

Reactive Coatings Literature Review

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Reactive Coatings Literature Review

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Executive Summary

This document is a review of reactive coatings to protect military personnel from chemical and biological warfare (CW/BW) agents. Decontamination of surfaces exposed to chemical or biological agents presents a major challenge to U.S. forces. Present decontaminants may have problems with toxicity or corrosion; all decontamination solutions present the logistical challenge of supplying them when and where they are needed. Reactive coatings would be available at any time, enhancing protection while simplifying logistics. Ideally, a reactive coating would not add significantly to the cost or weight of the coating system and would not compromise other properties of the coating.

The purpose of this review is to identify available technologies and ongoing research in reactive coatings for military equipment. We define a reactive coating as a surface coating that neutralizes chemical or biological threats by a chemical reaction. We first considered requirements for reactive coatings. Key elements are the rate of decontamination, effectiveness against the full range of threats that U.S. forces are exposed to, ability to maintain performance under all conditions, safety and environmental friendliness, and the ability to preserve critical coating properties such as camouflage and corrosion protection. While the systems surveyed reported activity against one or more threats, none reported performance against a full range of threats, which would be necessary for a complete systems evaluation. For example, activity against agents deposited on particulate materials ("dusty" mustard or weaponized anthrax) has not been addressed. Clearly, durability in field conditions is also critical, but this aspect was seldom addressed in the systems we surveyed and would require much more extensive testing.

In performing this review TDA Research, Inc. (TDA) searched available databases, including the Defense Technical Information Center (DTIC), the Chemical and Biological Information and Analysis Center (CBIAC), and the U.S. Patent and Trademark Office. We also searched the scientific and technical literature, including proceedings of the Scientific Conference on Chemical and Biological Defense Research. We prepared a survey requesting information on reactive coatings that was sent to individuals and organizations identified as potentially having technologies of interest. For each reactive coatings technology identified, we asked the following questions: What is the technology? What is the proposed mode of action? What threat(s) does it address? What procedures were used to evaluate it?

As background to this review we summarized the applicable chemistry, identifying three fundamental types: stoichiometric reactants, rechargeable stoichiometric systems (principally containing active halogen), and catalytic systems. We carried out calculations to estimate the capacity of stoichiometric systems, and found that stoichiometric systems could be effective against vapor threats or light to moderate aerosol threats. Catalytic systems, assuming rapid kinetics and high turnover numbers, would be suitable even for heavy challenges with CW agent aerosols. In reviewing the applicable mechanisms for detoxification we considered oxidation and hydrolysis, as applied to a range of CW agents. We concluded that a practical system will likely involve more than one detoxification mechanism in order to address the full range of threats.

We also identified some additional opportunities for reactive coatings that were not addressed in any of the systems now reported to be in development. Catalytic reactive coatings systems are under development, and enzymatic catalysis has previously been applied to chemical defense, but we found no systems using enzymes in coatings. This represents an area for future R&D. With an enzymatic or any other catalytic process there is the potential for complete inhibition to decrease the rate of the catalyzed reaction. We cited research relevant to this area and recommend that it be carefully considered in future work.

TDA also considered the optimal diffusivity of threat agents in a reactive coating. If the reactant is evenly distributed throughout the coating, then the agent must diffuse relatively rapidly in order to use all of the available capacity. However, standard practice in chemical agent resistant coatings (CARCs) is to decrease the agent diffusivity in order to minimize re-emission. Low diffusivity of the agent in the coating implies that only the reactive component on the surface will be effective. In considering means to control diffusivity of small molecules in coatings we reviewed recent work on reactive barriers in coatings. This could be a useful approach to reactive coatings. Our study also pointed out that a systematic assessment of the diffusion rate of threat agents in coatings would be useful to the development of reactive coatings in general and catalytic reactive coatings in particular.

TDA identified a range of reactive coating technologies under development, but none that was commercially available. Most of the technologies surveyed appeared to be at an early stage of development. We considered the projected cost of the systems, but found insufficient data to make any conclusions on cost. In general we found little consistency in the way that the systems had been evaluated. We classified the systems reviewed as primarily focused on either chemical or biological defense, although there is clearly some overlap. Both stoichiometric and catalytic CW protective systems were identified, with the stoichiometric systems being closer to commercialization. Surprisingly little effort has been directed at systems for catalytic detoxification of VX, and this appears to be an area requiring further focused research.

Several coatings with antimicrobial properties were identified. We found no generally accepted test methods or standards for performance of antimicrobial protective coatings. For example, we asked whether coatings were effective against bacterial spores but found little indication that these tests had been performed. We also asked about measures of lethality (e.g., 6-log kill) but again found no consistency. One approach to antimicrobial coatings was systems that slowly release halogen, which could potentially also afford some defense against CW agents. We classify these systems as stoichiometric coatings since there is an irreversible reaction. One technology, by Triosyn, is fairly well advanced toward commercial application. Another technology, licensed to Halosource, can be recharged by surface application of a reactant such as bleach. We classified this as a regenerable stoichiometric system. Other antimicrobial coatings used fixed groups such as quaternary ammonium ions. While these systems might offer a longer service life than those that release halogen, we found no conclusive tests of durability in service. Antimicrobial systems could be deactivated by formation of a dust, oil or protein fouling layer on the surface, but this issue has not been addressed.

In summary, we find that the potential advantage of reactive coatings has led to development of systems using a wide range of approaches. Although none of these are yet commercial, some are fairly well advanced. Spurred by recent threats to the U.S. military and the civilian population, several active research projects are making significant progress. To support this research we make the following recommendations:

Reactive coatings research and development would benefit if technology developers had a generally accepted list of threat scenarios. A task force under Government direction could compile a list of scenarios that should be considered, which would facilitate broader understanding and comparison of competing technologies.

Similarly, research into chemical defense has long suffered from use of a wide range of simulants and test methods. At least for the limited area of reactive coatings, it should be possible to establish a systematic series of protocols to facilitate evaluation of developmental

technologies. For example, the R&D process could begin with experiments using threat agent analogs selected to screen for activity in specific area. The most effective materials could then be tested against other analogs or under more realistic conditions. The development process should move as rapidly as feasible to tests with live agents. Durability or longevity under field conditions has generally not been addressed. To assure that research efforts are properly directed, performance under field conditions should also be considered as early as is feasible.

Diffusion of chemical agents in coatings is well known but has not been quantified or modeled. For catalytic chemical protective coatings the solubility and diffusion of (for example) O₂ and H₂O in the matrix may also be critical. Additional data on the diffusivity of agents in coatings, and means to lower that diffusivity if needed, would contribute to the development of new reactive coatings.

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1. Introduction

This document is a review of reactive coatings to protect military personnel from chemical and biological warfare (CW/BW) agents. After an attack with chemical or biological weapons, exposed equipment must be decontaminated to ensure the safety of personnel and permit continued operation. Some current decontamination systems, such as DS2, are potentially toxic or corrosive. The logistical problem of providing the decon solution at any time or place it may be needed remains a problem with any formulation. Clearly a desirable part of any chemical/biological (CB) protective system would be a coating that could eliminate harmful materials without addition of other reagents.

In this review we have focused on coatings for military equipment, and have not specifically considered coatings for fabrics (fabric finishes), although we recognize that chemistry useful in coatings may also be applicable to fabrics with some modification. We have also not considered coatings applied directly to the skin, such as the active topical skin protectants now under development by the Army. In terms of the categories often used with systems for CW/BW defense, this review focuses on materials for protection and decontamination. Coatings whose only function is in the areas of detection or demilitarization have not been considered. Similarly, systems relying on physical adsorption (activated carbon, Fuller's earth) are well known and are not reviewed here. Decontaminants applied as solutions, foams, or as particles and powders, (such as the reactive sorbents prepared from alkaline earth oxides and the beads in the CW protective wipe) were not considered. We have covered coatings that are described as providing improved chemical agent resistance through a combination of sorption and chemical reaction.

We define a reactive coating as a surface coating that neutralizes chemical or biological threats by a chemical reaction. The reaction converts the CW agent to a harmless (or at least less harmful) product and/or neutralizes BW agents. We have focused on reactive coatings for passive applications, as opposed to active systems such as those requiring a pump to move air through a filter element or catalyst bed.

Reactive coatings potentially have a wide range of non-military commercial applications, both in combating harmful materials such as hazardous industrial pollutants (HIPs) and in neutralizing harmful microorganisms. We have considered the level of commercialization of specific coatings technologies identified.

This review was performed by TDA Research, Inc. (TDA). Some active projects at TDA involve CW/BW defense systems, including efforts led by some of the authors of this study. We have attempted to be fair and objective in our assessments of all technologies. TDA projects are clearly identified in the review.

In the following sections we first outline essential or desirable properties of reactive coatings in general. We then discuss the methodology used in this review and the questions asked. We then address the mode of action of reactive technologies in general: what types of reactions are usable, the mechanism of action, and related issues. Next we address several additional opportunities for improvements in reactive coatings that were identified in the course of this review, along with associated testing required to assess potential problems. We then survey existing technologies, beginning with systems focused primarily on defense against CW agents and continuing to those focused on BW agents, recognizing that there is substantial overlap.

We conclude with a summary of our findings and recommendations for actions that would enhance development of reactive coatings.

2. Requirements of Reactive Coatings

Practical systems must provide useful protection in a practical time frame: minutes preferred, but certainly in hours and not days. There are reports of systems that deactivate harmful chemical by a photocatalytic reaction (for example, on TiO₂; Stevens et al. 1998), but this approach was not considered because it does not appear to be consistent with Army requirements. There would inevitably be surfaces that are not decontaminated because they are not exposed to light; a potential requirement to wait for daylight to begin decontamination is also not realistic. Further mission requirements are that the system must be applicable with existing technology, safe, environmentally friendly (no or minimal hazardous waste on application or paint stripping), durable, consistent with the low observables (camouflage) requirements for military vehicle coatings, protective against corrosion, and available at an acceptable cost.

An area related to but distinct from reactive coatings (as here defined) are the chemical agent resistant coatings (CARCs). When exposed to a chemical agent, any coating will tend to absorb some amount of the agent. Even after the exposed surface has been decontaminated, the absorbed agent may be re-emitted. This agent desorbing from the coating can be dangerous to soldiers, and even in very low concentrations can activate chemical agent detection systems. At that point the soldiers would not know whether they were detecting residue from a previous episode or were the subject of a new attack, and would be required to take precautions, with accompanying loss in effectiveness. Current Army combat vehicle coatings must meet a standard (MIL-C-46168) for re-emission of CW agents. For recent developments in CARC coatings see Escarsega and Duncan 1996, Escarsega et al. 1997, Escarsega and Chesonis 1997, Duncan et al. 1998, Stone and Tolle 1998 and STANAG 2001. CARC coatings by definition require the use of some material or method for decontamination. Reactive coatings would provide that decontamination through their inherent reactivity, and may therefore be said to be self-decontaminating. While these two systems are distinct in definition and application, clearly some of the chemical approaches useful in CARC coatings could be applied to reactive coatings, and vice versa.

An effective coating must retain activity during a reasonable period of service. All of the mechanisms proposed for neutralization of chemical or biological agents are potentially subject to loss of capacity through one or more mechanisms. Sorbents could become loaded with heavy hydrocarbons from fuel vapors; stoichiometric reactants could react with environmental materials (e.g., strong bases would react with CO₂) or could be lost through desorption from the coating; catalysts are subject to deactivation by materials that bind to the catalytic site. Some reactive coatings could be deactivated by formation of a dust, oil or protein fouling layer on the surface, but this issue has not been addressed. Particularly in the case of antimicrobial coatings, the literature on prevention of biofouling provides many examples of surfaces designed to minimize colonization by living cells that rapidly become covered with a biological slime and thereafter provide a surface well suited to growth.

The threat agent must contact the reactive material in the coating if it is to be decontaminated. Clearly, several problems could arise in this area. Chemical agents may not come in contact with the reactive material because the coating does not match the hydrophobic or hydrophilic properties of the agent. Bacterial spores may not be deactivated because their size does not permit them to come in close contact with the reactive material in the coating. These problems are compounded when the chemical or biological agent is deposited on the surface of a particulate material, as in the case of "dusty" mustard and "weaponized" anthrax spores.

3. Methodology

In performing this literature survey TDA searched available databases, including the Defense Technical Information Center (DTIC), the Chemical and Biological Information and Analysis Center (CBIAC), the U.S. Patent and Trademark Office and the Internet. We also searched the scientific and technical literature, including proceedings of the Scientific Conference on Chemical and Biological Defense Research. We also identified and contacted individuals and organizations who were potential developers of or customers for reactive coatings, through past expedience in the CW/BW defense area and through the membership listing in the NBC Industry Group, an association of organizations supporting nuclear, biological and chemical defense. We prepared a survey requesting information on reactive coatings that was sent to all of the identified individuals and organizations.

For each reactive coatings technology identified, we asked the following questions:

1. What is the technology? What is the proposed mode of action?
2. What threat(s) does it address?
3. What test procedures were used to evaluate it?
4. What are the projected system costs?

In evaluating chemical defense technologies, developers have used both surrogates and live agents. While testing with live chemical agents is unarguably the most realistic challenge, it is also far and away the most expensive. A wide range of surrogates has been used: for example, chloroethyl ethyl sulfide (CEES) is widely used as a simulant for sulfur mustard (agent HD) and spores of *B. globigii* are widely used as a simulant for anthrax spores. In reviewing performance data we considered how the reported results might be used to compare competing technologies. For systems designed to protect against biological threats, we considered which organisms the system was tested against, and whether vegetative cells, spores or both were used. We also asked whether the system had been tested in the field, and whether any potential problems (e.g., safety, environmental hazards) had been identified and addressed. We asked whether any model to predict performance had been reported.

In a review of this type it would be reasonable to consider projected system costs, in order to identify technologies with apparent cost advantages. We found, however, that the technologies were not sufficiently developed for us to carry out a meaningful cost comparison.

4. Mode of Action of Reactive Coatings

In this section we first review types of reactions available for reactive coatings and then consider the detoxification of CW agents in general.

4.1. Stoichiometric vs. Catalytic Neutralization of Chemical Warfare Agents

There are three basic types of reactive coating active sites: stoichiometric, regenerable stoichiometric and catalytic. These three types may be generally described as follows, using CBA as the chemical or biological warfare agent.

Stoichiometric: CBA + reactant -----> products

Examples include amines that can react with CW agents in an irreversible reaction, as well as the iodine-generating system pioneered by Triosyn.

Regenerable stoichiometric:

Step 1: CBA + active reactant -----> neutralized CWA + deactivated reactant
Step 2: deactivated reactant + activation solution -----> active reactant

The primary examples are the N-halamines, which may react with a CW/BW agent in an irreversible reaction, and then may be regenerated by application of a bleach solution.

Catalytic: CBA + (O₂/H₂O in presence of catalyst) -----> products

Examples include hydrolysis and oxidation catalysts. If an active material reacts to oxidize a CW agent and is itself reduced, but can then subsequently be re-oxidized by atmospheric O₂, we refer to this material as a catalyst rather than a regenerable reactant because no additional action is required for continued activity.

It is reasonable to ask what range of CW challenges stoichiometric coatings can meet, and this issue is addressed with a few simple material balances. We assume that the CW agent is deposited on the surface as an aerosol, and that the diameter of a typical aerosol droplet is on the order of 5 μm. Assuming a density of 1.0 g/cc, for an agent with a molecular weight of roughly 150 AMU this corresponds to about 4 x 10⁻¹³ mols of the agent. Upon contact with a surface, this droplet might be expected to interact with a circular patch with diameter of about 10 μm. A typical architectural or vehicular coating is on the order of 100 μm thick. We assumed that the coating has a density of 1 g/cc and that all of the reactant in the coating is accessible for the detoxification reaction. To neutralize all of the CW agent, a stoichiometric reactant would then need to be present at concentrations of approximately 0.1 mols/L in the coating solids (ca. 1% by mass for active sites with an equivalent weight of 100). This same active site concentration could accommodate a total contaminant load of roughly 1 g/m², an order of magnitude less than current chemical protection doctrine prescribes, but still a reasonably heavy contamination (Institute for Defense Analyses 1999). The above calculations assume favorable equivalent weights of stoichiometric reagents and a simple 1:1 stoichiometry between active reagents and chemical agents.

We see from the above that the stoichiometric neutralization of chemical agents can be effective for protection from single contamination events at low to moderate levels of contamination.

Stoichiometric systems may therefore find utility in plans to handle modest aerosol contamination or exclusively vapor phase agents. Regenerable stoichiometric systems would likely require regeneration after each contamination event. For systems featuring stoichiometric or regenerable stoichiometric decontaminants, it is clear that the active site concentration in a reactive coating must be matched to the assumed level of contamination.

4.2. Detoxification Mechanisms of Chemical Warfare Agents

While there are many chemical warfare agents, three in particular are most commonly considered since they are either readily synthesized, known to be stockpiled, or are particularly toxic. These three are sulfur mustard (agent HD), the fluorophosphonate G-series nerve agents (which are considered as a group due to their similar mechanisms of action and detoxification), and the nerve agent VX. Each of these agent types presents particular challenges for detoxification and each will be explored in some detail below.

It is important here to distinguish between destruction of the chemical agent and its detoxification. Particularly with agents HD and VX, some common reactions of the agent with potential decontaminants can produce byproducts that are nearly as toxic as the agents themselves. When developing new reagents or catalysts for decontamination, it will continue to be important to study product distributions to ensure true detoxification of the chemical agents.

Sulfur mustard (HD) can be effectively detoxified by either nucleophilic substitution at the aliphatic chlorine or by partial oxidation of the sulfide to the sulfoxide, as shown in Figure 1. Further oxidation of the sulfoxide leads to the sulfone; both HD and the sulfone are vesicants, while the sulfoxide is not (Marshall and Williams 1921, Lawson and Reid 1925, Anslow et al. 1948).

The hydrolysis reaction shown is perhaps the most appealing, but while the half life for mustard in water is about 4 minutes, the solubility of HD in water is so low that a 100 μm droplet has a half life of about 6 years (Harvey et al. 1997). This is not likely to be a problem in reactive coatings, but it does serve to highlight the need to accommodate the various polarities of the reactants in any neutralization reaction. Amines have also been shown to react with HD (Lawson and Reid 1925, Day 1996). In reactive coating applications, HD will most likely be detoxified by catalyzed partial oxidation or hydrolysis reactions. In the case of hydrolysis reactions, the catalyst must be robust in the presence of the HCl reaction product.

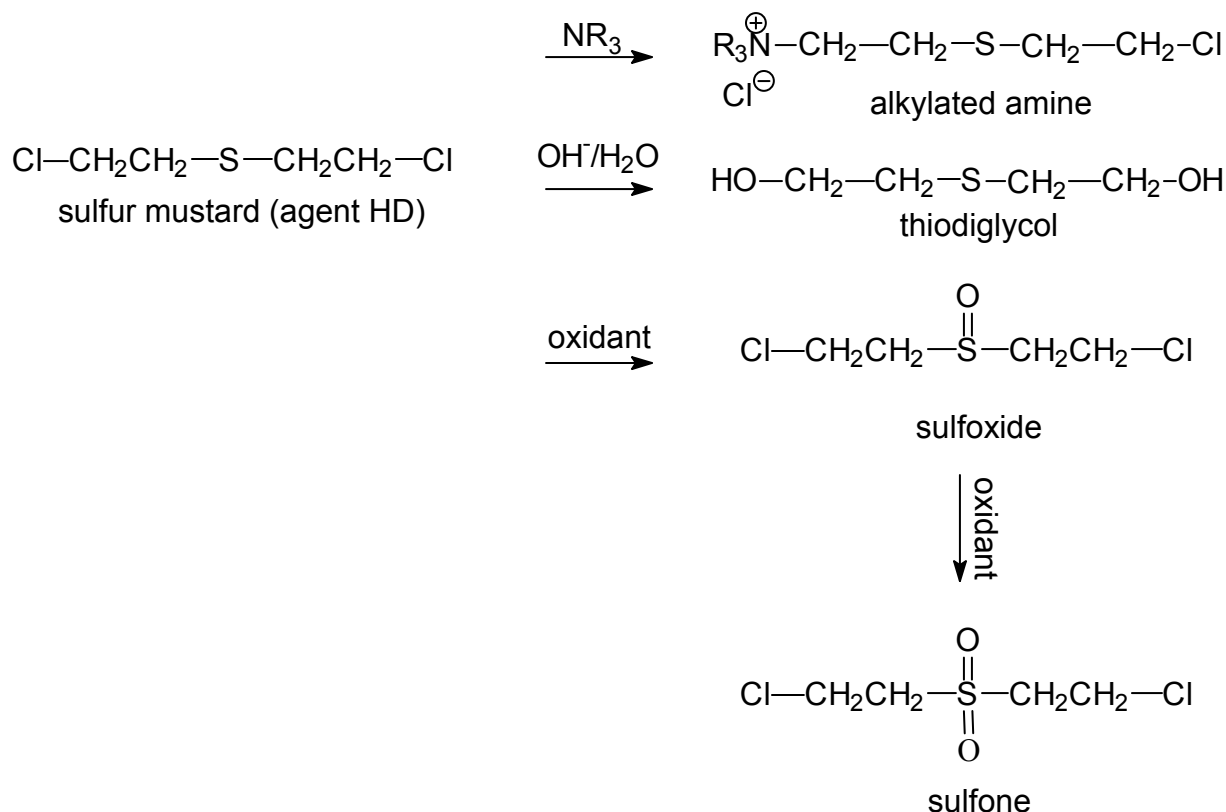


Figure 1. Common reactions of sulfur mustard. The amine in the first reaction may be primary, secondary, or tertiary.

The fluorophosphonate G-agents are readily susceptible to detoxification by hydrolysis of the P-F bond as shown in Figure 2. As with hydrolysis of HD, the hydrolysis of G-agents produces strong acids (both hydrofluoric acid and the phosphorous-based acid), and to maintain long-term activity and high turnover, any hydrolysis catalyst would need to be insensitive to these products. While G-agents have been decontaminated by a variety of oxidant solutions and solid powders (see e.g. Wartel 1999, Table 5-3), all of these systems have had aqueous or basic sites capable of hydrolytic detoxification and there is no evidence of exclusively oxidative decontamination reactions. It seems likely that, in reactive coatings, G-agents will be neutralized by hydrolytic catalysts.

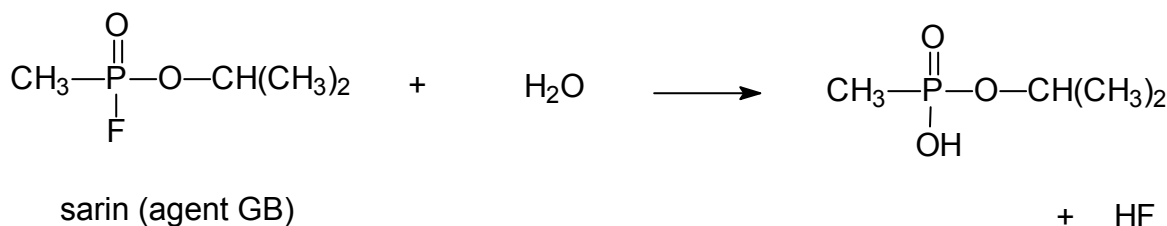


Figure 2. Hydrolysis of sarin, agent GB.

The nerve agent VX presents a particular problem in decontamination. It reacts with aqueous bases, but one of the hydrolysis products is still very toxic and not readily susceptible to further hydrolysis (Figure 3). Detoxification of VX requires cleavage of the P-S bond. Yang (1999) has

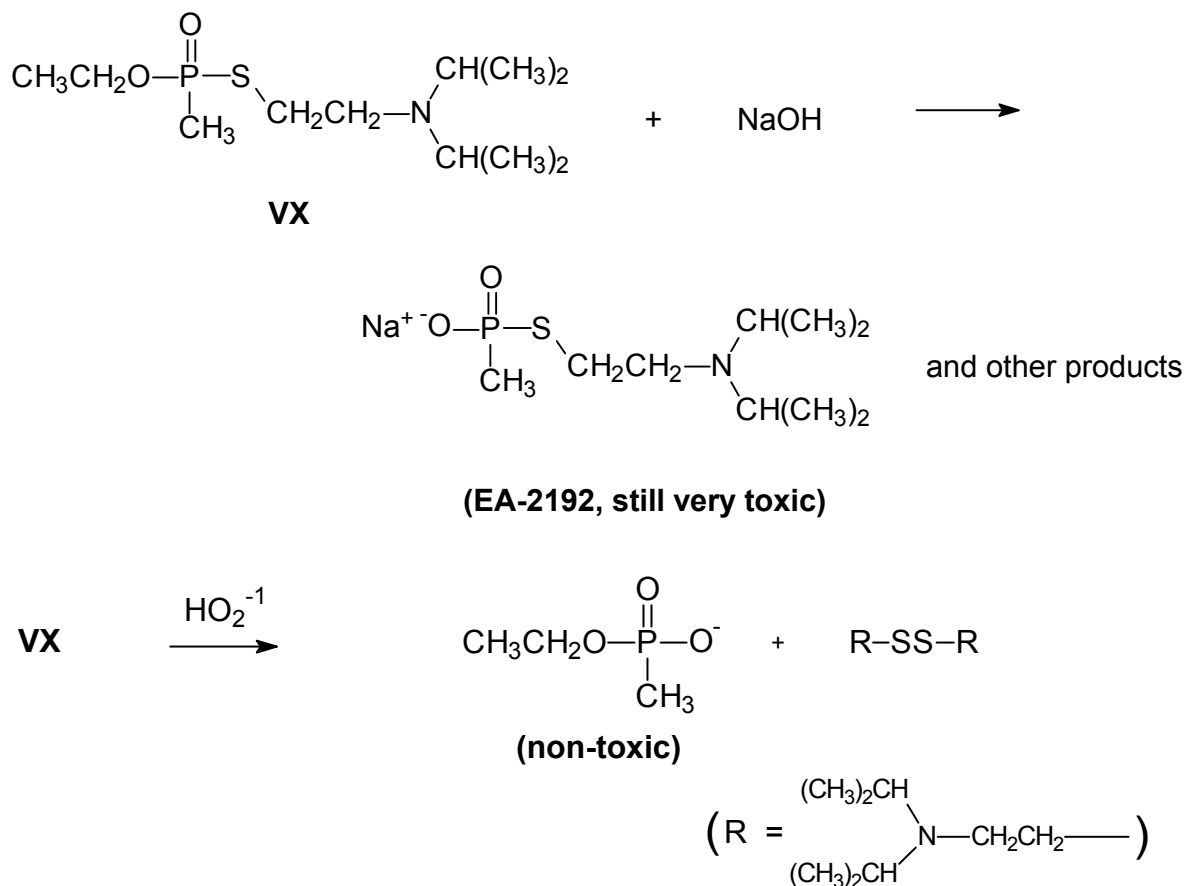


Figure 3. Reaction of VX with base (hydroxide ion) produces several products, one of which (EA-2192, about 15% of total products) is almost as toxic as VX itself. Reaction of VX with the hydroperoxide ion HO_2^{-1} yields a non-toxic product after cleavage of the P-S bond. The initially formed disulfide (RSSR) is oxidized further to the corresponding sulfonic acid salt.

shown that basic solutions of hydrogen peroxide detoxify VX rapidly at room temperature. The active species is the hydroperoxide anion, HO_2^{-1} ; the rate constant is 40 times greater than the corresponding rate constant for reaction with OH^{-1} (e.g., at 23 °C and 0.1 M, $t_{1/2} = 31$ min for HO^{-1} and 0.75 min for HO_2^{-1}). Further oxidation reactions occur, including oxidation of the disulfide to the sulfonic acid salt and, in alkaline media, oxidation of the amine nitrogen, so considerable excesses of oxidant are required (Yang et al. 1992 and Yang 1995). VX has also been detoxified by aqueous persulfate solutions (Mikolajczyk 1989) and a variety of hypochlorites (Wartell 1999). In a catalytic reactive coating, VX could be detoxified by either a selective hydrolysis catalyst or an oxidation catalyst. As noted below, product inhibition of catalytic activity may be a concern. Surprisingly little effort has been directed at systems for catalytic detoxification of VX, and this appears to be an area requiring further focused research.

5. Additional Opportunities and Testing Requirements

During this literature review we identified several aspects of detoxification chemistry that could be applied to reactive coatings but which have not yet been reported in these systems. At the same time there are specific challenges associated with current and potential reactive coatings that will require further testing. In this section we discuss three of those issues. We first consider enzymatic catalysis, identifying high reported reaction rates as a positive aspect and potential instability to environmental conditions as an area requiring testing. We then discuss competitive inhibition, which could affect the rate of any catalyzed detoxification processes. Again additional testing will be required to identify any potential problems. Finally we consider diffusivity of CW agents and potential reactants within coatings, focusing on recent work on reactive barrier additives as one method to decrease the permeability of a coating to specific materials.

5.1. Enzymatic Catalysis

Enzymatic detoxification of chemical warfare agents is an appealing approach. While G-agent detoxification is readily achieved by organophosphorus acid anhydrolases (OPAAs, Cheng et al. 1999), none of these enzymes or organophosphorus hydrolases (OPHs) are particularly well suited to cleavage of the P-S bond in VX, which is required for detoxification, although progress is being made on this point (Kolakowski et al. 1997; DiSioudi et al. 1999a and b). Further, enzymes suitable for nerve agent hydrolysis are generally inhibited by the acidic conditions produced by ester hydrolysis and are largely ineffective below pH values of about 4.5, which limits their capacity to neutralize agents (LeJeune 2001). Current enzymatic hydrolysis catalysts are also deactivated and presumably denatured by mustard (HD) alkylation, so that their utility for long-term application in the field must be verified. This highlights the need to ensure that agents do not deactivate target sites in any coating system containing mixed catalysts; the solution to this problem may be either designing catalysts that are robust to all agents or designing a combination of catalysts such that the kinetics of catalyst deactivation by agents is much slower than agent neutralization.

While all of the desired enzymatic catalysts are not presently available, the first steps toward incorporating enzymes in polymeric materials have already been taken. Researchers at the University of Pittsburgh incorporated enzymes into polyurethane foams while retaining much of the catalytic activity (LeJeune and Russell 1996, LeJeune et al. 1997). Agentase, LLC, has commercialized this technology and expanded it into urethane and acrylic gels (see www.agentase.com and Andreopoulos et al. 1999). Researchers at Altus Biologics have stabilized hydrolytic enzymes while retaining their activity by lightly crosslinking crystals of the enzymes (Margolin and Navia 2001). Another technology, now apparently at Roche Vitamins in NJ, incorporates active enzymes in a protective sol-gel matrix which can then itself be incorporated into a variety of polymers (Gill and Ballesteros 2000a and b, Gill 2001). Fused OPH and cellulose binding proteins have served to immobilize active enzymes on cellulose materials (e.g. filters) in a one-step process (Richins et al. 2000).

As the active site chemistry of OPAA and OPH catalysts becomes more fully understood, perhaps it will be possible to design biomimetic catalysts that are less susceptible to deactivation by alkylation and/or low pH environments. Some work on biomimetic catalysts is underway (Yamazaki et al. 2001) and the design of OPH active sites (DiSioudi et al. 1999a and b) and may lead to further improvements in catalyst stability to HD and to low pH values.

5.2. Competitive Inhibition in Catalytic Detoxification

A catalytic reactive coating must maintain a useful turnover frequency at ambient temperature. It is well known from the literature on low-temperature catalysis that desorption of the reaction product from the catalyst site can limit turnover frequency. Lowering of the rate of a catalyzed reaction by the binding of a species other than the target substrate to the catalyst site is known as competitive inhibition, and has been extensively investigated for enzyme-catalyzed reactions. Although the large majority of studies and examples relate to enzymatic catalysis, these considerations would apply to any catalytic reactive coating. Among catalyzed reactions relevant to decontamination, hydrolysis of phosphonate esters has been studied in the greatest detail. Competitive inhibition has been observed in these systems, as described below.

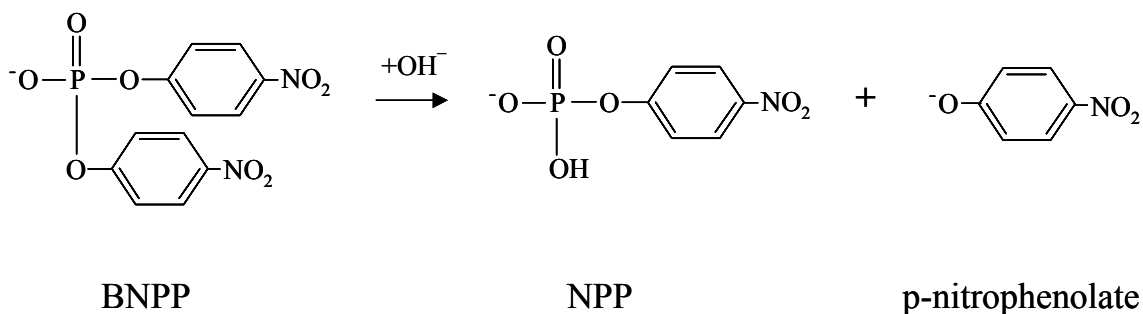
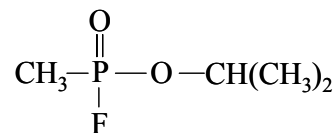


Figure 4. Basic hydrolysis of BNPP.

The basic hydrolysis of bis(*p*-nitrophenyl)phosphate (BNPP) produces *p*-nitrophenyl phosphate (NPP) and *p*-nitrophenolate (Figure 4). The monoester NPP can be further hydrolyzed to produce *p*-nitrophenolate as well. The chemical structure of BNPP is similar to the fluorophosphonate G-agents, such as sarin (Figure 5), as both have a phosphorous-oxygen double bond with an attached ester group. Catalysts that are effective on both BNPP and NPP are expected to effectively catalyze the hydrolysis of the G-type chemical warfare agents, either at the ester linkage or at the phosphorous-fluorine bond.

The uncatalyzed hydrolysis of BNPP is very slow, with a pseudo-first order rate constant on the order of $10^{-11} \text{ sec}^{-1}$. Certain metal complexes can substantially improve the rate of reaction, yielding apparent first order rate constants on the order of 10^{-8} to 10^{-4} sec^{-1} . Unfortunately, with many of these catalysts, the monoester can competitively inhibit the reaction through complex formation with the catalyst, effectively inactivating the catalyst for diester hydrolysis. This inhibition is seen with many different metal catalysts: for example, Ott (1998) reports a decrease in reaction rate after one turnover with a zirconium catalyst complex; Baldwin (2001) reports inhibition of hydrolysis by phosphate using a manganese dioxide catalyst; both Deal (1996, 2001) and Gajda (2001) report inhibition using copper(II) catalyst complexes. Deal (1996) found that the concentration dependence of inhibition by the monoester NPP did not fit a simple competitive inhibition model, although the analysis is complicated by both the monoester NPP and the diester BNPP producing the same phenolate product. Gajda (2001) theorized that the monoester may have stronger complex formation properties than the diester, while Morrow (1988) reported kinetic data on the hydrolysis of NPP with copper catalysts which shows a reaction rate constant approximately 10 times smaller than for the hydrolysis of BNPP with the same catalyst. These two observations may account for the deviation from a simple competitive inhibition model. Deal (2001) found



sarin (agent GB)

Figure 5. Structure of sarin.

that pyrophosphate, phosphate, phenyl phosphate, and nitrophenyl phosphate all inhibited copper(II)-promoted hydrolysis, and that the inhibition was stronger with increasing basicity of the phosphate. No inhibition was seen using an analog of the phenolate product.

These potential problems could be overcome by appropriate catalyst design, and should certainly be tested at an early stage in the reactive coating development process.

5.3. Diffusion and Reactive Barriers in Coatings

TDA found no systematic consideration of the optimal diffusivity of threat agents in a reactive coating. If the reactant is evenly distributed, then the agent must diffuse relatively rapidly throughout the coating in order to use all of the available capacity. However, standard practice in CARC coatings, as already noted, is to decrease the agent diffusivity in order to minimize re-emission. Low diffusivity of the agent in the coating suggests only the reactive component on the surface will be effective in neutralizing threat agents. If the reactive component is localized on the surface, it becomes important to lower the diffusivity of the agent in the coating to prevent its re-emission. It is well known that increasing crosslinking may decrease the permeability of coatings, but this approach may also yield coatings that are too brittle and are easily damaged.

The use of additives to improve resistance of films and coatings to diffusion of small molecules has been extensively investigated. These additives are typically either reactants (e.g., to absorb oxygen or water) or particulate material (to improve the barrier properties by increasing the tortuosity of the path that a small molecule must follow in diffusing through the film or coating.). Although we found no reports of reactive barrier materials used in reactive coatings for chemical defense, research in reactive barriers may be relevant to reactive coatings in general.

Desiring to understand the improvements that reactive particulate materials provide to the barrier properties of plastic packaging films to water and oxygen permeation, Cussler and co-workers at the University of Minnesota have explored the fundamental mathematics of permeation in the presence of homogeneous stoichiometric reactants and non-reactive impermeable flake (Cussler and Yang 2000, Yang et al. 2001). These models, which incorporated both chemical reactivity and tortuosity effects of reactive and inert fillers, accurately predicted permeation and penetration through a reactive film.

This work could be applied to model CW agent penetration, reaction and desorption from coatings containing reactive groups. To be useful for reactive coatings for chemical warfare agents, the present model would need to be expanded to account for several features: catalytic reactions and permeation of co-reactants (e.g. H₂O, O₂); inhomogeneous distribution of reactant or catalyst; permeation vs. reaction vs. vaporization of a limited amount of CWA challenge as opposed to an unlimited challenge of e.g. atmospheric oxygen. Perhaps finite element analysis along the lines of Gusev and Lusti (2001) may be a more appropriate approach to this more complicated problem. For catalytic reactive coatings, these modeling studies would allow one to predict the ultimate agent disposition as a function of agent challenge level, catalytic activity, catalyst concentration and catalyst dispersion.

We conclude that additional data on the diffusivity of agents in coatings, and means to lower that diffusivity if needed, would contribute to the development of new reactive coatings.

6. Reactive Coatings Reported

In this section we summarize reactive coatings technologies that were identified through this review. When an organization provided detailed responses to the survey, these are included in Appendix A. We first describe systems developed primarily for CW agent defense, followed by those developed primarily for BW agent defense, and note any systems reported to be active in both areas. We begin each section with the systems that are closest to commercial available and move on to those that are in earlier stages of research and development.

6.1. Systems Developed Primarily for CW Agent Defense

The standard for performance of a reactive coating to protect against CW agents appears relatively straightforward: Performance should be measured by the time required to reduce a given level of applied agent to an acceptable concentration, such as the threshold limit value (TLV) or permissible exposure level (PEL). However, TDA found no reports of coatings tested in this manner. This may be appropriate in view of the early stage of development. The lack of published reports may also reflect the perceived importance of the technology and the potential market size, which may influence developers to withhold data pending publication of patents. The variety of ways in which results are reported indicate the desirability of accepted performance standards.

1. Mine Safety Appliances Company (MSA; Pittsburgh, PA) has developed coatings for polycarbonate respirator/gas mask lenses that are CW agent hardened for up to 24 hours. MSA provided this information in response to TDA's survey request, but no further information was available. It is clear that this is a commercially available product, but no information was provided to indicate that this is actually a reactive coating, rather than a coating designed to remain transparent on exposure to CW agent.

2. There are also reactive coatings designed to facilitate decontamination by a water rinse. These coatings wash off with the contamination and are therefore suitable only for a single use before reapplication. In this case a stoichiometric coating can be very effective. A reactive coating of this type is under development at TDA, and may be offered for sale as early as December 2002. No information on the chemistry of the system is available at this time. A primary substrate of interest is Nomex cloth, although solid surfaces (e.g., aircraft crew helmet) have also been coated. Coated cloth samples have retained only 1/25 of the residual contamination of uncoated samples after contamination with agent HD and rinsing with water. Further details are found in Appendix A.

3. Brendley et al. (1987) at the U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, investigated use of a reactive ion exchange resin (RIER) in acrylic and solvent-based polyurethane coatings. The coatings were tested with diisopropylfluorophosphate (DFP), a simulant for G-agents. They found that the inclusion of RIER improved the chemical agent resistant capacity of the coatings. The particles were thought to function as both sorbents and catalysts, which is consistent with a high surface area and the presence of fixed acid or base sites that can promote hydrolysis of phosphonate esters. We are not aware that this work is continuing, or that any commercial systems have resulted to date.

4. The research group of Craig Hill at Emory University has reported extensively on catalytic detoxification of CW agents using polyoxometalate (POM) catalysts (Gall et al. 1994, Hill and

Gall 1996, Zeng and Hill 1997, Rhule et al. 2001). These materials have principally been tested against chloroethyl ethyl sulfide (CEES), a simulant for mustard. From the reported work with CEES, a particular strength of the POM catalysts is the ability to selectively oxidize HD to the less-toxic sulfoxide. The stability of POM catalysts to environmental catalysts poisons such as sulfur is claimed as an advantage. The chemistry of polyoxometalates has recently been reviewed (Hill 1998). TDA is currently developing catalytic self-decontaminating coatings incorporating POM catalysts. This work is in the laboratory stage of development. Further details are found in Appendix A.

6.2. Systems Developed Primarily for BW Agent Defense

Antimicrobial coatings are commonly found on metal surfaces such as air conditioner cooling coils (see, for example, Steele 2001) and as anti-fouling coatings on ship hulls. Most contain an active principle such as silver metal (in the form of silver oxide) or trialkyltin compounds, which slowly dissolves into water in contact with the surface and is absorbed into microbial cells, thereby inhibiting growth. Similarly, many commercial antifungal additives for coatings include chlorothalonil, a halogenated aromatic compound that slowly leaches from the surface into the target microorganism. In this review TDA has not covered such commercial systems using a leachable antimicrobial agent.

The definition of an acceptable level of performance is particularly challenging in systems targeting biological agents (see, for example, Ritter 2001). Systems can be active toward vegetative organisms and not bacterial spores, but it is generally accepted that systems effectively killing spores will be effective on vegetative organisms. While any level of protection has some value, developers have not generally referred to any commonly accepted standard or method of measurement. While a 6-log kill is sometimes quoted as a target effectiveness for decontamination systems, in this review TDA found references citing 94% elimination (1.2 log kill) in one case and 99.98% (3.7 log kill) in another, both against vegetative organisms. We stress that all of the reported values may be valuable indicators of potential and progress in developing systems. Only one group (Triosyn) reported effectiveness against bacterial spores; in all other cases there were no reports of any tests against spores. These observations point out the need for broadly acknowledged performance standards and test methods.

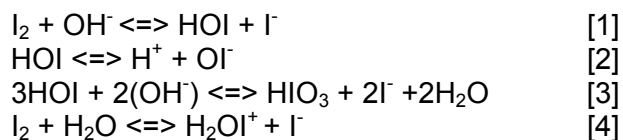
TDA identified several novel systems having antimicrobial activity (and also activity against CW agents, in some cases), which are described in the following paragraphs. Again we begin each section with the systems that are closest to commercial availability and move on to those that are in earlier stages of research and development.

1. Triosyn (South Burlington, VT and Mirabel, Canada) has developed quaternary ammonium triiodide coatings that display antimicrobial activity, and which may provide chemical protection as well. Because the active principle is iodine, this appears to be a stoichiometric reactive coating. There is no indication that these materials can be recharged if they lose capacity. The following summary is condensed from Triosyn's response to TDA's survey; more details are found in Appendix A.

Triosyn® biocidal resin is an interactive broad-spectrum biocidal polymer effective against bacterial spores, viruses, protozoa, algae and fungi. Triosyn® biocidal paints and coatings have been developed to protect a wide variety of surfaces from disease-causing microorganisms existing in civilian and military settings. Harmful microorganisms deposited on surfaces painted with Triosyn® paints/coatings are destroyed and the sterility of the surface material is maintained. Current base formulations include enamels, latexes (flat and semi-gloss), epoxies,

urethanes (water and solvent-based), marine paints and wood tinctures. Testing against suspensions of *Erwinia herbicola* (Eh) *Escherichia coli* (*E. coli*) on chemical agent resistant coating CARC paint panels proved that Triosyn® can be added to standard urethane-based CARC formulations and still be effective against bacteria. In addition, water-based flat latex yielded >99.96% reduction of Eh and an alkyd oil-based enamel showed >99.98% reduction. Finally, the U.S. Marine Corps sponsored a test program performed to evaluate the effectiveness of Triosyn® in the destruction of chemical agents and determine whether Triosyn® can be added to CARC. Exposure of VX to Triosyn® led to its degradation and the possible formation of rearrangement products. This degradation is to be further investigated and characterized to determine all degradation products associated with the process. Toxicity studies of the products from the reaction are also to be conducted (CBIAC 2001).

Triosyn® resin is an anionic polymer containing quaternary ammonium ion moieties, whose charge is balanced by I_3^- in immediate proximity. When the cellular entities such as bacteria, viruses, and fungi, encounter the resin, they preferentially attract the charged ion sites from the polymer matrix. Once bound to these sites, a redox (oxidation-reduction) reaction occurs whereby the I_3^- emits I_2 , the remaining iodide ion staying in proximity to the ammonium ion moiety.



Triosyn's technology appears to be the most developed of any of the reactive coatings surveyed, and is nearing commercial application

2. Worley and co-workers at Auburn University have developed N-halamine biocidal monomers and polymers (Eknoian et al. 1998, Worley et al. 1996 to 2001). The antimicrobial activity of these materials is due to the halogen (typically chlorine). They lose capacity over time, but can be recharged by rinsing the material with a bleach solution. Halosource (Seattle, WA) holds the rights to the N-halamine polymer technology. Their website (www.halosource.com) indicates that biocidal paints and coatings will be offered under the Haloshield brand.

3. Veridian (Charlottesville, VA) has been developing aerogel coatings for enhanced biological agent collection and detection for the DoD (DARPA and TSWG). During this research, they have identified an aerogel coating, optionally containing covalently-attached moieties that exhibit antimicrobial activity. This system is reported to be in advanced development. Veridian quotes an inhibition factor of 3, which TDA tentatively interprets as equivalent to a 3-log kill. Further information is attached in Appendix A.

4. Tiller and co-workers at MIT (2001) describe a method to covalently attach poly(4-vinyl-N-alkylpyridinium bromide) to glass slides to create a surface that kills airborne bacteria on contact. The resultant surfaces were able to kill up to 94% of *Staphylococcus aureus* cells sprayed on them. On similarly modified surfaces the numbers of viable cells of another Gram-positive bacterium, *Staphylococcus epidermidis*, as well as of the Gram-negative bacteria *Pseudomonas aeruginosa* and *Escherichia coli*, dropped more than 100-fold compared with the original amino glass. There were no reports that the coating was effective against bacterial spores. Tiller et al. suggest that such materials could be used to coat the surfaces of common objects touched by people in everyday life (e.g., door knobs, children's toys, computer keyboards, telephones, etc.) to render them antiseptic and thus unable to transmit bacterial

infections. As noted in the introduction, an effective surface must be shown to resist fouling and retain activity, which would need to be demonstrated in this case also.

Chen et al. (1999, 2000) reported that quaternary ammonium compound dendrimers are exceptionally effective biocides. TDA found no reports that these materials have been incorporated onto surfaces, but given their reported activity they would be expected to be more effective on surfaces than the structures of Tiller et al. cited above, but subject to the same potential limitations with respect to fouling.

7. Summary and Recommendations

It is clear that reactive or self-decontaminating coatings could enhance America's capabilities against chemical and biological weapons by increasing the speed and simplifying the logistics of decontamination. In this review we identified several promising new technologies systems that address this need, most of which appear to be in the early stages of development. The antimicrobial paint developed by Triosyn is reported to be in advanced development, and the aerogel-based antimicrobial paint from Veridian is reported to be at a less advanced stage. While CARC coatings are well developed, we found no indication that any reactive coatings intended to provide chemical protection have advanced beyond laboratory testing.

The technologies surveyed here all appear to have a single mode of action (stoichiometric substitution, catalytic oxidation, etc.). Since protection is required against a range of threats and circumstances, it appears likely that some combination of modes of action will be required. This could be, for example, a combination of catalysts for oxidation and hydrolysis, or systems that selectively hydrolyze HD, G agents, and VX through separate mechanisms. Enzymatic catalysis has previously been applied to chemical defense, but we found no systems using enzymes in coatings. This represents an area for future R&D. Surprisingly little effort has been directed at systems for catalytic detoxification of VX, and this also appears to be an area requiring further focused research.

To assist this important ongoing research we make the following recommendations:

Research and development would benefit if technology developers had a generally accepted list of threat scenarios. For example, chemical agents may be used as vapors, aerosols or dusts and at widely varying concentrations. Biological weapons (such as bacterial spores) may be used pure or deposited on powders (weaponized). A task force under Government direction could compile a list of scenarios that should be considered, which would facilitate broader understanding and comparison of competing technologies.

Similarly, research into chemical defense has long suffered from use of a wide range of simulants and test methods. At least for the limited area of reactive coatings, it should be possible to establish a systematic series of protocols to facilitate evaluation of developmental technologies. For example, the R&D process could begin with experiments using threat agent analogs selected to screen for activity in specific area. The most effective materials could then be tested against other analogs or under more realistic conditions. The development process should move as rapidly as feasible to tests with live agents. Durability or longevity under field conditions has generally not been addressed. To assure that research efforts are properly directed, performance under field conditions should also be considered as early as is feasible.

Diffusion of chemical agents in coatings is well known but has not been quantified or modeled. For catalytic chemical protective coatings the solubility of (for example) O₂ and H₂O in the matrix may also be critical. Additional data on the diffusivity of agents in coatings and means to lower that diffusivity if needed, would contribute to the development of new reactive coatings.

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8. Appendix A: Results of Survey on Reactive Coatings for Chemical Protection

Responding organization:

Veridian

Contact person (name, title):

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Technology description: In your response please be as specific as possible. Please indicate the type(s) of coating system where the technology can be applied. If known, please indicate whether the protective reaction is catalytic or non-catalytic. Indicate whether any reactive component leaches out of the coating during use. Indicate whether the coating is intended to protect against biological warfare agents.

Veridian has been developing aerogel coatings for enhanced biological agent collection and detection for the DOD (DARPA and TSWG). During this research, we have identified an aerogel coating which exhibits antimicrobial activity, see Figure 1.

VERIDIAN Inhibition Testing of Aerogels

Method developed to assess inhibition of aerogel polymer on bacterial growth (*E. coli*)

Consecutive dilutions of bacterial culture (1:10) performed in presence of aerogel. Allow to grow overnight and record final dilution in which growth occurred.

	Solution	Concentration	% solids	Inhibition factor
controls	none		NA	0
	ethanol	1:100 dilution	NA	0
aerogels	B2 aerogel	1:100 dilution	3%	0
	aerogel (20% antimicrobial dopant)	1:100 dilution	3%	3

•The inhibition factor represents the orders of magnitude (logarithmic) less of cell growth obtained compared to the control.

•The % solids characterizes the amount (wt/wt) of aerogel polymer present in the liquid form tested.

Figure 1. Aerogel antimicrobial study.

Aerogel is a term used to describe very low-density, highly porous polymeric materials. These characteristics give rise to a solid-wispy material which is mostly air-filled, hence the name aerogel. This unique material is one of the lightest solids known and has properties consistent with both a solid and a gas. Typically, aerogel possesses a complex, adjustable pore structure, high internal surface area, high porosity, and adjustable surface chemistry. These properties can be independently controlled during synthesis. Aerogel's exceptionally high surface area acts as a sample concentrator. In addition, the internal surface area can be coated with collection enhancing compounds to increase the absorption capacity; aerogel has been proven to substantially enhance biocollection efficiency.

Specifications:

Pore size: 50nm (statistical average)

Porosity: typically 5% solids, 95% air, open connected pore structure

Density: (3 - 400 kg/m³)

Surface area: typically 1400 m²/g

Backbone: typically silica (SiO₂)

Surface chemistry:

- Hydrophilic or hydrophobic
- Variable concentration of covalently attached (prevents leaching) antimicrobial moieties.

Coating description: dip, spin, or spray coatings; typically 100-1000nm thick. Adhere to glass, plastic, wood, fabric (dependent on surface prep and compatible surface chemistries).

Other: transparent; significant thermal stability

Additional information (e.g., research collaborations, technology licensees)

Collaboration with Sandia National Labs

Availability (10 = commercially available now, 1 = basic research)

6

Other information relating to the technology:

Reports in scientific or other readily accessible literature:

Descriptions now available on the Internet, with URL:

Patents:

Reports with limited distribution (e.g., reports to U.S. Government agencies sponsoring research):

Survey on Reactive Coatings for Chemical Protection

Responding organization:

Triosyn® Corp.

Contact person (name, title):

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E-mail:

l.dionno@hydrobiotech.ca

Technology description:

Triosyn® biocidal paints / Coatings have been developed to protect a wide variety of surfaces from disease causing microorganisms existing in civilian and military settings. Harmful microorganisms deposited on surfaces painted with Triosyn® paints / coatings are destroyed and the sterility of the surface material is maintained. Current base formulations include enamels, latexes (flat and semi-gloss), epoxies, urethanes (water and solvent-based), marine paints and wood tinctures. Work performed for the U.S. government and U.S. department of defense has successfully demonstrated the decontaminating effect of Triosyn® biocidal paints / Coatings. Testing against suspensions of *Erwinia herbicola* (Eh) *Escherichia coli* (*E. coli*) on chemical agent resistant coating CARC paint panels proved that Triosyn® can be added to standard urethane-based CARC formulations and still be effective against bacteria. In addition, water-based flat latex yielded >99.96% reduction of Eh and an alkyd oil-based enamel showed >99.98% reduction. Finally, the U.S. Marine Corps sponsored a test program performed to evaluate the effectiveness of Triosyn® in the destruction of chemical agents and determine whether Triosyn® can be added to CARC. Exposure of VX to Triosyn® lead to its degradation and the possible formation of rearrangement products. This degradation is to be further investigated and characterized to determine all degradation products associated with the process. Toxicity studies of the products from the reaction are also to be conducted. **Ref:** *CBIAC: Development and Evaluation of CARC with Triosyn® Additive, May 2001*

The Triosyn® paints have been tested under ASTM D3273 entitled, "Standard Test Method for Resistance to Growth of Mold on the Surface of Interior Coatings in an Environmental Chamber". Wood panels coated with Triosyn® wood stain, Triosyn® marine paint, and Triosyn® alkyd epoxy, have exceeded the 4 week period specified in the ASTM and is ongoing with no fungal growth as compared to their respective wood panels coated with the paints containing no Triosyn®.

Total iodine method is used to measure the iodine that leaches out of the coating using spectrophotometer at a wavelength of 592 nm for absorbance. Preliminary toxicological studies

were performed on latex and acrylic paint and these showed threshold limit values of 0.0013 mg/m³ over 150 hours and 0.1061 mg/m³ over 194 hours, respectively. These values are way below the acceptable standard of 1 mg/m³ (ACGIH). All toxicology studies need to be performed under OSHA standard protocols and there is ongoing investigation as to the different types of paints.

The regulatory procedures for registration of biocide paints include the performance of a number of recognized standard protocols. The following includes a summary of international requirements for the various biocidal product type;

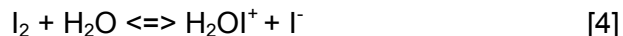
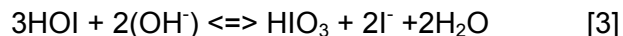
Wood Preservation Standard; laboratory efficacy testing against fungi and field efficacy testing
Paint film Preservation Standard; evaluation of the resistance or susceptibility of paint films to microorganisms mainly fungi and algae

In-can Preservation Standards; test methods for the evaluation of bacterial efficacy in the container

Antifouling products; include a number ASTM protocols involving field-testing for durations of up to 2 years.

The Triosyn® additive is suitable for a wide variety of paints for a wide variety of applications and may be applied by conventional spray equipment as well as brush and roller. The manufacturing cost incurred will be minimal on Triosyn® based paints, as the procedure entails a simple addition and mixing of the Triosyn® into the commercially available paint formulation. No large equipment or human resources are required.

Triosyn® resin is an anionic polymer whose molecular chain lengths are ammonium ion moieties (NR₃⁺) whose charge is counter balanced by I₃⁻ in immediate proximity. When the cellular entities such as bacteria, viruses, and fungi, encounter the resin, they preferentially attract the charged ion sites from the polymer matrix. Once bound to these sites, a redox (oxidation-reduction) reaction occurs whereby the I₃⁻ emits I₂ in unit surges, the remaining iodide ion staying in proximity to the ammonium ion moiety.



Additional information (e.g., research collaborations, technology licensees)

Battelle Medical Research & Evaluation Facility West Jefferson, Ohio

Availability (10 = commercially available now, 1 = basic research)

For the immediate future, Triosyn® is available for research and development purposes only. Triosyn® based paints have undergone numerous efficacy studies to be classified as 8 for microbiological degradation and 2 for chemical degradation on a scale from 1 to 10.

Other information relating to the technology:

Triosyn® biocidal resin is an interactive broad-spectrum biocidal polymer effective against bacterial spores, viruses, protozoa, algae and fungi. It interacts with microorganisms through an ionic reaction sensitive to their presence and concentration. Triosyn® harnesses the power of iodine through the non-toxic application of demand-release polymer technologies. Performance attributes include; full-spectrum biocidal efficiency greater than 99.9%, environmentally safe, devitalizes on contact, no hazardous by-products, self-sterilizing, chemically stable, no demonstrated microbial resistance, cost-effective, and engineering flexibility.

Reports in scientific or other readily accessible literature:

Aviation Week's Business & Commercial Aviation, January 2001, p. 80
Commerce, Mai 1994, p. 89
CBIAC Newsletter, Winter 2001, Volume 2, Number 1, "Development of the Biocide Casualty Care System" p.2
CDIA Report, Spring 2001, Volume IX / Issue 5, "Member Profile" p. 9

Descriptions now available on the Internet, with URL:

WWW.TRIOSYN.COM

Triosyn® Corp. Public scientific recognition:

links to third party statements

Battelle Memorial Institute:

<http://www.battelle.org/army/sae/columbus/coatings.stm>

<http://www.battelle.org/army/sae/columbus/ccs.stm>

<http://www.battelle.org/army/sae/columbus/canteen.stm>

<http://www.battelle.org/army/sae/columbus/bodybag.stm>

Applied Science and Analysis

Session 12: presentation on Biocidal resin Triosyn® by Dr. Moore:

<http://www.asanltr.com/cbmts/cbmts/III/cbmts-iii-summary.htm>

U.S. Defense Information Systems Agency

Chemical and Biological Defense Information Analysis Center

Story 2: Casualty Care System:

<http://www.surviac.wpafb.af.mil/mss/cbiac/cbiac.htm>

Edgewood Chemical Biological Center:

Visit new archives past stories and click on *Quarter 2* or

<http://www.surviac.wpafb.af.mil/mss/archives.htm>

Patents:

Patent Title: Iodine / Resin Disinfectant and a Procedure for the Preparation Thereof

Country	Application #	Patent #
Australia		688276
Belgium		0660668
Canada		2,140,639
Denmark		0660668
Europe		0660668
Europe (divisional)	97109103.8	
France		0660668
Germany		0660668
Hong Kong		HK1011259
Hong Kong (divisional)	99106101.5	
Hong Kong (divisional)	99106102.4	
Ireland		0660668
Italy		0660668
Japan	06-507628	
Liechtenstein		0660668
Luxembourg		0660668
Malaysia	PI 9500752	
Monaco		0660668
Netherlands		0660668
New Zealand		255299
New Zealand (divisional)		299530
New Zealand (divisional)		299531
New Zealand (divisional)		299532
Philippines	50850	
Singapore	9502057-4	
South Korea	95-701017	
Spain		0660668
Sri Lanka		10774
Sweden		0660668
Switzerland		0660668
UK		0660668
US		5,639,452
US (divisional)		6045820
Vietnam	S-1060/95	

Patent Title: Use of Iodinated Resins to Disinfect Air-Containing Microorganisms

Country	Application #	Patent #
Australia		719355
Australia (divisional)	48770/00	
Europe	97108792.9	
US		5,980,827
Vietnam	S-1060/95T3	

Patent Title: Use of Iodinated Resins in Sterilization Dressings and Articles of Clothing

Country	Application #	Patent #
Australia	71865/98	
Vietnam	S-1060/95T2	
US	09/267056	
US (divisional)	09/465968	

Patent Title: Biostatic Air Filter

Country	Application #	Patent #
United States		6224655
International	PCT/CA99/00080	
Australia	N/A	
Brazil	N/A	
Mexico	PA/2001/004443	
International	N/A	

Patent Title: Water Filter Cartridge

Country	Application #	Patent #
Canada	2,267,511	
United States	09/534,621	
International	PCT/CA00/00325	

Combined chemical / biological protective coatings

***Patent Title: Composition for Deactivating Chemical/
Biological Active Agents and Method of Making the Same***

Country	Application #	Patent #
US	09270636	
International	PCT/US99/05862	
Canada	234209	
Australia	30094/99	
Brazil	PI9908876-2	
China	99805735.5	
Europe	99911455.6	
Hong Kong	N/A	
Indonesia	P-5151	
India	N/A	
Mexico	009196	
Malaysia	PI20004357	
New Zealand	507013	
Philippines	1-2000-02576	
Pakistan	848/2000	
Singapore	200005288-6	

Aerosolized Decontamination System

***Patent Title: Composition for Deactivating Chemical/
Biological Active Agents and Method of Making Same***

Country	Application #	Patent #
US	109270636	
International	Pct/ca00/00909	

Patent Title:

Topical Antiseptic Composition

Country	Application #	Patent #
United States	09/369,133	
International	PCT/CA00/00909	

Patent Title:

Deactivation of Toxic Biological Agents in Biological Fluids such as Blood

Country	Application #	Patent #
Canada	2279683	
International	PCT/CA00/00891	
United States	09/631,125	

Patent Title: Deactivation of Toxic Chemical Agents

Country	Application #	Patent#
United States	09327827	
International	Pct/ca00/00685	

Patent Title: Process for the Immobilization of Particles in a Three Dimensional Matrix Structure

Country	Application #	Patent#
Canada	2297513	
Canada (divisional)	2333435	
US	09/772560	
International	PCT/CA/00104	

Reports with limited distribution (e.g., reports to U.S. Government agencies sponsoring research):

Study Title	Testing Institute / Sponsor	Challenge
Technology Development of Triosyn® in Biological Warfare Environment	Battelle Medical Research & Evaluation Facility West Jefferson, Ohio Chemical & Biological Defense Information Analysis Center (CBIAC) / US Department of Defense 2000	P. pseudomallei, F. tularensis, Bacillus subtilis spores, B. Anthracis
Triosyn® Laminated Advanced Materials Face Masks	Hydro Biotech Inc. Mirabel, Canada / US Department of Defense 2000	MS2 phage, Bacillus subtilis var niger spores
Integrated Filter Canteen	Hydro Biotech Inc. Mirabel, Canada / US Department of Defense 2000	Klebsiella terrigena, MS2 phage, Cryptosporidium parvum oocysts
Inanimate Surface Decontamination Electronics Decontamination Casualty Care System Overgarment	Hydro Biotech Inc. Mirabel, Canada / US Department of Defense 2000	Klebsiella terrigena, MS2 phage, Bacillus subtilis var niger spores
Skin Decontamination Field Wound Dressing Body Bag	Hydro Biotech Inc. Mirabel, Canada / US Department of Defense 1999	Klebsiella terrigena @ 10 ⁵ PFU/ml, MS2 phage @ 10 ⁵ PFU/ml, Bacillus subtilis var niger spores (BG) @ 10 ⁵ CFU/ml Bacillus subtilis var niger spores (BG), Staphylococcus aureus @ 10 ⁹ CFU, Pseudomonas aeruginosa @ 10 ⁹ CFU Bacillus subtilis var niger spores (BG) @ 10 ⁸ CFU, MS2 phage, Klebsiella terrigena @ 10 ⁸ CFU
Triosyn® Infused Pellethane Triosyn® Infused BF Goodrich Materials	Battelle Medical Research & Evaluation Facility West Jefferson, Ohio Chemical & Biological Defense Information Analysis Center (CBIAC) / US Department of Defense 1999-2000	MS2 phage

Development and Evaluation of CARC with Triosyn® Additive	Battelle Medical Research & Evaluation Facility West Jefferson, Ohio Chemical & Biological Defense Information Analysis Center (CBIAC) / US Marine Corps 2000	Erwinia herbicola, Escherichia coli, GD, HD, VX
Acute Oral Toxicity Testing of Triosyn® in Rats Acute Inhalation Toxicity Testing of Triosyn® in Rats Acute Eye Irritation Study in Rabbits Acute Dermal Toxicity Testing of Triosyn® in Rabbits Chromosome Aberration Assay AS-52 Point Mutation Mouse Micronucleus Assays	Battelle Medical Research & Evaluation Facility West Jefferson, Ohio Chemical & Biological Defense Information Analysis Center (CBIAC) / US Department of Defense 2000	GLP Studies as per EPA Guidelines

Survey on Reactive Coatings for Chemical Protection

Responding organization:

TDA Research, Inc.

Contact person (name, title):

William Bell

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Telephone:

303-940-2355

E-mail:

wbell@tda.com

Technology description: In your response please be as specific as possible. Please indicate the type(s) of coating system where the technology can be applied. If known, please indicate whether the protective reaction is catalytic or non-catalytic. Indicate whether any reactive component leaches out of the coating during use. Indicate whether the coating is intended to protect against biological warfare agents.

Equipment exposed to chemical or biological (CB) agents must be decontaminated to ensure the safety of personnel and allow continued use of the equipment. Current decontamination systems, such as the DS2 solution, tend to be corrosive and incompatible with sensitive electronics. Some less-aggressive decontamination systems produce a hazardous byproduct (e.g., sorbent or liquid waste containing unaltered toxins) whose disposal introduces an additional logistics burden. An ideal solution to decontamination of equipment after a CB attack would be a self-decontaminating coating that could deactivate the threat agents by a catalytic reaction.

TDA has developed a coating for military vehicles (which could also be extended to other systems) that neutralized a simulant for mustard (agent HD) by a catalytic reaction at room temperature. The coating also demonstrated activity against a simulant for the BW agent anthrax. TDA is now preparing and evaluating additional catalysts and coatings to increase the rate of the CW agent decontamination reaction. We are also evaluating catalysts that improve effectiveness against phosphonate nerve agents. Previous tests have used simulants for CW agents. Planned work includes tests with live CW agents and simulants for two BW agents. We also plan to verify that the self-decontaminating coating can meet all other requirements of military vehicle coatings and carry out a field test. An independent consultant will investigate safety and environmental considerations associated with the coating.

Additional information (e.g., research collaborations, technology licensees)

Collaboration with Emory University (research group of Prof. Craig Hill)

Availability (10 = commercially available now, 1 = basic research)

2

Other information relating to the technology:

NA

Reports in scientific or other readily accessible literature:

NA

Descriptions now available on the Internet, with URL:

NA

Patents:

NA

Reports with limited distribution (e.g., reports to U.S. Government agencies sponsoring research):

Bell, W.L., T.A. Scholten, C.L. Hill, A. Bailey, E Boring and J. Rhule (2001). "Catalytic Self-Decontaminating Coatings." Final report submitted to the Defense Advanced Research Projects Agency under contract DAAH01-00-C-R127.

Survey on Reactive Coatings for Chemical Protection

Responding organization:

TDA Research, Inc.

Contact person (name, title):

Bryan M. Smith, Senior Chemical Engineer

Mailing address:

12345 West 52nd Avenue, Wheat Ridge, CO 80033

Telephone:

303-940-2331

E-mail:

smithbm@tda.com

Technology description: In your response please be as specific as possible. Please indicate the type(s) of coating system where the technology can be applied. If known, please indicate whether the protective reaction is catalytic or non-catalytic. Indicate whether any reactive component leaches out of the coating during use. Indicate whether the coating is intended to protect against biological warfare agents.

TDA Research, Inc. (TDA) is developing, a water-based aerosol coating designed to facilitate the decontamination of coated substrates by a simple water rinse. This project is funded through a Small Business Innovation Research contract sponsored by the Naval Air Warfare Center. The intention is to protect valuable substrates from contamination by chemical warfare agents so that they may be reused without jeopardizing the health and safety of personnel working in a contaminated environment. Typical substrates might be flight suits and helmets, Self Contained Breathing Apparatus (SCBA) equipment, night-vision goggles, etc. This coating will be especially useful for substrates containing screws, rivets, cloth, creases, or absorbent plastics – all places where chemical agents can hide from standard decontamination procedures – since it helps prevent agent penetration.

Mode of Use:

The decontamination-aid coating is designed to be applied prior to any exposure to chemical agents, and is easily applied in the field by one person with no special training, equipment, or safety precautions. Within 30 minutes the coating is effective in preventing substrate contamination. After exposure to chemical contamination, the substrates are rinsed with water (e.g. from a garden hose or similar source) to remove residual contamination. Seawater also serves to decontaminate substrates. Since the coating prevents the contamination from absorbing into the substrate, the rinsed substrates will present no hazard from desorbing chemical agents. After substrate decontamination by rinsing with water, the coating must be re-applied to maintain peak effectiveness.

The coating is clear (although it may be dyed for quick visual reference of coverage) and water-based. It presents no flammability hazard and offers excellent compatibility with all potential substrate materials, including optical surfaces. It is non-corrosive and is not expected to induce any eye or skin irritation. It is expected to be shelf stable for many years and may be applied long before substrate exposure to chemical agents.

Preliminary data, acquired by an independent laboratory working with agent HD on nylon cloth substrates, indicates that control substrates retained typically 25-times more contamination than did pre-treated substrates after a simple water rinse. The coating formulation is not yet optimized and we expect the performance to improve substantially. We will also be testing the coating performance against agents VX and GB.

Additional information (e.g., research collaborations, technology licensees)

Availability (10 = commercially available now, 1 = basic research)

Other information relating to the technology:

Reports in scientific or other readily accessible literature:

Descriptions now available on the Internet, with URL:

Patents:

Reports with limited distribution (e.g., reports to U.S. Government agencies sponsoring research):