

# THE NEXT GENERATION OF CHEMICAL AND BIOLOGICAL PROTECTIVE MATERIALS UTILIZING REACTIVE NANOPARTICLES

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## ABSTRACT

NanoScale Materials and Gentex recently finished a Phase III SBIR program entitled "Nanoparticles as Reactive Technologies for Decontamination and Soldier Protection", funded by AF, Contract F33615-01-C-6063. This program showed that reactive nanoparticles can be successfully attached to textiles, while retaining their ability to detoxify chemical agents. This paper and resulting poster presentation will summarize the work completed and some of the results gained from this effort.

## 1. INTRODUCTION

Protection of personnel from harmful chemical and biological agents has been an issue since their first use on the battlefield during World War I. Today, chemical protection is provided by separate material systems that are only worn when needed, adding weight, cost, and heat stress to a soldier's load. The result of these materials is reduced functionality and higher metabolic work rate when being worn. Although these materials provide good chemical protection they do nothing to detoxify the materials they adsorb.

Activated carbon has been used as the material of choice for protection against chemical agents for many years. Activated carbon works by trapping organic compounds in its extremely high surface area, thereby keeping the agent from getting to the skin and causing damage. Because this is a physical process, activated carbon does nothing to react or destroy the agents it adsorbs, resulting in limited protection times and disposal issues.

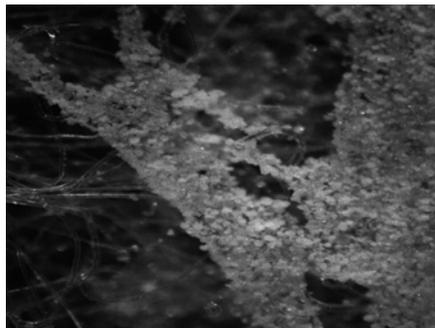
It has recently been discovered that specially created, metal oxide nanoparticles have the potential to completely replace the use of activated carbon. NanoScale Materials, Inc. of Manhattan, KS has pioneered the creation of highly engineered nanoparticles for use in detoxifying chemical and biological (CB) agents. In laboratory tests, these materials have demonstrated the ability to detoxify and destroy chemical agents and their simulants by breaking down their chemical structure. They have also

been determined to be effective in destroying biological agent simulants including virus and bacteria spores in initial tests.

## 2. ATTACHMENT MECHANISMS

Before the efficacy of nanoparticle doped textiles could be tested, robust attachment mechanisms had to be developed and validated. Due to the small particle size of nanoparticles, the attachment mechanisms utilized must fix the particles properly to the surface of the textile but not cover it. Since existing activated carbon beads are many orders of magnitude greater in size than the nanoparticles, the ability to provide good adhesion and coverage to the textile surface while not overly occluding the nanoparticle surface becomes even more difficult. To address this problem, Gentex utilized a number of different attachment methods and promising samples were then tested and downselected. A Scanning Electron Microscope (SEM) was used to verify the nanoparticle attachment and to quantify the amount of occlusion of the nanoparticles. Figure 1 shows nanoparticles successfully attached to a textile substrate with good adhesion and uniformity.

**Figure 1 Nanoparticles Attached to a Textile**



A variety of different attachment methods were evaluated as part of this program. As would be expected, some methods worked better than others. Squeeze coating and electrostatic attachment were determined to be the best two methods. Squeeze coating involves the use of adhesives to wet the surface of the material and then the excess is squeezed out of the material.

Once the excess is removed, the nanoparticles are then sprinkled onto the surface and then the adhesive is cured. In the electrostatic attachment method, the nanoparticles are exposed into a electrostatically charged field which facilitates attachment to a textile substrate. The particles are then fixed to the surface using a proprietary process. As part of this work, a variety of nanoparticle formulations and particle size distributions were evaluated using these two methods. From this work, Gentex discovered that the molecular weight and particle size distribution of the nanoparticles utilized had a significant effect on resulting packing density and total add-ons.

### 3. MATERIAL TESTING

Successful candidates coming out of the attachment mechanism trials were then tested for their performance against chemical agents. Chemical agent testing was performed in accordance with method CRDC-SP-84010 with a liquid contamination/vapor penetration at 10 g/m<sup>2</sup> concentration. Swatch testing was performed at ambient temperature (23°C) and 50% relative humidity. Control samples were also tested at the same time (identical in construction but with no active materials attached), to establish a percentage reduction in cumulative mass. Live chemical agents Sulfur Mustard (HD) and the nerve agent Soman (GD) were used for the testing. Test results are shown in Table 2 below.

From this testing, the following conclusions can be made. Reactive nanoparticle doped

materials can successfully and very efficiently decompose both HD and GD. These test results show that the attachment methods selected do not overly occlude the nanoparticles. The data also shows a relationship between agent detoxification and loading, with higher loading resulting in better protection. Presently used carbon laminates are allowed a maximum breakthrough of 4µg/cm<sup>2</sup> for HD and 1 µg/cm<sup>2</sup> for GD over a 24-hour period. It takes around 150-180 g/m<sup>2</sup> of activated carbon to provide this amount of protection. It is interesting to note that the maximum loading tested in this experiment was 99.7 g/m<sup>2</sup>, while meeting present protection requirements.

### CONCLUSION

The results from this program show that nanoparticle doped textile systems are capable of destructively destroying a variety of chemical agents and *can provide comparable levels of protection to existing carbon-based systems, but at lower weights.* Due to their small size, high surface area, and destructive chemical capabilities, nanoparticles represent a major leap in protection capabilities. Work is still needed to validate that these material systems are robust enough to survive the military environment, but initial test results are very positive. If successful, these materials have the potential to meet the holy grail of protective materials, a self-detoxifying material.

Sample ID/ Attachment Method	Particle Type	Particle Loading (g/m <sup>2</sup> )	HD Cumulative Mass Summary µg/cm <sup>2</sup>			GD Cumulative Mass Summary µg/cm <sup>2</sup>		
			Test Sample	Control	% reduction	Sample	Control	% reduction
021902-7 Electrostatic Attachment	TiO <sub>2</sub>	87.0	<3.93	33.7	86	<0.09/<0.08	28.9/29.4	99.8
			<5.36	28.0		<0.05/<0.04	32.8/33.1	
			<4.14	N/A		<0.03/<0.03	NA	
			mean<4.48	30.9		<0.06/<0.05	30.9/31.3	
TR-0752 Squeeze Coating	Coated MgO	99.7	<8.00	<19.9	75	0.05	45.2/46.5	99.9
			<8.63	<28.9		0.03	36.7/37.6	
			<6.03	<42.1		0.02	30.9/31.9	
			<7.55	<30.3		0.03	37.6/38.7	
TR-0753 Squeeze Coating	Uncoated MgO	25.7	<10.5	<19.9	52	<0.06	45.2/46.5	99.5
			<21.5	<28.9		<0.55	36.7/37.6	
			<11.6	<42.1		0.01	30.9/31.9	
			<14.5	<30.3		<0.21	37.6/38.7	

**Table 2 Results of Chemical Agent Testing**