
Solution	95% MEA 5% NaOH	90	68	50
Fresh microcapsules 8699-72	95% MEA 5% NaOH	94	80	70
Aged microcapsules 8573-130	90% MEA 5% NaOH 5% H ₂ O	95	85	76
Solution	89% MEA 5% NaOH 5% H ₂ O 1% 4-(N,N-dimethyl- amino)pyridine	88	60	40
Fresh microcapsules 8699-94	89% MEA 5% NaOH 5% H ₂ O 1% 4-(N,N-dimethyl- amino)pyridine	94	82	68

decontaminated only 30% of the HD over the same period of time. Microcapsules that had been aged in closed containers for three months showed only a slight reduction in decontaminating ability as they destroyed 24% of the HD in eight hours. We do not view this slight reduction in reactivity for the aged microcapsules as significant since we have observed $\pm 5\%$ variations in the HD assays. We are currently evaluating microcapsules that have been aged in open containers, and these evaluations should provide us with valuable information concerning deactivation by sorbed carbon dioxide. Our results with alkali-metal hydroxides and aliphatic amine solutions containing 1% of the hypernucleophilic agent 4-(N,N-dimethylamino)pyridine indicate no significant acceleration in decontaminating ability for HD. As shown in Table II, we found 60% of the HD deactivated after eight hours of contact with a solution comprising 89% of monoethanolamine, 5% of sodium hydroxide, 5% of water, and 1% of 4-(N,N-dimethylamino)-pyridine. These results are similar to those of solutions containing only monoethanolamine and sodium hydroxide. We plan to evaluate at least one more solution containing this accelerating agent at an increased concentration of about 20%.

As indicated in Table III, we found the reactivity of polyamide microcapsules containing either a organic solution of CC2 or a slurry of XXCC3 to be very low for HD. In each case, less than 2% of the HD was deactivated over a period of 4 hours for either of the core components or the microcapsules. We reasoned that CC2 was inefficient as a decontaminating agent when used without the benefit of moisture.

When we evaluated microcapsules comprising XXCC3 cores and ethyl cellulose walls, we found rapid decontamination of HD. As indicated in Table IV, only 13% of the mustard remained after the first hour of contact with microcapsules. We view these results as most promising and intend to apply these microcapsules to fabric. We are currently assessing the stability of the microcapsules during exposure to heat, ultraviolet light, and moisture. Table IV also indicates that ethyl cellulose microcapsules containing the commercial bleach HTH decontaminate HD very slowly. After eight hours these microcapsules deactivated only 28% of the agent. In addition, we found no difference between microcapsules that were kept dry and those allowed to adsorb water vapor at 25°C for several days.

V. DISCUSSION OF RESULTS

In general, we have been successful in preparing a number of candidate microcapsule systems for evaluation. Earlier

Table III. Deactivation of HD by Polyamide Microcapsules
Containing CC2 in CHCl_3 and XXCC3 Slurried in CCl_4

Sample	Core Reagents	Agent Remaining,		
		1 hr %	2 hr %	4 hr %
Solution	0.12 <u>M</u> CC2 in CHCl_3	>98	>97	>98
Microcapsules 8699-126	0.12 <u>M</u> CC2 in CHCl_3	>98	>98	>98
Solution	XXCC3 slurried in CCl_4	>97	>99	>98
Microcapsules 8699-120	XXCC3 slurried in CCl_4	>98	>98	>98

Table IV. Deactivation of HD by Ethyl Cellulose
Microcapsules Containing HTH or XXCC3

Sample	Core Reagent	Agent remaining,		
		<u>1 hr</u> %	<u>4 hr</u> %	<u>8 hr</u> %
8699-71 (dry)	HTH	96	84	72
8699-71 (wet)	HTH	94	80	70
8699-82 (dry)	XXCC3	13	10	10

our screening procedures were hindered by the use of unsatisfactory simulants. During this period, however, we have developed screening procedures based on the gas-chromatographic analysis of HD. Our preliminary results indicated the need for optimizing our assays. We observed some inaccuracies in our techniques, but the errors were minimized by careful control of gas chromatographic conditions and by the use of internal standards.

The most significant observation thus far is the slow reactivity of polyamide microcapsules containing monoethanol amine and sodium hydroxide. In the following sections, we present the variables we have explored and discuss the problems we have encountered.

A. Screening Procedures

In our recent screening procedures we have analyzed for unreacted HD based on the gas chromatographic (GC) assay using peak heights as an estimate for HD concentration. We found we could not always depend on accurate results due to slight variations in chromatographic conditions. Accordingly, we minimized these errors by the use of internal standards. We also found that a more uniform method of contamination was needed for reproducible results. In our current procedure a portion of the microcapsules sorb the agent resulting in a wet clump of microcapsules. Since the clump of microcapsules occludes some of the HD, we have been unable to wet all of the microcapsules evenly. We, therefore, have been unable to measure the total deactivating capacities of the microcapsules. In the future, we plan to contaminate the microcapsules with dilute solutions of HD and remove the solvent by application of a mild vacuum.

B. Reactivity of Candidate Microcapsules

Since we observed slow reactivity for polyamide microcapsules containing monoethanolamine and sodium hydroxide cores, we searched for other core reagents and wall materials that would give faster deactivation. As one approach, we added the hyper-nucleophilic acylating agent 4-(N,N-dimethylamino)pyridine to the core material. In addition, we used the interfacial polymerization technique to encapsulate a number of known organic decontaminating agents including RH-195, XXCC3, and CC2. Our most promising results have come from ethyl cellulose microcapsules containing solid XXCC3. We observed fast kinetics of deactivation, less than 1 hr, but several questions remain unanswered. In future work we must determine the stability of these microcapsules, particularly in view of the light sensitivity of XXCC3.

VI. CONCLUSIONS

The progress made during the first three quarters of this project have been substantial. We have optimized the interfacial polymerization method of microencapsulating alkali-metal hydroxides and aliphatic amines. We have modified this method to incorporate other agent-reactive materials including XXCC3, CC2, and RH-195. The phase-separation technique has been successfully adapted, and we have encapsulated solid XXCC3 and HTH in ethyl cellulose. Our preliminary reactivity studies indicate that polyamide microcapsules containing monoethanolamine and sodium hydroxide cores may be too slow in deactivating HD. These microcapsules are not suitable for protection against mustard. Fast deactivation of HD was found for microcapsules comprising XXCC3 in ethyl cellulose, and an investigation of the stability of these microcapsules is extremely important as we enter the last quarter of this project.

VII. FUTURE WORK

In the future, we will continue to screen candidate microcapsules for agent reactivity. With our improved assay procedures, based on the gas chromatographic analysis of HD, we should be able to eliminate the variability that we have observed in the past. The encouraging results with the ethyl cellulose microcapsules containing XXCC3 will be followed by stability studies. These will include evaluations of heat, light, and moisture sensitivity.

We selected a number of candidate resin finishes that are used as durable fabric binders. During the next period we will apply several formulations of microcapsules and binders to fabrics and evaluate their effects on the fabric hand. We plan to examine the treated fabrics by obtaining scanning electron micrographs, and we will then use agents to evaluate the reactivity of the treated fabrics by the Edgewood permeation-cell technique.

DISTRIBUTION LIST

Administrator
Defense Documentation Center
Attn: Accessions Division
Cameron Station
Alexandria, VA 22314

2

Commander/Director
Chemical Systems Laboratory
Attn: DRDAR-CLW-P/Mr. Sheldon Day
Aberdeen Proving Ground, MD 21010

20

Dir of Proc, ARRADCOM
Attn: DRDAR-PRB-S

1

Chief, Dev Spt Div
Attn: DRDAR-CLJ-L
DRDAR-CLJ-R
Chief, Phys Prot Div
Attn: DRDAR-CLW

3

1

1

Chief, Ind Prot Br
Attn: DRDAR-CLW-P

1

Phys Prot Div
Ind Prot Br
RECORD COPY

1

Mr. Sheldon E. Day
Contract Project Officer
Phys Prot Div
Ind Prot Br

6

Commander
US Army Natick Research and Development
and Development Command
Attn: DRXNM-VCC
DRXNM-VMP/Dr. R. Macnair
DRXNM-TRL
Natick, MA 01760

1

1

1

Commander
US Army Development and
Readiness Command
Attn: DRCDE-DW-S
Alexandria, VA 22333

2

Office of Technical Director

1