

ARMY RESEARCH LABORATORY



## Dendritic Polymers as Fire Suppressants

Nora C. Beck Tan  
Daniel C. DeSchepper  
Lajos Balogh

ARL-TR-2071

OCTOBER 1999

Starburst® is a registered trademark of Dendritech, Inc.

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.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

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

# Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5069

---

---

ARL-TR-2071

October 1999

---

## Dendritic Polymers as Fire Suppressants

Nora C. Beck Tan  
Daniel C. DeSchepper  
Weapons & Materials Research Directorate, ARL

Lajos Balogh  
University of Michigan

---

Approved for public release; distribution is unlimited.

---

---

---

---

## Abstract

---

This report describes an evaluation of the applicability of one of the latest advances in polymer technology (dendritic polymers) to suppressing fires, one of the greatest survivability threats to military personnel and vehicles. Certain types of alkali and transition metal complexes are known to have the capability to act as fire suppression super-agents. Unfortunately, the most effective of these agents are also highly toxic. Dendritic polymer molecules, because of their unique architecture, have been found to have the ability to make tens to hundreds of metal ions complex, either in their interior or on their surface. This “complexation” allows the dendrimer to act as a non-toxic carrier of metal ions. Because the solubility of the complex is controlled by the polymer, the dendrimers can be used to carry the metal ions in various fire suppression fluids, such as water. In this study, our aim was to investigate the effectiveness of dendrimer-metal complexes as fire suppression agents in an aqueous solution. This project was undertaken as a 1-year, proof-of-concept effort as part of the Strategic Environmental Research and Development Program (SERDP)-Next Generation Fire Suppression Technology Program (NGP). We found that the dendritic polymers do enhance the fire suppression effectiveness of water. Our results indicate that the fire suppression effectiveness depends on the type of complexed ion delivered and the mechanism of delivery. Our results also uncovered a need to develop new fire suppression agent screening methods suitable to evaluate experimental liquid and solid powder fire suppressants.

## ACKNOWLEDGMENTS

We would like to express our thanks to Dr. Jiann Yang and Ms. Nikki Privé for assisting with the execution and interpretation of results from all the experiments that were run using the dispersed liquid agent fire suppression screen (DLAFSS) apparatus at the National Institute of Standards and Technology, and to Dr. Yang for his critical review of this report. The advice of Dr. Tony Finnerty is also gratefully acknowledged. This research is part of the Department of Defense's (DoD) Next Generation Fire Suppression Technology Program, funded by the DoD Strategic Environmental Research and Development Program (SERDP).

INTENTIONALLY LEFT BLANK

## TABLE OF CONTENTS

	<u>Page</u>
LIST OF FIGURES .....	vii
LIST OF TABLES .....	ix
1. INTRODUCTION .....	1
2. MATERIALS .....	1
3. FIRE SUPPRESSION EXPERIMENTATION .....	5
4. TECHNICAL RESULTS: FIRE SUPPRESSION INVESTIGATION .....	7
4.1 Fire Suppression Experiments, Part I: DLAFSS Evaluation .....	8
4.2 Fire Suppression Experiments, Part II: JP8 Fuel Fire Screening Investigation . . . .	18
5. IMPORTANT FINDINGS AND CONCLUSIONS .....	21
6. IMPLICATIONS FOR FUTURE RESEARCH .....	21
REFERENCES .....	23
DISTRIBUTION LIST .....	25
REPORT DOCUMENTATION PAGE .....	27

INTENTIONALLY LEFT BLANK



## LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Chart of Fire Suppressant Effectiveness, Babushok and Tsang . . . . .	2
2. Schematic Representation of the DFLASS Apparatus . . . . .	6
3. Picture of (a) an Envelope Flame and (b) a Wake Flame . . . . .	6
4. Setup for JP8 Fire Suppression Experiments . . . . .	8
5. Air Blow-off Velocity Recorded Using Different Propane Burner Elements . . . . .	9
6. Water Blow-off Velocity Recorded Using Different Propane Burner Elements . . . . .	10
7. Average Air Blow-off Velocity Recorded Using Different Propane Burners . . . . .	11
8. Average Water Blow-off Velocity Recorded Using Different Propane Burners . . . . .	12
9. Ratio of Average Blow-off Velocities Measured for Water and Air Using Different Propane Burners . . . . .	12
10. Blow-off Velocity Ratios for Various Candidate Agents to Air, and Reference Ratios for Water to Air Measured With the Same Conditions (pump rate of suppressant fluid to nebulizer is 0.3 ml/min in all cases) . . . . .	14
11. Blow-off Velocity Ratios for Various Candidate Agents to Air, and Reference Ratios for Water to Air Measured With the Same Conditions (pump rate of suppressant fluid to nebulizer is 0.5 ml/min in all cases) . . . . .	14
12. Times for Various Experimental Fire Suppression Agents to Extinguish a 200-ml JP8 Fuel Pan Fire . . . . .	19
13. Amounts of Various Experimental Fire Suppression Agents Required to Extinguish a 200-ml JP8 Fuel Pan Fire . . . . .	19
14. Mass Flow Rates for Various Experimental Fire Suppression Agents Deployed During JP8 Fire Suppression Agent Screening Experiments . . . . .	20

INTENTIONALLY LEFT BLANK

## LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	Elemental Composition of Pure Dendrimers and Dendrimer Salt Complexes . . . . .	4
2.	Average Blow-off Velocities for Various Candidate Agents . . . . .	13
3.	Ranking of Fire Suppression Effectiveness for Aqueous Solutions of Various Experimental Agents . . . . .	16

INTENTIONALLY LEFT BLANK

# DENDRITIC POLYMERS AS FIRE SUPPRESSANTS

## 1. INTRODUCTION

Dendritic polymers or dendrimers are a new polymer technology just recently come to fruition as commercial products. They are ultra-branched, three-dimensional polymeric molecules possessing a low density core surrounded by a crowded, high density surface.[1,2] The interior of the dendrimer has a high concentration of branching junctions, which number in the tens to hundreds, depending on the overall degree of polymerization of the dendrimer. In the chemistries most commonly synthesized, these branching points are tertiary amines. Thus, the nitrogen at the branch junction has a lone pair of electrons that may be used for “complexation<sup>1</sup>.” The ends of these branching paths are located on the dendrimer’s surface and may also number in the tens to hundreds. The chemistry of these end groups is easily tailored to incorporate a desired chemical moiety or to encourage complexation with a specific ion. The isolation of multiple nitrogen branch points and end groups within the 5- to 10-nanometer (nm)-diameter dendritic molecule leads to an excessively high local concentration of complexation sites and potentially to a very effective delivery vehicle. It is possible to carry dozens of metal ions within or on the surface of a single dendrimer molecule.

Previous research has shown that transition metal complexes and alkali metal salts may act as super-agents for fire suppression, performing as much as 60 times more efficiently than Halon 1301 [3,4] (see Figure 1). Unfortunately, the most effective of the complexes also suffer from high toxicity. We postulated that by encapsulating the metal ion inside the dendrimer or by attaching it to a dendrimer surface, we could create the best case scenario for a Halon replacement: a super-effective agent encapsulated in an inert, bio-compatible shell that decomposes upon contact with flame. Thus, our conceptual hypothesis was that dendrimer-metal complexes could be used as high efficiency, low toxicity fire suppression agents. We have examined this hypothesis by evaluating the fire suppression capacity of two classes of dendrimer-metal complexes: dendrimer-alkali metal salts, and dendrimer-transition metal complexes. Our results indicate that dendrimer-metal hybrids show promise for use as fire suppression agents.

## 2. MATERIALS

Poly(amidoamine) dendrimers were purchased from Dendritech, Inc., of Midland, Michigan. Two types of dendrimers were used in this study: Generation 3.5 sodium carboxylate salt

---

<sup>1</sup>The process of making a metal ion complex.

terminated dendrimers, designated G3.5-ONa, and Generation 4.0 primary amine terminated dendrimers, designated G4.0. Both types of dendrimers were synthesized from an ethylenediamine (EDA) core. All other starting materials (inorganic salts, solvents) were purchased from Aldrich Chemical.

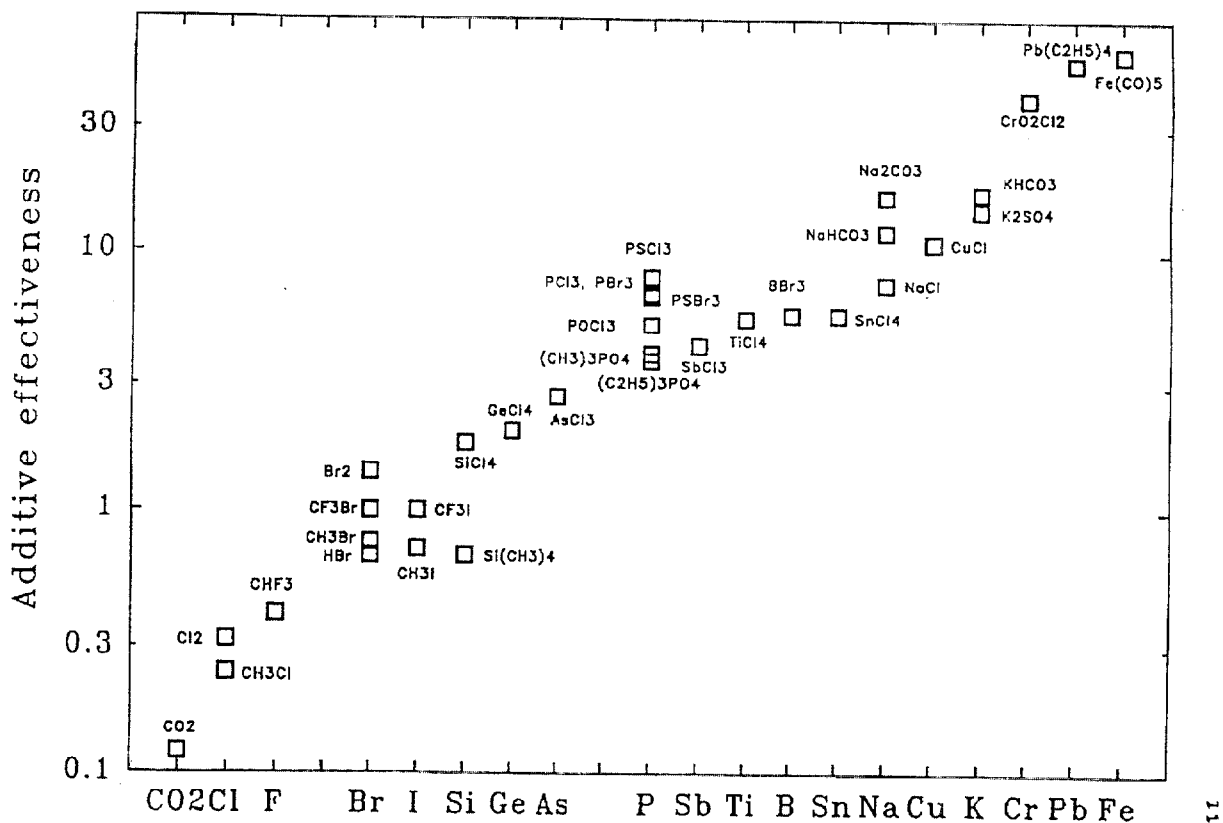


Figure 1. Chart of Fire Suppressant Effectiveness. Babushok and Tsang [4]

The G3.5-ONa dendrimers have 64 –COONa end groups per molecule and a nominal molecular weight of 14,019 g/mole. These materials were used in the as-received condition.

The G4.0 dendrimers have 64 –NH<sub>2</sub> end groups per molecule, and nominal molecular weight of 14,215 g/mole. These G4.0 dendrimers were used as starting materials from which the potassium salts and transition metal complexes were prepared. The –NH<sub>2</sub> end groups of the G4.0 dendrimers can cause instability and intermolecular aggregation in the transition metal complex form. For this reason, the end groups were converted to the more stable succinic acid form by reaction with succinic anhydride in methanolic solution before the salts and complexes were prepared. After reaction, the modified G4.0 dendrimer was dried, and the product was purified by

dissolution and vacuum stripping three times to ensure removal of all methanol residue. The modified dendrimer, designated G4.SA, has an end group chemistry of  $[-\text{NHCO}(\text{CH}_2)_2\text{COOH}]$ . The final product was characterized using hydrogen and carbon nuclear magnetic resonance (NMR). The proton spectrum showed no trace of residual succinic acid but showed a sharp peak at 30.4 ppm, which is characteristic of methylene protons next to the terminal carboxylate groups, and therefore confirms the expected reaction. Molecular weight determination by matrix-assisted laser desorption ionization spectroscopy indicated a molecular weight for G4.SA of 19,271 g/mole. This molecular weight value indicates that, on average, each G4.0 molecule has had 52 of the 64 primary amine end groups converted to succinic acid. (A molecular weight of 20,619 g/mole would indicate 100% conversion.)

After the reaction was verified, the final G4.SA product was then re-dissolved in deionized water to 25% concentration, by weight, and split into four equivalent batches. One batch was retained as control, one converted to potassium salt, one converted to iron complex, and one converted to chromium complex. Conversion to potassium salt was accomplished by adding potassium carbonate ( $\text{K}_2\text{CO}_3$ ) in a quantity equivalent to that required to allow for 64 potassium ions per dendrimer molecule.

Preparation of iron and chromium salts was first attempted in the same manner as the potassium salts. Upon addition of the inorganic salt precursors used in the generation of the transition metal complexes (ammonium sulfate hexahydrate ( $[\text{Fe}(\text{NH}_3)_2\text{SO}_4]_2 \cdot 6\text{H}_2\text{O}$ ) and chromium chloride hexahydrate ( $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ ) to small amounts of the 25% G4.SA solutions during ambient conditions, gelation occurred within 1 minute. Similar results were obtained using 10% solutions, although gelation took considerably longer. Both solutions were found to be stable only if prepared and stored in the absence of oxygen. For this reason, only 1-gram amounts of the iron and chromium complexes were prepared initially, to be used in characterization, and the remaining dendrimer and metal salt solutions were kept separately for mixing immediately before fire suppression experiments. The transition metal complexes were formed by mixing a quantity of either the iron or the chromium salt into an aqueous solution of G4.SA under nitrogen atmosphere in ratios so that each G4.SA molecule would complex with 21 metal ions, on average. One-gram batches of the G4.SA potassium salt, designated G4.SA-K, the G4.SA iron complex, designated G4.SA-Fe, and the G4.SA chromium complex, designated G4.SA-Cr, were dried by lyophilizing (i.e., freeze drying) and were subsequently characterized using elemental analysis for verification and quantification of the metal content.

Elemental analysis of G4.SA, G4.SA-K, G4.SA-Fe, G4.SA-Cr, and G3.5-ONa materials was conducted by Galbraith Laboratories. The metal-containing species were analyzed only for carbon, nitrogen, hydrogen, and the metal species expected. The G4.SA starting material was analyzed for carbon, nitrogen, hydrogen, and oxygen, which should give 100% elemental content of that material. Oxygen analysis was not conducted on the metal-containing species for budgetary reasons. The results of the elemental analysis are given in Table 1, along with the calculated amounts for C, O, N, H, and the appropriate metallic species, for comparison.

Table 1. Elemental Composition of Pure Dendrimers and Dendrimer Salt Complexes

Sample	Element	Weight Percent	Atom Percent
G4.SA	Hydrogen	8.08	53.9
	Carbon	48.03	26.7
	Nitrogen	14.7	7
	Oxygen	29.1	12.5
G4.SA-Cr	Hydrogen	6.94	51.2
	Carbon	42.07	25.6
	Nitrogen	12.76	6.72
	Oxygen*	33.6	15.5
	Chromium	4.63	0.66
G4.SA-Fe	Hydrogen	6.81	51
	Carbon	37.9	23.7
	Nitrogen	13.63	7.29
	Oxygen*	37.3	17.5
	Iron	4.37	0.6
G4.SA-K	Hydrogen	6.7	50.9
	Carbon	42.2	26.7
	Nitrogen	12.62	6.84
	Oxygen*	28.7	13.6
	Potassium	9.8	1.9
G3.5-ONa	Hydrogen	7.38	52.5
	Carbon	43.37	25.7
	Nitrogen	12.9	6.55
	Oxygen*	29.4	13.1
	Sodium	6.92	2.14

\*calculated



### 3. FIRE SUPPRESSION EXPERIMENTATION

Fire suppression capacity for various liquids was evaluated using two separate techniques, one developed at the National Institute of Standards and Technology (NIST) under the Next Generation Fire Suppression Technology Program (NGP), and one that was a modification of a method developed at the U.S. Army Research Laboratory (ARL) by Dr. Anthony Finnerty under U.S. Army funding.

The technique and equipment developed at NIST is called the dispersed liquid agent fire suppression screen (DLAFSS) apparatus.[5,6] This technique was developed specifically for screening experimental agents and has very good reproducibility in comparison to other screening methods. The DLAFSS apparatus consists of a cylindrical, opposed flow burner (located in a vertical wind tunnel) and a nebulizer used as a droplet generation device (mounted in the settling chamber of the tunnel). Propane gas injected into the burner serves as fuel for the diffusion flame emanating from the opposed flow burner (see Figure 2). A syringe pump is used to deliver the agent candidate to the nebulizer at a constant, preset volumetric flow rate. During the experiment, liquid agents are entrained into the air flow stream in the wind tunnel and travel upward where they impinge on the propane flame. The candidate liquid is delivered into the air stream at a constant rate, and the air velocity is slowly increased. When air velocity reaches a critical value, the stable, blue enveloped propane flame at the burner will be blown off, forming a wake flame (see Figure 3). The transition to a wake flame is essentially equivalent to extinguishing the fire. A wake flame remains because of anchoring effects associated with the burner design. The air velocity at which the transition from a envelope flame to a wake flame occurs depends on the effectiveness and delivery rate of the fire suppressant liquid, and this velocity is therefore used as a criterion for screening the effectiveness of various candidate liquids. More details about the design, development, and implementation of this experimental technique are given in references [5] and [6]. Although this was by far the best method found for screening experimental liquid fire suppression agents, some difficulties were encountered in the application of this method, which are described in subsequent sections.

All experiments using the DLAFSS apparatus were conducted with the propane flow rate set to 2.0 liters per minute and the nebulizer air flow rate at 0.25 liter per minute. The procedure involved first turning on the air in the wind tunnel at a minimum rate, opening the propane valve, turning on the nebulizer air, setting the syringe pump to the desired agent delivery rate, and lighting the burner. The initial state of the flame under these conditions is an enveloped diffusion flame. The system was then allowed to thermally equilibrate for 2 to 5 minutes. Following system stabilization, the air flow in the wind tunnel was increased slowly until the transition

from the enveloped flame to the wake flame occurred. The air flow rate at the transition point was recorded. Before each agent experiment was run, control values of transition flow rate, or blow-off point, were recorded for pure air (no agent) and pure water. Two to three values of air and water velocity were recorded for each burner element used on a given day. Three values of blow-off velocity were recorded for each sample.

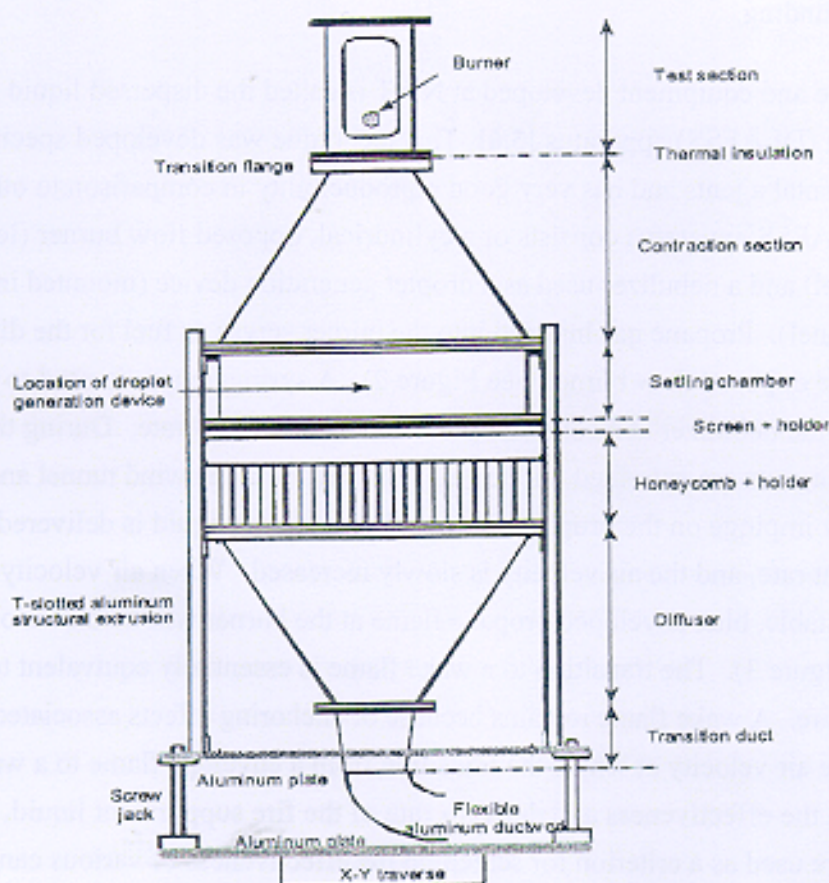


Figure 2. Schematic Representation of the DLAFFS Apparatus.

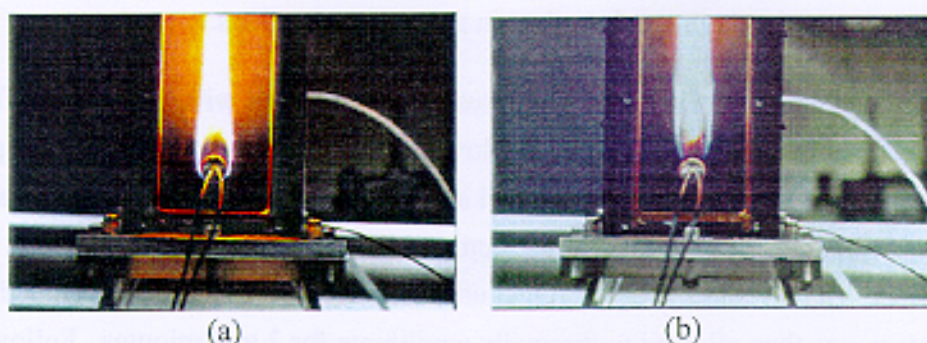


Figure 3. Picture of (a) an Envelope Flame and (b) a Wake Flame.

The second method used was a modification of the JP8 fuel fire suppression agent screening method developed by Dr. Finnerty at ARL.[7] The experiment involves simply spraying a stream of the agent directly onto a small JP8 fire during controlled conditions. The time to extinguish the fire is the criterion used to evaluate the effectiveness of various agents. It was our original intention to follow the Finnerty procedure exactly; however, upon closer scrutiny, we discovered that this procedure required a larger amount of sample per experiment than was available to us. We modified the sample delivery procedure to accommodate the limited sample availability. A Binks model 15 paint spray gun was used as the agent delivery device, with a 1.58-mm nozzle operating at a pressure of 40 psi. This gun produces a fine stream of fluid droplets entrained in a forced air flow from a relatively small container of fluid. We found that we were able to fill the agent dispersion container with as little as 50 ml of fluid and achieve an acceptable droplet stream. The spray gun was aimed at a 30° angle to the fuel reservoir, a 160-mm diameter aluminum pan. The apparatus was adjusted so that the droplet spray distribution pattern covered the entire surface of the fuel container. In order to ensure that the surface was covered entirely, it was necessary to set the apparatus so that the distribution actually exceeded the size of the fuel container. Preliminary investigations indicated that for water, the rate of flow out of the spray gun was 4.6 ml/sec, while the rate of collection in the fuel container was 1.7 ml/sec. Before each experiment, the fuel pan was filled with 200 ml of JP8 jet fuel. The fuel was at ambient temperature, 23° to 25° C. The procedure involved filling the fuel pan and agent dispersion container with pre-weighed amounts of fluid, setting the fuel on fire with a propane torch, waiting 60 seconds after the entire surface of the fuel was engaged for the system to stabilize, engaging the spray device, and recording data. The data included the amount of time required to extinguish the fire, the amount of agent fluid remaining in the spray gun, and the amount of fluid remaining in the fuel pan. All experiments were recorded using a video camera, and exact fire-out times were extracted from the recordings. A photograph of an experiment in progress is shown in Figure 4.

#### **4. TECHNICAL RESULTS: FIRE SUPPRESSION INVESTIGATION**

Fire suppression screening experiments were conducted on water and aqueous solutions of pure dendrimer, dendrimer sodium salts, dendrimer potassium salts, dendrimer iron complexes, dendrimer chromium complexes, sodium acetate, potassium carbonate, chromium (III) chloride hexahydrate, and ammonium iron(II) sulfate hexahydrate. The water, dendrimer solutions, and pure salt solutions were investigated as controls. In the case of the pure salts, the concentrations were adjusted so that the atom concentration of the metal ion was either equivalent to that in the corresponding dendrimer-metal complex solution (sodium, iron, and chromium salts) or set at 10 times the equivalent weight (potassium salts).

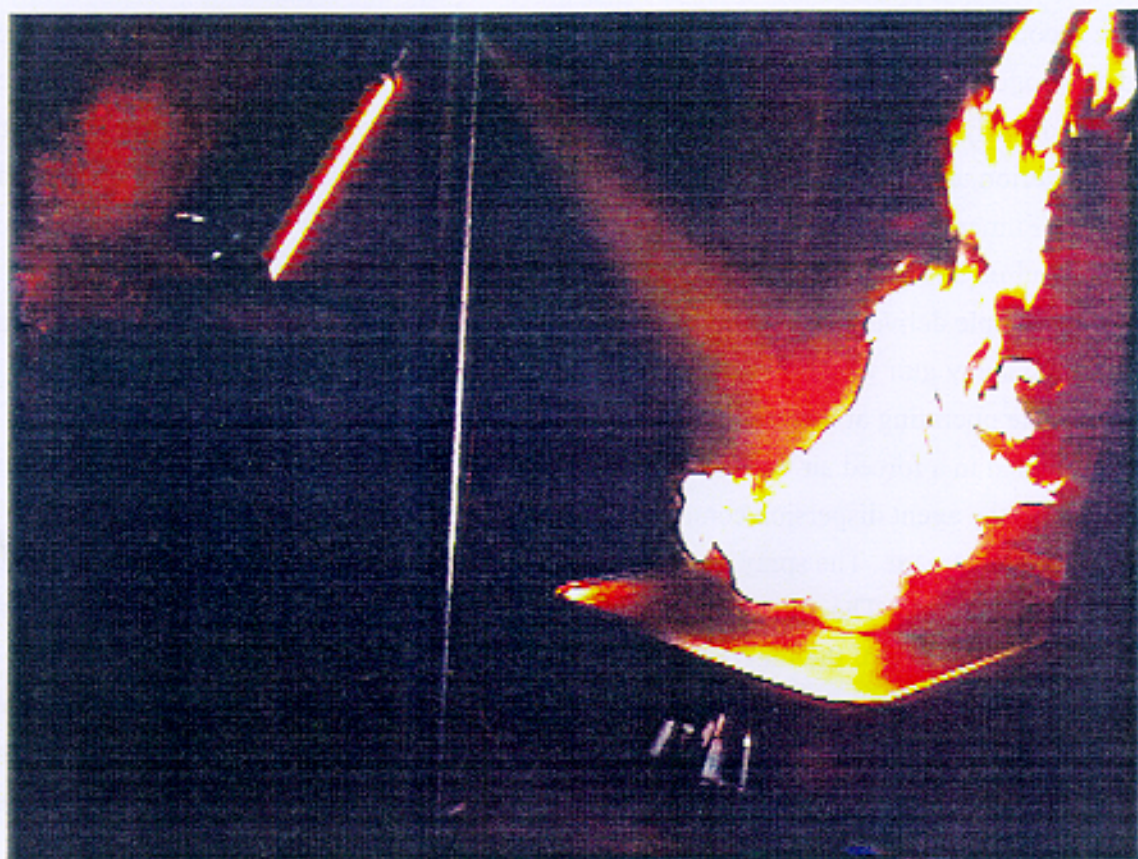


Figure 4. Setup for JP8 Fire Suppression Experiments.

#### 4.1 Fire Suppression Experiments, Part I: DLAFSS Evaluation

##### 4.1.1 *Data Collection and Analysis*

The DLAFSS experiment was developed at NIST concurrently with this program. For this reason, procedures and data reduction protocols were not well established for the duration of the study, and some consideration must be given to the evaluation of reproducibility and proper interpretation of data collected using the DLAFSS experiment.[8]

As described previously, the DLAFSS experiment essentially involves recording the air flow required to destabilize or “blow off” an enveloped propane flame in a wind tunnel. Incorporation of a fire suppression agent into the air stream reduces the flow rate required to blow off the flame. The procedure employed involves first establishing the critical air flow for blow-off without any introduced agent, followed by determining the critical blow-off air flow when water is introduced into the air stream as a fire suppression agent, and finally determining the critical blow-off air flow required when the experimental suppression agent is introduced into

the flow. Thus, to evaluate a given experimental agent, at least three separate critical air flow values are recorded. In addition, the procedure involved multiple determinations of air and water blow-off values per experiment. The result is that we ultimately recorded more than 36 values of air blow-off velocity and water blow-off velocity during the 2-month period over which the experiments were conducted. In Figures 5 and 6, the air and water blow-off velocities are plotted against the ID number of the burner that was used in the study. Multiple burners were used because it was necessary to constantly replace the burners after experimentation because of contamination by polymer char products.

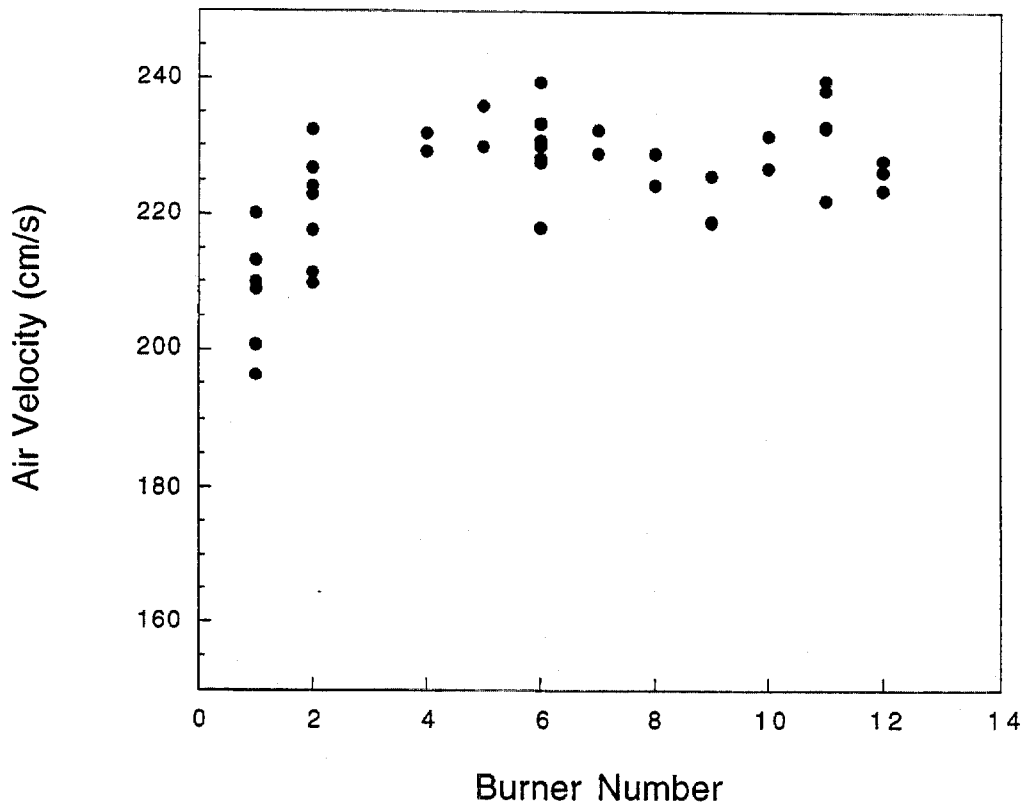


Figure 5. Air Blow-off Velocity Recorded Using Different Propane Burner Elements.

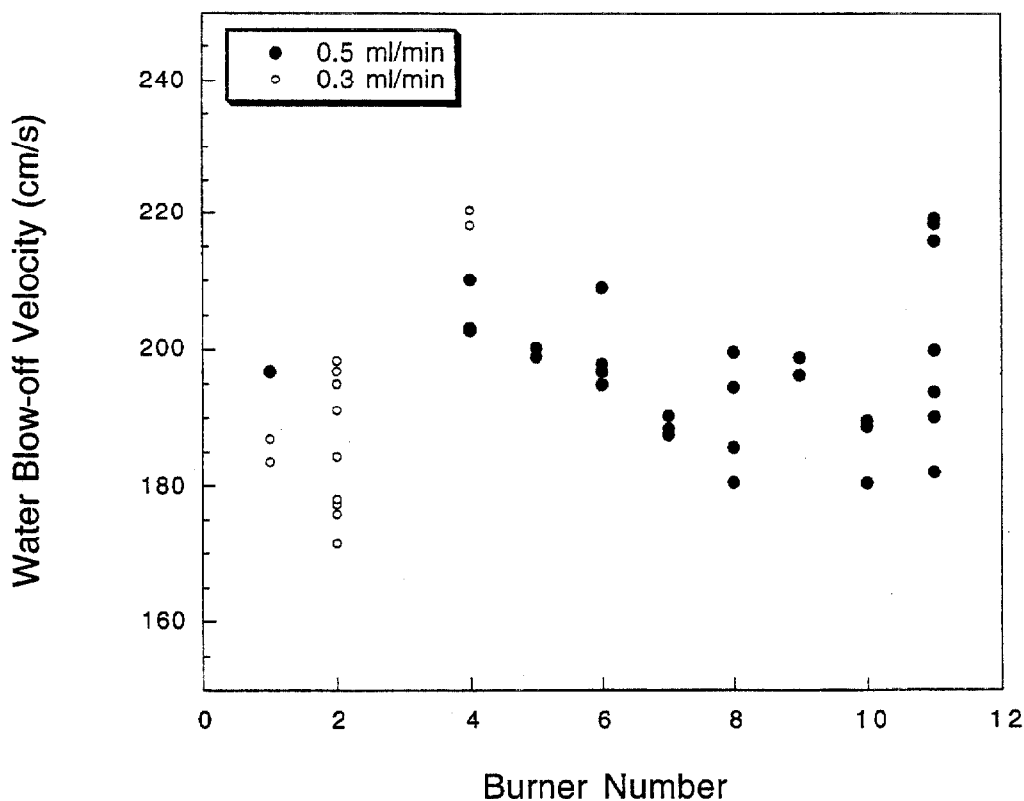


Figure 6. Water Blow-off Velocity Recorded Using Different Propane Burner Elements (open circles, water pumped to nebulizer at 0.3 ml/min; closed circles, water pumped to nebulizer at 0.5 ml/min).

Clearly, there is considerable scatter in the values of the blow-off velocities measured for a given burner or with different burners. The scatter in the data is 20% to 30%, which is high enough to mask any effects of the experimental suppressants, making the absolute values of the blow-off velocity unacceptable for quantification of fire suppression effectiveness. Reducing the data to averages of all measured blow-off velocities using a given burner on a given day improves the situation somewhat but still results in 10% to 20% scatter in the data (see Figures 7 and 8). The double data points in Figure 7 for burners 1, 2, and 6 give an indication of the day-to-day variation in average air blow-off velocity, which is in the 5% to 7% range. Note that the scatter in the air blow-off velocities (see Figure 7) is considerably less than in the water blow-off velocities (see Figure 8), which may be symptomatic of the difficulty associated with screening liquid fire suppression agents.

In this study, we found that the best parameter for quantifying the data collected using the DLAFSS apparatus was the ratio of the water or sample blow-off velocity to the air blow-off velocity (see Figure 9). A compilation of water to air blow-off velocity ratios collected over the course of the experiments indicates that the scatter in these ratios is in the range of 10% to 13%.

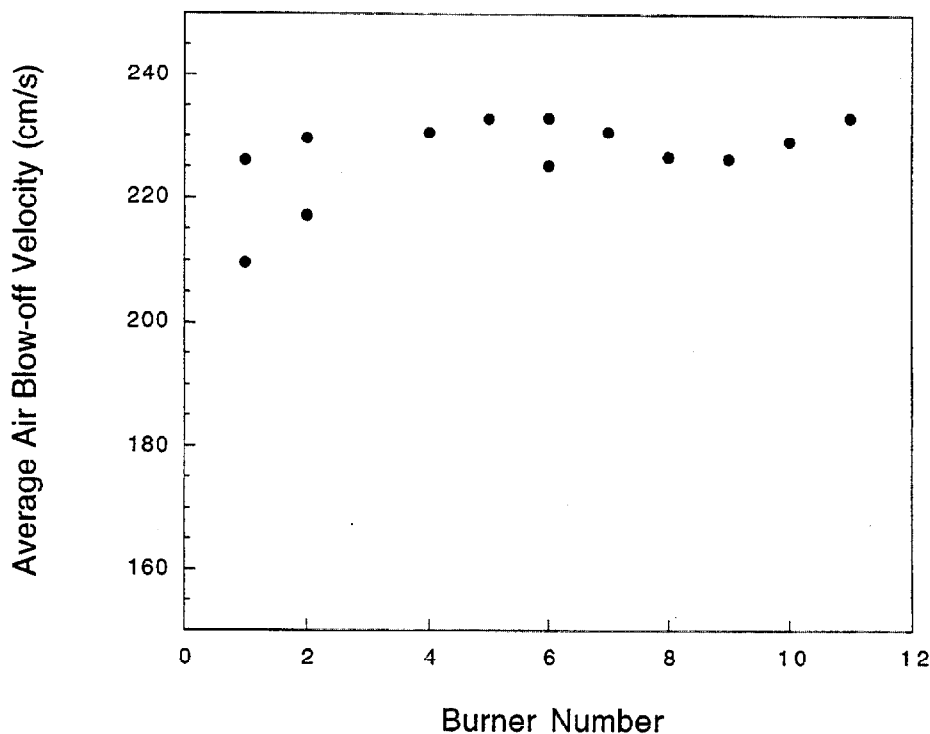


Figure 7. Average Air Blow-Off Velocity Recorded Using Different Propane Burners (all values collected using a given burner on a given day were included in the arithmetic average).

Based on the considerations just outlined, the procedure adopted for reducing the data was as follows. During evaluation of a given candidate fire suppressant, several measurements of air blow-off velocity and water blow-off velocity were taken before we experimented with the screening agent. After the screening agent's performance was measured, an additional air blow-off velocity measurement was taken. If this measurement differed significantly from the pre-sample measurement, the apparatus was shut down, and the burner was removed and either cleaned or replaced. If the burner was cleaned but not replaced, an additional air blow-off velocity measurement was taken to ensure that the system had returned to its starting performance, and a second sample was measured. If the burner needed to be replaced in between samples, as was generally the case for the dendrimer samples, several measurements of air blow-off velocity and water blow-off velocity were recorded before the measurement was repeated on the sample. The procedure was repeated until at least three measurements had been collected for each sample.

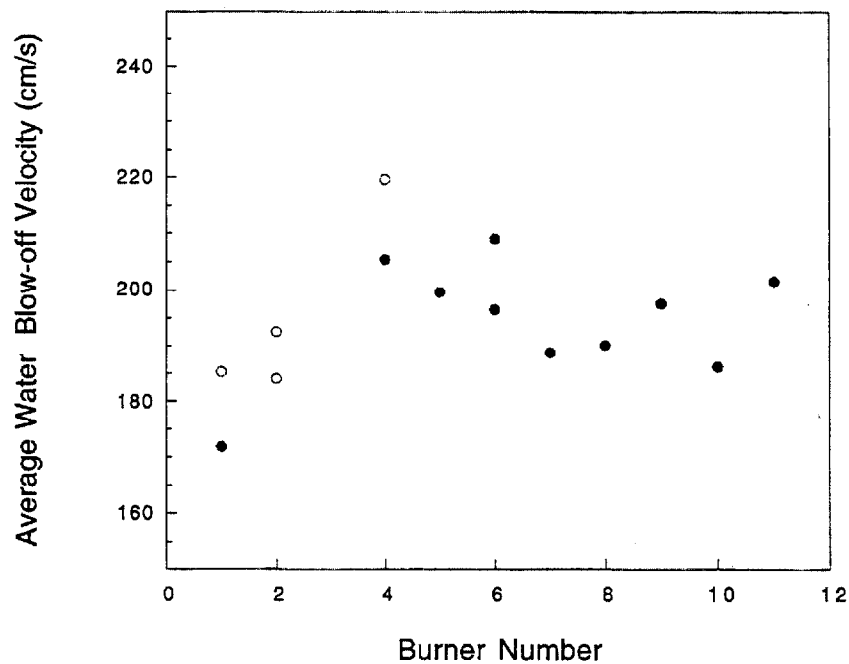


Figure 8. Average Water Blow-Off Velocity Recorded Using Different Propane Burners (all values taken on a given day using a given burner were included in the arithmetic average; open circles, water pumped to nebulizer at 0.3 ml/min; closed circles, water pumped to nebulizer at 0.5 ml/min).

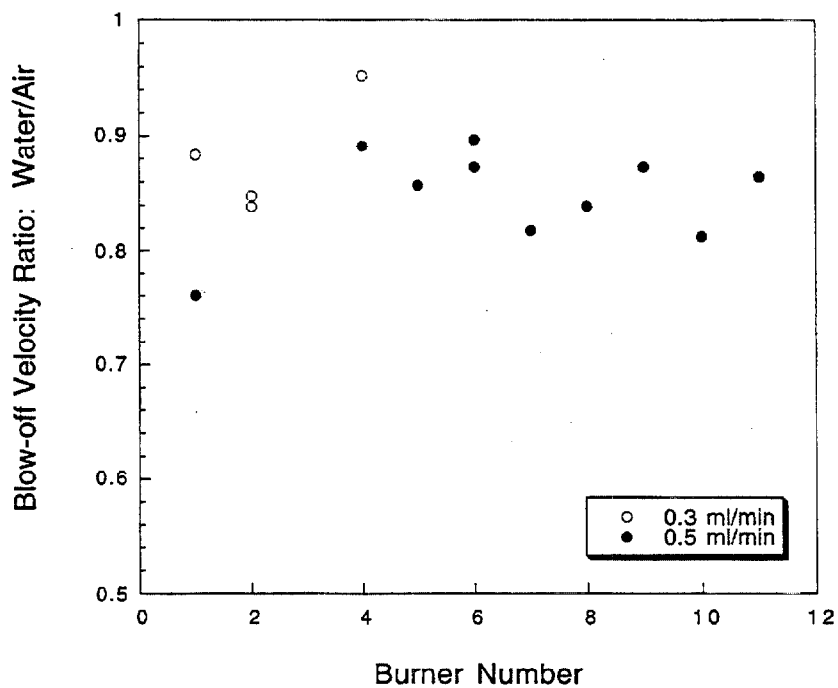


Figure 9. Ratio of Average Blow-Off Velocities Measured for Water and Air Using Different Propane Burners (open circles, water pumped to nebulizer at 0.3 ml/min; closed circles, water pumped to nebulizer at 0.5 ml/min).



Data for air blow-off velocity and water blow-off velocity for a given burner collected on a given day were averaged and used in calculating blow-off velocity ratios of water to air, sample to air, and sample to water for samples that were evaluated using that same burner. Then, the ratios calculated for each sample were averaged. These average ratios are the recorded parameters used to evaluate the candidate suppressant's performance.

#### 4.1.2 DLAFSS Results

The actual values of average blow-off velocities calculated for each agent screened are tabulated in Table 2. These values are similar to those collected by Yang et al.[5,6] for a variety of potassium and sodium small molecule salts.

The results of the DLAFSS fire suppression experiments on aqueous solutions of pure dendrimers, modified dendrimers, and sodium and potassium salt solutions are summarized in Figures 10 and 11. As discussed before, because of uncertainties in the data, the most valid comparisons may be made between the water-to-air ratio and the sample-to-air ratios calculated from data recorded during very similar conditions. To avoid misinterpretation of the figures, the water-to-air blow-off velocity ratio measured during the same conditions as the sample-to-air blow-off velocity ratio is given in each case. The effectiveness of the agent should be interpreted based on that reference.

Table 2. Average Blow-off Velocities for Various Candidate Agents

Agent	Blow-off Velocity (cm/s) 0.3 ml/min	Blow-off Velocity (cm/s) 0.5 ml/min
10% G4.SA	170	
25% G4.SA-K	152	
4.8% K <sub>2</sub> CO <sub>3</sub>	189	
15% G4.SA		193
15% G4.SA-K		180
3.23% K <sub>2</sub> CO <sub>3</sub>		204
15% G3.5-ONa		152
0.65% CH <sub>3</sub> CO <sub>2</sub> Na		171

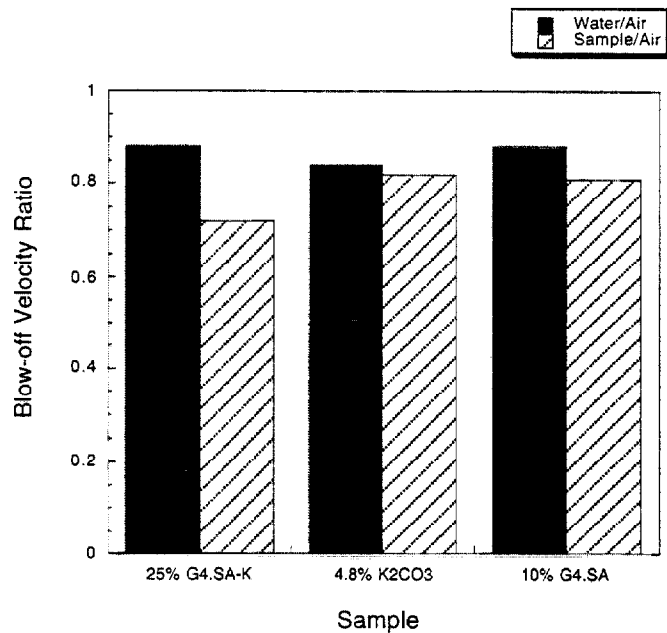


Figure 10. Blow-off Velocity Ratios for Various Candidate Agents to Air, and Reference Ratios for Water to Air Measured With the Same Conditions (pump rate of suppressant fluid to nebulizer is 0.3 ml/min in all cases).

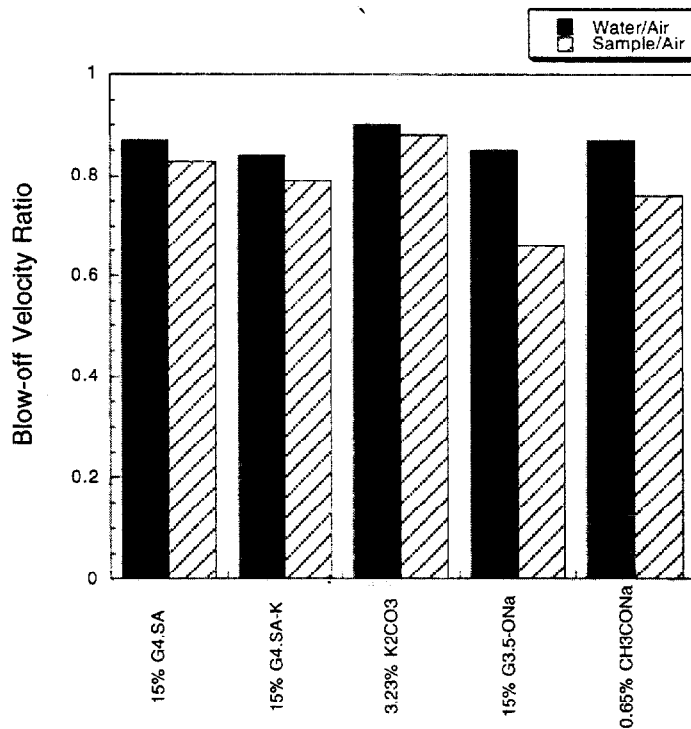


Figure 11. Blow-off Velocity Ratios for Various Candidate Agents to Air, and Reference Ratios for Water to Air Measured With the Same Conditions (pump rate of suppressant fluid to nebulizer is 0.5 ml/min in all cases).

Figure 10 summarizes the results of fire suppression experiments conducted with a sample delivery rate of 0.3 ml/min. These were among the first experiments conducted. The most interesting results from the 0.3-ml/min experiments are those from the 25% G4.SA-K and the 4.8%  $K_2CO_3$  solutions. Although the potassium carbonate actually contains ten times more potassium ions than the G4.SA-K dendrimer salt solution, the dendrimer solution is clearly more efficient as a fire suppression agent. Another important finding that can be seen from Figure 10 is that the pure dendrimer solution, 10% G4.SA, has fire suppression capacity that is better than pure water. This is significant because there were initial concerns that the polymer may act as fuel and thereby be detrimental to fire suppression effectiveness.

The original experimental plan had been to conduct fire suppression experiments on all dendrimers and modified dendrimers from 25% aqueous solutions, by weight, with the sample delivery rate of 0.3 ml/min. However, the sample delivery device, a commercial syringe pump, stalled repeatedly upon attempts to deliver a 25% solution of G4.SA and again upon attempt to deliver a 20% solution of the same material. This failure of the pump is related to the high viscosity of the solution. We resolved this issue by dropping the solution concentration used to 15% and at the same time increasing the sample delivery rate to 0.5 ml/min. These new settings allowed for the same delivery rate of sample ( $0.5 \cdot 15 = 0.3 \cdot 25$ ), without causing the sample delivery device to stall.

The results from DLAFSS experiments conducted with the sample delivery rate of 0.5 ml/min are summarized in Figure 11. These results include velocity blow-off ratios for 15% solutions of pure G4.SA dendrimer, G4.SA-K dendrimer salt, and G3.5-ONa dendrimer sodium salt. Results from small molecule potassium and sodium salts are also included for comparison. The results for the 15% G4.SA solution indicate that once again, the addition of the pure dendrimer to water is not detrimental to fire suppression effectiveness. A modest improvement in fire suppression effectiveness is seen for both the 15% G4.SA and the 15% G4.SA-K samples. The comparison of G4.SA-K to the  $K_2CO_3$  solution shows that the dendrimer salt performs better than the pure salt by a small amount. This may be more significant than it appears, given that the potassium ion concentration in the salt solution is actually ten times that in the dendrimer solution.

The agent that showed the most significantly enhanced fire suppression capability was the G3.5-ONa dendrimer potassium salt. The blow-off velocity of the dendrimer-sodium salt is reduced nearly 20% relative to the blow-off velocity ratio for water measured when the same conditions are used. The 0.65% sodium acetate solution, which has the same sodium ion

concentration as the G3.5-ONa dendrimer salt, also showed promise for enhancing the fire suppression effectiveness of water but to a lesser extent than the dendritic salt solution.

The blow-off velocity ratios of sample fire suppression effectiveness to water fire suppression effectiveness measured when the same conditions were used are tabulated in Table 3. All ratios are less than 1.0, indicating that the experimental agents performed better than water in all cases. For the case of the pure G4.SA dendrimer solutions and the potassium salts, the effectiveness of the experimental agent was very close to that of water, within 10%. In a few cases, the effectiveness of the agent was significantly better than water. For example, the sodium salts (both dendrimer and small molecule) and the dendrimer-potassium salt delivered at 0.3 ml/min from 25% solution are considerably more effective than water.

Table 3. Ranking of Fire Suppression Effectiveness for Aqueous Solutions of Various Experimental Agents

Agent	Sample-to-Water Blow-off Ratio
Water	1.00
10% G4.SA, 0.3 ml/min	0.91
25% G4.SA-K, 0.3 ml/min	0.82
4.8% K <sub>2</sub> CO <sub>3</sub> , 0.3 ml/min	0.98
15% G4.SA, 0.5 ml/min	0.96
15% G4.SA-K, 0.5 ml/min	0.94
3.23% K <sub>2</sub> CO <sub>3</sub> , 0.5 ml/min	0.98
15% G3.5-ONa, 0.5 ml/min	0.78
0.65% CH <sub>3</sub> CO <sub>2</sub> Na, 0.5 ml/min	0.87

In the case of the sodium salts, it appears that the sodium cation in this system is the active species. Both the small molecule salt and the dendrimer salt show promise as fire suppression agents. It is noteworthy that the sodium acetate showed an effect when present in only 0.65% by weight. Since this salt is inexpensive, non-hazardous and readily available, it may be prudent to investigate its fire suppression effectiveness more fully. Clearly, the G3.5-ONa dendrimer performed better than the small molecule salt solution of equivalent sodium ion concentration. A similar effect is observed in comparing the 25% G4.SA-K and the 4.8% K<sub>2</sub>CO<sub>3</sub> solutions. Since the pure dendrimer solutions were not found to be significantly more effective than water, the observed effect must be related to the combination of the cation with the dendrimer “carrier.” This is exactly the type of effect we were hoping to achieve at the outset of the project and

offers some proof of the concept that the use of dendritic polymers as carriers for active fire suppressant species can be beneficial.

The mechanism responsible for observed enhancement in the fire suppression effectiveness of the sodium and potassium through coupling with the dendrimer carrier cannot be easily extracted from the data. One possibility is that the organization of the cations on the dendrimer surface, which results in an extremely high *local* concentration of them, has a beneficial effect on the kinetics of the radical recombination reaction believed to be responsible for flame suppression. This type of kinetic effect has recently been observed for other situations in which an active species is localized on the surface of a dendrimer.[9] A second possibility is that the size and size distribution of the droplets being delivered to the flame were altered by the dendrimers in such a way as to improve the fire suppression effectiveness of the fluid, based on purely geometrical considerations. (It is generally believed that the droplet size and distribution are an important factor in determining the effectiveness of water sprays for fire suppression.) The droplet diameter from a nebulizer, which is the sample delivery device incorporated into the DLAFSS device, is known to be related to the properties of the nebulizing fluid, such as density, surface tension, and viscosity.[10] The density of dendrimer solutions is not substantially different than that of pure water, and the surface tension of polymer and salt solutions is generally not changed by more than about 10% to 20%. Thus, these two factors are probably not influencing the droplet distribution strongly. However, the viscosity of dendrimer solutions is much greater than that of pure water. Although measurement of the viscosity of the various dendrimer solutions was beyond the scope of the present investigation, other recent work on poly(amidoamine) dendrimers indicates that the viscosity of 15% to 25% dendrimer solutions at room temperature should be on the order of tens of centipoise[11], an order of magnitude greater than that of pure water (~1.0 centipoise).[12]

The idea that the viscosity effects may alter the fire suppression effectiveness through changes in the delivery spray may explain the apparent discrepancy between the fire suppression effectiveness observed for 25% G4.SA-K dendrimer solution delivered at 0.3 ml/min and the 15% G4.SA-K solution delivered at 0.5 ml/min. The mass flow rate of polymer into the flame is identical in both cases (0.08 g/min), but the fire suppression effectiveness of the 25% solution is considerably better than the 15% solution. This may be a reflection of the viscosity difference between the two fluids, which could be as much as a factor of 6 to 8, and its effect on the droplet size and distribution in the sample delivery spray. Although recent results by Yang et al.[8] indicate that the droplet size and distribution generated in the DLAFSS experiment are not strongly dependent on fluid viscosity in low viscosity solutions (~1-4 centipoise), they did not

measure droplet size distributions in polymer solutions that have viscosities that are much greater than that of water.

Although it is likely that the viscosity issue is playing a role in the determination of apparent fire suppression effectiveness, we emphasize that in the sodium salt and sodium dendrimer systems, chemical mechanisms are also probably contributing significantly. Note that both the 15% pure dendrimer solution and the 15% G4.SA-K solution were much less effective than the 15% G3.5-ONa solution, though the viscosities should be of similar magnitude (see Table 3). In addition, a change in the flame color was also observed upon introduction of the sodium-containing agents into the air flow, indicating a chemical interaction. Given this evidence of chemical interaction, it is in the sodium-containing systems where the kinetic benefits of localizing the active species on the surface of a dendrimer should be most readily apparent. The results from the G3.5-ONa solution provide the most concrete evidence that using a dendrimer carrier to deliver active species into a flame has a positive effect on the fire suppression effectiveness of that active species.

#### 4.2 Fire Suppression Experiments, Part II: JP8 Fuel Fire Screening Investigation

The analysis of data from the JP8 fuel fire screening experiments was very straightforward. The relevant parameters recorded were the time to extinguish the fire and the amount of agent that was dispersed in extinguishing the fire. Because a relatively large amount of agent was required to perform this experiment and the results were not found to be highly reproducible, this experiment was used only for the dendrimer-iron complexes that could not be studied using the DLAFSS apparatus because of their high viscosity. The associated transition metal salt and pure dendrimer controls were also studied (chromium [III] chloride hexahydrate, ammonium iron[II] sulfate hexahydrate, and G4.SA). The dendrimer chromium complexes could not be studied because the supply of material was insufficient.

The results from the JP8 fuel fire screening experiments are summarized in Figures 12 and 13. The fire-out times recorded for the iron salt and the dendrimer solutions appear to be slightly higher than those recorded for pure water, while the time for the chromium salt solution to extinguish the fire appears to be slightly less. Unfortunately, the scatter in the data is such that it is not possible to draw any strong conclusions regarding the relative fire-out times for any of the agents studied.

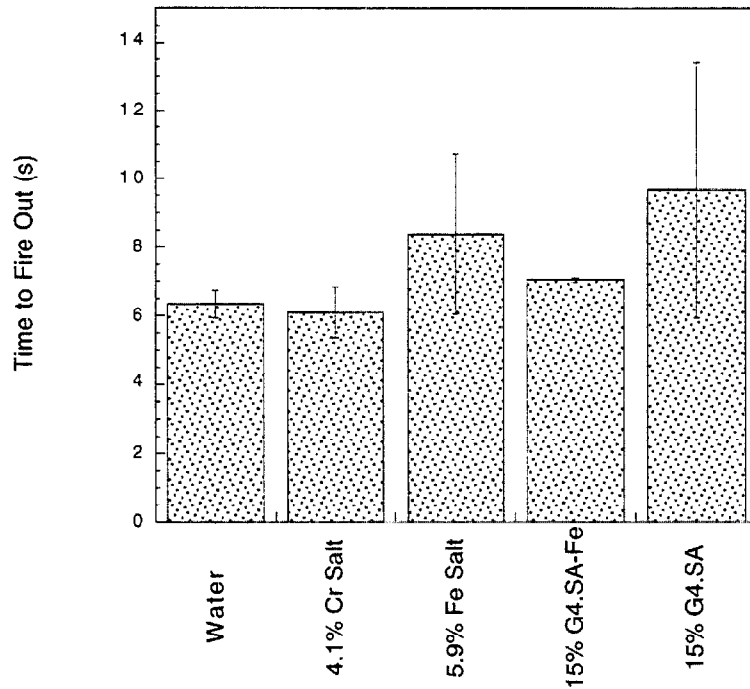


Figure 12. Times for Various Experimental Fire Suppression Agents to Extinguish a 200-ml JP8 Fuel Pan Fire (error bars represent  $\pm 1$  standard deviation).

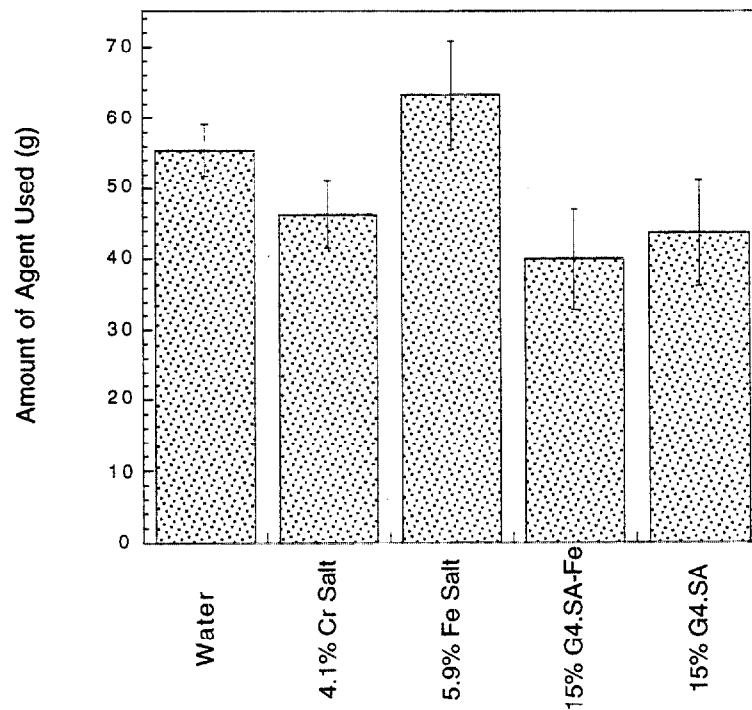


Figure 13. Amount of Various Experimental Fire Suppression Agents Required to Extinguish a 200-ml JP8 Fuel Pan Fire (error bars represent  $\pm 1$  standard deviation).

The amounts of the various agents required to extinguish the JP8 fuel fire vary within a range of about 10% (see Figure 13). The results suggest that while the fire-out times for the dendrimer agents may be slightly higher than for water, the total amounts of the dendrimer agents required to extinguish the fire were smaller than the total amounts of water and transition metal salt solutions required. Thus, it is not possible to judge the relative efficiency of the agents from these experiments because of the discrepancy in the agent delivery rates. These rates are calculated from the amount deployed and the time of deployment and are plotted in Figure 14. It appears that the paint sprayer was delivering higher viscosity solutions at slower rates. This difficulty in uniform agent dispersion for solutions of varying viscosity is a challenge to be addressed during the development of screening techniques for experimental fire suppression agents.

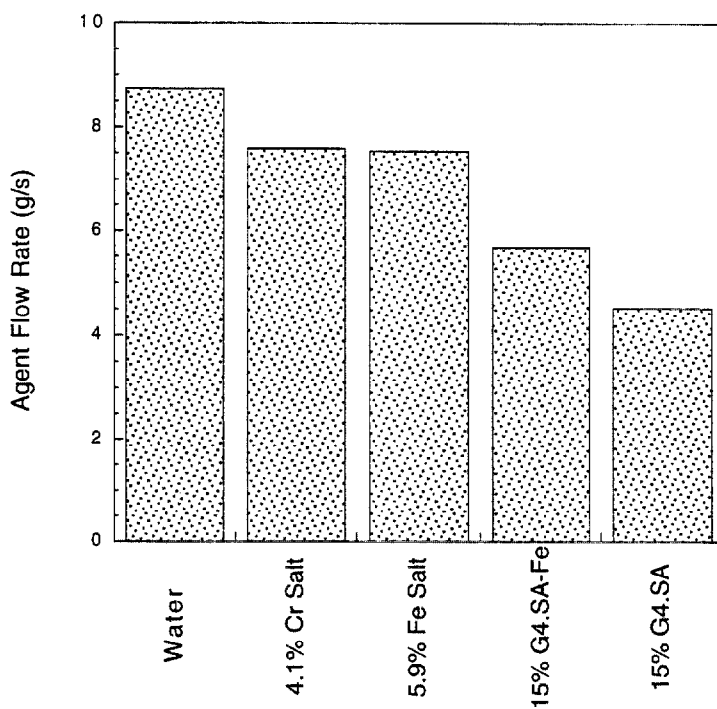


Figure 14. Mass Flow Rates for Various Experimental Fire Suppression Agents Deployed During JP8 Fire Suppression Agent Screening Experiments.

Because of the difficulties encountered in investigating the transition metal complexes using the JP8 fuel fire screening experiment, it is not possible to draw any strong conclusions regarding the fire suppression effectiveness of the dendrimer-transition metal complexes. However, despite the difficulties, we believe that the experiment was sensitive enough that if super-agent behavior were being displayed, i.e., the experimental agents were actually 50 or more times more effective than water, we would have detected it. Our studies indicate that the dendrimer-iron complexes are



most likely not exhibiting the super-agent performance that has previously been observed for iron pentacarbonyl and other volatile transition metal complexes.[4]

## 5. IMPORTANT FINDINGS AND CONCLUSIONS

The most significant of our research findings can be summarized as follows:

- Poly(amidoamine) dendrimers incorporated as an additive to water at substantial concentrations have no deleterious effect on the fire suppression effectiveness of water and can actually improve the fire suppression effectiveness of water marginally.
- The use of dendritic polymer carriers to deliver fire suppression agents such as potassium and sodium can increase the effectiveness of these agents substantially.
- Dendrimer-sodium salts are more effective fire suppression agents than dendrimer-potassium salts.
- The addition of sodium acetate to water improves its fire suppression effectiveness significantly, even in concentrations of <1% by weight.
- Potassium carbonate does not significantly improve the fire suppression effectiveness of water at concentrations as great as 5% by weight.
- More work is needed in the development of versatile experiments for screening experimental fire suppressants.

## 6. IMPLICATIONS FOR FUTURE RESEARCH

A very interesting and somewhat unexpected result of this work is that the organic polymers we dispersed into flames as additives to water did NOT act as fuel for the fire. Thus, it seems that one can safely introduce organic polymers, or at least some types of polymers, into a fire without detrimental effects. This finding opens up at least three interesting possibilities for producing more effective fire suppressants. One possibility is to improve the efficiency of water by introducing organic agents or super-agents into it using polymer micelles as carriers. This technique may be used to solubilize otherwise insoluble agents in a harmless way and could potentially boost the effectiveness of water into an acceptable range. A second possibility is that toxic compounds with proven effectiveness, such as fluorine- and phosphorous-containing

species, could be oligomerized or polymerized and incorporated into foam, fluid, or solid fire suppressants. The polymerization would reduce the toxicity and the volatility of the compounds, making them safer to handle and more environmentally friendly. A third possibility is to exploit the viscosity accumulation that accompanies the solubilization of polymers for control of droplet size in fire suppression fluids. Our results hinted that the 8- to 10-fold increase in viscosity that can accompany polymer solubilization may be a good way to achieve droplet size control and could potentially enhance the effectiveness of agents. One could easily achieve even larger viscosity increases by using higher molecular weight polymers. Dendritic polymers are particularly well suited for this sort of purpose because they display Newtonian viscosity behavior (i.e., their viscosity is independent of shear rate), which will make them easier to deliver reliably than conventional polymers, by using nozzles or other high shear devices.

Finally, our findings indicate that the organization of a fire suppression agent using a polymer to achieve a high local concentration may be effective in increasing the efficiency of that agent. This idea is tantalizing. The applicability of this effect and the mechanisms responsible for it could be more fully investigated using polymers of various sizes and architectures to determine how it could be optimized to achieve superior performance in next generation fire suppressants.

## REFERENCES

1. Tomalia, D.A., "Dendrimer Molecules," Scientific American, vol. 272, pp. 62-66, May 1995.
2. Tomalia, D.A., A.M. Naylor, and W.A. Goddard, "Starburst Dendrimers: Molecular Level Control of Size, Shape, Surface Chemistry, Topology, and Flexibility from Atoms to Macroscopic Matter," Angewandte Chemie, International Edition, vol. 29, pp. 138-175, 1990.
3. Tapscott, R.E., "Current Topics on New Halon Replacements," National Industrial Research Institute, Agency of Industrial Science and Technology, Nagoga, Japan, 10 April 1997.
4. Babushok, V.I., and W. Tsang, "Superagent Fire Extinguishing Compound Relative Effectiveness," Report to the Next Generation Fire Suppression Technology Program, National Institute of Standards and Technology, April 1997.
5. Yang, J.C., M.K. Donnelly, N.C. Prive, and W.L. Grosshandler, "An Apparatus for Evaluating Liquid Fire Suppression," Proceedings of the 1998 Halon Options Technical Working Conference, pp. 471-481, Albuquerque, New Mexico, 12-14 May 1998.
6. Yang, J.C., M.K. Donnelly, N.C. Prive, and W.L. Grosshandler, "Dispersed Liquid Fire Suppression Screen Apparatus," NISTIR-6319, National Institute of Standards and Technology, 1999.
7. Finnerty, A.E., R.L. McGill, and W.A. Slack, "Water-Based Halon Replacement Sprays," Technical Report ARL-TR-1138, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, July 1996.
8. Yang<sup>2</sup>, J.C., M.K. Donnelly, N.C. Prive, and W.L. Grosshandler, "Recent Results From the Dispersed Liquid Agent Fire Suppression Screen," submitted to the Halon Options Working Group Technical Conference, April 1999.
9. Chen, C.Z., N.C. Beck Tan, and S.L. Cooper, "Incorporation of Dimethyldedecylammonium Chloride Functionalities onto Poly(propylene amidoamine) Dendrimers Significantly Enhances Their Anti-bacterial Properties," Chemical Communicators, vol. 16, pp. 1585-1586, August 1999.
10. Nukiyama, and Tanasawa, "Experiments on the Atomization of Liquids in Air-Stream," Transactions of the Society of Mechanical Engineers of Japan, Reports No. 4, 5, 6, 1938 through 1940.
11. Uppuluri, S., P.R. Dvornic, N.C. Beck Tan, and G. Hagnauer, "The Properties of Dendritic Polymers II: Generation Dependence of the Physical Properties of Poly(amidoamine) Dendrimers," ARL-TR-1774, U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, January 1999.
12. Weast, R.C. (Ed.) CRC Handbook of Chemistry and Physics, 67th edition, CRC Press, Inc., Boca Raton, Florida, 1986.

---

<sup>2</sup>As a result of analytical method development at NIST occurring concurrently with the present program, Dr. J. Yang has suggested an alternate method for quantifying fire suppression effectiveness using the DLAFSS apparatus. Unfortunately, these procedures were not fully developed before the execution of this project and could not be used effectively, given the available data. Details of the new procedure are available in the manuscript.

INTENTIONALLY LEFT BLANK

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
2	ADMINISTRATOR DEFENSE TECHNICAL INFO CENTER ATTN DTIC OCP 8725 JOHN J KINGMAN RD STE 0944 FT BELVOIR VA 22060-6218	1	DR JEARLDINE NORTHRUP ENERGY AND UTILITY SYSTEMS US ARMY CORPS OF ENGINEERS CONST ENGINEERING RSCH LABS PO BOX 9005 CHAMPAIGN IL 61826-9005
1	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL CS AS REC MGMT 2800 POWDER MILL RD ADELPHI MD 20783-1197	1	DR ALBERT MCMANUS US ARMY INST OF SURGICAL RSCH 3400 RAWLEY CHAMBERS ROAD FT SAM HOUSTON TX 78234-6315
1	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL CI LL TECH LIB 2800 POWDER MILL RD ADELPHI MD 207830-1197	1	MR ZHISHENG CHEN DEPT OF CHEMICAL ENGINEERING UNIVERISTY OF DELAWARE NEWARK DE 19716-3110
1	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL DD 2800 POWDER MILL RD ADELPHI MD 20783-1197	1	DR BARRY BAUER BLDG 224/POLYMER BLENDS GROUP NATIONAL INST OF STDS & TECH GAITHERSBURG MD 20899
5	DR LAJOS BALOGH UNIVERSITY OF MICHIGAN CTR FOR BIOLOGIC NANO- TECHNOLOGY INT MED ALLERGY 4010 KRESGE II ANN ARBOR MI 48109-0533	1	DR ANDRE M STRIEGEL USDA/ARS/NCAUR 1815 N UNIVERSITY ST PEORIA IL 61604
5	BLDG AND FIRE RSCH LABORATORY ATTN CHIEF FIRE SCIENCES DIV DR RICHARD GANN BLDG 224 RM B250 NIST GAITHERSBURG MD 20899	1	DR GARY WASHINGTON DEPT OF CHEMISTRY US MILITARY ACADEMY WEST POINT NY 10996
3	BLDG AND FIRE RSCH LABORATORY ATTN DR JIANN YANG (2 CYS) DR WM GROSSHANDLER BLDG 224 NIST GAITHERSBURG MD 20899	1	DR JOHN WALKER US ARMY NATICK RD&E CENTER BIOTECHNOLOGY/MATERIALS DIV SCIENCE & TECH DIRECTORATE KANSAS ST NATICK MA 01760-5020
1	MR FRANK GAMBOA NGP SUPPORT OFFICE GAMBOA INTERNATIONAL CORP 3920 OAK STREET FAIRFAX VA 22030	1	DR WILLIAM BELL TDA RESEARCH INC 12345 WEST 52ND AVENUE WHEAT RIDGE CO 80033
		1	DR HEIDI SCHREUDER GIBSON US ARMY SOLDIER SYSTEMS CMD NATICK SOLDIER CENTER ATTN SSCNC YM NATICK MA 01760 5020

<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>	<u>NO. OF COPIES</u>	<u>ORGANIZATION</u>
1	ENERGY AND UTILITY SYSTEMS US ARMY CORPS OF ENGINEERS CONST ENGINEERING RSCH LABS ATTN CHARLES MARSH PO BOX 9005 CHAMGAIGN IL 61826-9005	1	DR ABE TURETSKY EDGEWOOD CHEM AND BIO CTR ATTN AMSSB RRT B BLDG E3150 APG-EA
	<u>ABERDEEN PROVING GROUND</u>		<u>ABSTRACT ONLY</u>
2	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL CI LP (TECH LIB) BLDG 305 APG AA	1	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL CS EA TP TECH PUB BR 2800 POWDER MILL RD ADELPHI MD 20783-1197
20	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL WM MA N BECK TAN BLDG 4600		
5	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL WM MA D DESCHEPPER BLDG 4600		
5	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL WM MA G HAGNAUER BLDG 4600		
1	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL WM PC A MIZIOLEK BLDG		
2	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL WM TB A FINNERTY BLDG 391 RM 1		
2	DIRECTOR US ARMY RESEARCH LABORATORY ATTN AMSRL WM MA WAI CHIN S H MCKNIGHT BLDG 4600		
1	DR DUPONT DURST US ARMY ERDEC SCBRD RTL E3150 5232 FLEMING ROAD APG MD 21010		



