ENCAPSULATED MICRON AEROSOL AGENTS (EMAA)

Charles J. Kibert *
Douglas Dierdorf **

SUMMARY
A new class of fires suppressants, known as ***Encapsulated Micron Aerosol Agents*** (EMAA), having superior volumetric efficiency, low initial and life cycle costs, low toxicity, no known global atmospheric environmental impacts (ODP/GWP), and with the potential for a wide variety of applications, is being developed via a joint program between the private sector and the U.S. Air Force. The research program consists of developing solid compound formulations that, when pyrotechnically initiated, generate powerful fire suppressant aerosols that behave as lighter than air gases. Preliminary indications are that these aerosols are up to six times more powerful as fire suppressants than Halon 1301 on a mass basis. Using a solid, gel, or powder as the starting point for generation of an aerosol eliminates the need for piping and pressure cylinders, creating a potential for application in a wide variety of fire suppression roles: facilities, aircraft, portable rapid deployment shelters, fuel storage tanks, battery/UPS rooms, unmanned telecommunications facilities, and armored vehicle engine compartments. The speed of aerosol formation is dependent on system design and configuration. Mechanisms of aerosol fire suppression are discussed and the most recent test results are presented.

1. INTRODUCTION

The search for replacements and alternatives for the halon family of chemical fire suppressants has coincided with the development of novel materials and techniques that provide new options for fire protection. One class of materials that has good potential for filling several roles formerly performed by halons is aerosols. Originating as solid materials, micron size aerosol particles are generated via combustion of a combination of active compound, oxidizer, reducer, and binder. The U.S. Air Force has entered into a Cooperative Research and Development Agreement with Spectrex, Inc. to further the development of aerosol technology for a number of fire suppression applications. ***Encapsulated Micron Aerosol Agents (EMAA)*** is the title given by the U.S. Air Force to this research program.

Aerosol science or particle mechanics draws from several scientific disciplines to formulate the science that underlies its principle areas of research. Understanding the thermodynamic interaction of aerosols with fire propagation mechanisms is a new subset of aerosol science

* Project Officer, Wright Laboratories (Air Base Fire Protection and Crash Rescue Section) and Associate Professor, University of Florida
** Research Scientist, New Mexico Engineering Research Institute

that has the potential for creating a wide variety of fire suppression options.

2. AEROSOL CONCEPTS

Aerosol refers to a system of liquid or solid particles suspended in a gaseous medium. Aerosols are generally stable or quasi-stable systems with the bulk of particles being $\leq 1\mu m$ in diameter. Aerosols affect visibility, causing some degree of obscuration, especially in the size range of 0.1 to $1\mu m$. The collective term *particulate* is commonly used to refer to both solid and liquid (particle and droplet) components of an aerosol when differentiation of phases is unimportant. Several common aerosols are fumes, smoke, mists, fog, and haze.

Fumes resulting from chemical reactions may become aerosols via agglomeration of molecules due to high Brownian diffusion rates. Particle sizes vary greatly **as** a function of temperature and gas volume. Once formed, separation and rediffusion become very difficult. Metal fumes have particle sizes on the order of 0.5 pm.

Smoke is an aerosol resulting from combustion of fuels. Like fumes, smoke has particle sizes on the order of 0.5 pm.

Based on the state of the suspended substance, liquid or solid, dispersion and condensation aerosols are differentiated. Dispersion aerosols are formed by the atomization of solids and liquids while condensation aerosols are formed via the condensation of superheated vapors or chemical reactions in the gaseous phase. In general, dispersion aerosols are coarser than condensation aerosols.

EMAA is a dispersion aerosol that is delivered to the protected space via the combustion of the solid tablet. Prior to EMAA, dispersion aerosols have been created via crushing, grinding, blasting, or drilling of solid matter. The particle size reduction is directly related to the energy expended on crushing or grinding and other factors such **as** the brittle or plastic nature of the material, the porosity of the solid, and the presence of crystal flaws and sites of weakness. Physicochemical reactions using condensation processes have also been used to generate solid particle aerosols. Salts fused on heating wires have been used to generate aerosols via incandescence in inert gas atmospheres, the temperature being a function of the energy required to produce nuclei.

The dynamics of aerosols are important considerations for two reasons. First, the ability of the particles to remain suspended is obviously connected to the particle size and the residence time of the fire suppressant. Second, the aerosol, if it is to replace gases in certain applications, must be able to flow around obstacles.

The ability of the aerosol to remain suspended is governed by Stokes' Law which predicts the terminal velocity of the particle through air and consequently the residence time of the aerosol. As particle size increases the inertial and viscous forces of the fluid come into play. For larger particle sizes, the Stokes' Law predictions must be recalibrated for viscous drag forces.

The ability of the aerosol to flow around obstacles is necessary for the fire suppressant to be able to penetrate around and behind obstacles and into small spaces. The larger the particle size, the less able the particle will be to change direction, causing it to impinge on the obstacle. This property is called ***impaction*** and is governed by Stokes' number or the ***impaction parameter,*** the dimensionless ratio of the particle stopping distance to the characteristic dimension of the obstacle or flow geometry.

Dispersion of an aerosol fire suppressant is an important consideration in evaluating effectiveness. The dispersion characteristics of the aerosol are a function of the aerosol particle diameter, r. In general aerosol particles vary widely in size, from 1 nm to about 1 mm as the upper limit. Particle size is very important **as** the dispersion of the aerosol is affected by its diameter. Coarse particles with $r \geq 1\,\mu m$ have a dispersion rate that is a function of diameter. Particles in the range:

$$0.1\,\mu m \leq r \leq 1.0\,\mu m$$

have transition properties. Very fine particle aerosols with $r \leq 0.1\,\mu m$ are dispersed proportional to r^2 and the particle velocity, v.

The loss of aerosol particles in suspension can be attributed to several phenomena: sedimentation, diffusion, and coagulation. Again the size and velocity of the aerosol particles are the driving force. Larger particles, $r \geq 1\,\mu m$, will tend to fall and be lost via sedimentation. Smaller, submicron particles, will tend to diffuse out to the walls of containment via Brownian motion. Coagulation, the formation of larger particles from smaller particle via collisions, is caused by thermal, electrical, molecular, hydrodynamic and several other forces.

EMAA particles are on the order of $1\,\mu m$ in diameter. At 1 atm and 20°C these particles will have a terminal velocity of about 10^{-4} cm/s according to Stokes'Law. Diffusion losses are also predicted to be very small. The result is that EMAA will remain suspended in the protected space for times on the order of tens of minutes.

EMAA is initially a solid material that can originate in a variety of forms: solid, powder, or gel. The active component, an oxidizer, and a reducer are combined with a filler. These components are ground into a fine powder and mixed with an epoxy resin binder. Upon ignition of the material, the combustion products are ejected as a dispersion aerosol, with the solid particles floating in the air and the gaseous combustion products.

Some basic physical characteristics of the EMAA solid are:

Specific density:	**1.6 - 1.8** x 10^3 Kg/m^3
Combustion temperature:	**1500 - 2400** 'K
Shelf life (estimated):	15 years

The products of combustion are **40%** solid particles and **60%** gaseous products. The gaseous products consist of N„ CO„ CO, H_2O, **O,** and traces of hydrocarbons. The solid particles are various solid salts, depending on the formulation of the EMAA solid.

3. EXTINGUISHMENT MECHANISMS

Successful fire suppression requires that one or more of the four factors that tend to propagate a fire be interrupted. These factors together with their suppression mechanisms are:

Table 1 **Factors** governing **fire** propagation

Factor	Suppression **Mechanism**	Method
Fuel	Removal	Vapor seal
Oxygen	Exclusion	Smothering
Heat	Absorbance	Cooling
Chain reaction	Inhibition	Stop reactions

EMAA aerosols, like dry chemicals, are hypothesized to function via several mechanisms to suppress fire, the most prominent of which is chemical inhibition of the chain reaction. Other mechanisms such **as** heat absorption are also possible while oxygen exclusion is not a path for aerosol fire suppression. Depending on the temperature at the point of interaction, the aerosol particles act by heterogeneous or homogeneous inhibition (Birchall, **1970).** The aerosol particles, due to their small size, create a large total surface area for capturing the active species of the fire chain reaction. Heterogeneous reactions occur when the particle is still in a solid state and a recombination of the fire chain propagators occurs. As the particles enter higher temperature zones, homogeneous or gaseous phase reactions occur.

Heterogeneous processes typically undergo the following general reaction sequence:

(1) $A^{o} + S \text{ -----> } AS$

(2) $AS + A'' \text{ -----> } A_2 + S$

where A" is an active species in the fire chain reaction such as OH, H, or CH„ S is the surface of the solid aerosol particle, and A_2 represents a molecular species such **as** H_2O, CO„ or C_nH_{2n+2}. The newly created AS reacts with another active species in the fire chain reaction creating a stable molecule, A, At the same time a free aerosol particle, **S,** is regenerated and made available for further interactions.

Homogeneous processes have the following general pattern of interaction (Rosser, 1963):

(4) K + OH + M -----> KOH + M

(5) KOH + H -----> H_2O + K

(6) KOH + OH -----> H_2O + KO

where M is energy input from the fire, and H and **OH** are active species. The extinguishing process is similar to that of halon,

Chemical precursors that interact heterogeneously with the active species are based on cations of the alkali metals: K, Na, Cs, Rb, **Sr,** NH, and anions such as CO,, HCO_3, **SO,,** and **PO,.**

The alkali-metal salts have been shown to be especially effective fire suppressants. The potassium salts are generally superior to the sodium salts and the anion associated with each is an important factor in fire suppression effectiveness (Birchall, 1970). For example, alkali oxalates are particularly effective compared to bicarbonates.

In the form of dry chemicals, alkali-metal salts have to first decompose in the flame to provide a large specific area for interaction. To be effective as fire extinguishants, large dry chemical particles on the order of 70 μm in diameter decompose into submicron particles, reacting with the flames to produce inhibiting species such as alkali hydroxides. To allow such decomposition to occur, residence time in the flame is important. For large particles the appropriate residence time may be difficult to achieve because the shear mass of the particle will cause it to fall through the flame. In the case of 1 μm aerosol particles the residence time required to produce the reactive species is far shorter and the diffusion property of the small solid particle will tend to maintain its availability in the flame. The combination of these effects indicates the increased effectiveness of aerosols versus dry chemical fire extinguishants of similar composition.

Relatively recent evidence suggests that much of the effectiveness of dry chemicals can be attributed to thermal and heat extraction mechanisms such **as** heat capacity, fusion, vaporization, and decomposition (Ewing, et al., 1989a). At certain particle sizes, depending on the dry chemical powder composition, a sizable increase in extinguishing effectiveness is achieved that can be explained by flame heat removal (Ewing et al., 1989b and Ewing et al., 1992). This occurs at limit temperatures that are a function of the flame and extinguishant properties.

4. TEST RESULTS

A series of basic tests have been carried out to assess the performance of EMAA against a variety of fires. Table 2 contains a list of preliminary laboratory scale extinguishment tests that were conducted and Table 3 shows the results of these tests. Table 4 provides results for a group of intermediate to large scale tests. Testing indicates that EMAA has an extinguishment concentration of approximately 50 g/m^3 for n-heptane pool fires. This can be contrasted to the extinguishment concentration of Halon 1301, approximately 300 g/m^3 for the same fire.

Some of the known general characteristics of EMAA compared to gaseous agents are shown in Table 5.

Figure 1 shows an EMAA solid with active ignition system prior to testing and Figure 2 shows the aerosol emerging from the test chamber. Figure 3 shows the start of a passive ignition test while Figure 4 show the results of the ignition.

Table 2 EMAA Laboratory Scale Test Program

series	EMAA Location	Quantity	Fire Location	Description
1	MCSA	10 g.	Chamber Floor	Size: 4 cm dia. Fuel: n-heptane Preburn: 1 min.
2	Chamber Floor	10 g.	MCSA	Size: 4 cm dia. Fuel: n-heptane Preburn: 1 min.
3	MCSA	20 g.	Chamber Floor	Size: 4 cm dia. Fuel: n-heptane Preburn: 1 min.
4	MCSA	10 g.	Chamber Floor	Size: 10 cm dia. Fuel: n-heptane Preburn: 30 s.
5	MCSA	10 g.	Chamber Floor	Size: 10 x 18 an. fan Fuel: Brown paper Preburn: 30 s.

MCSA = mid-chamber

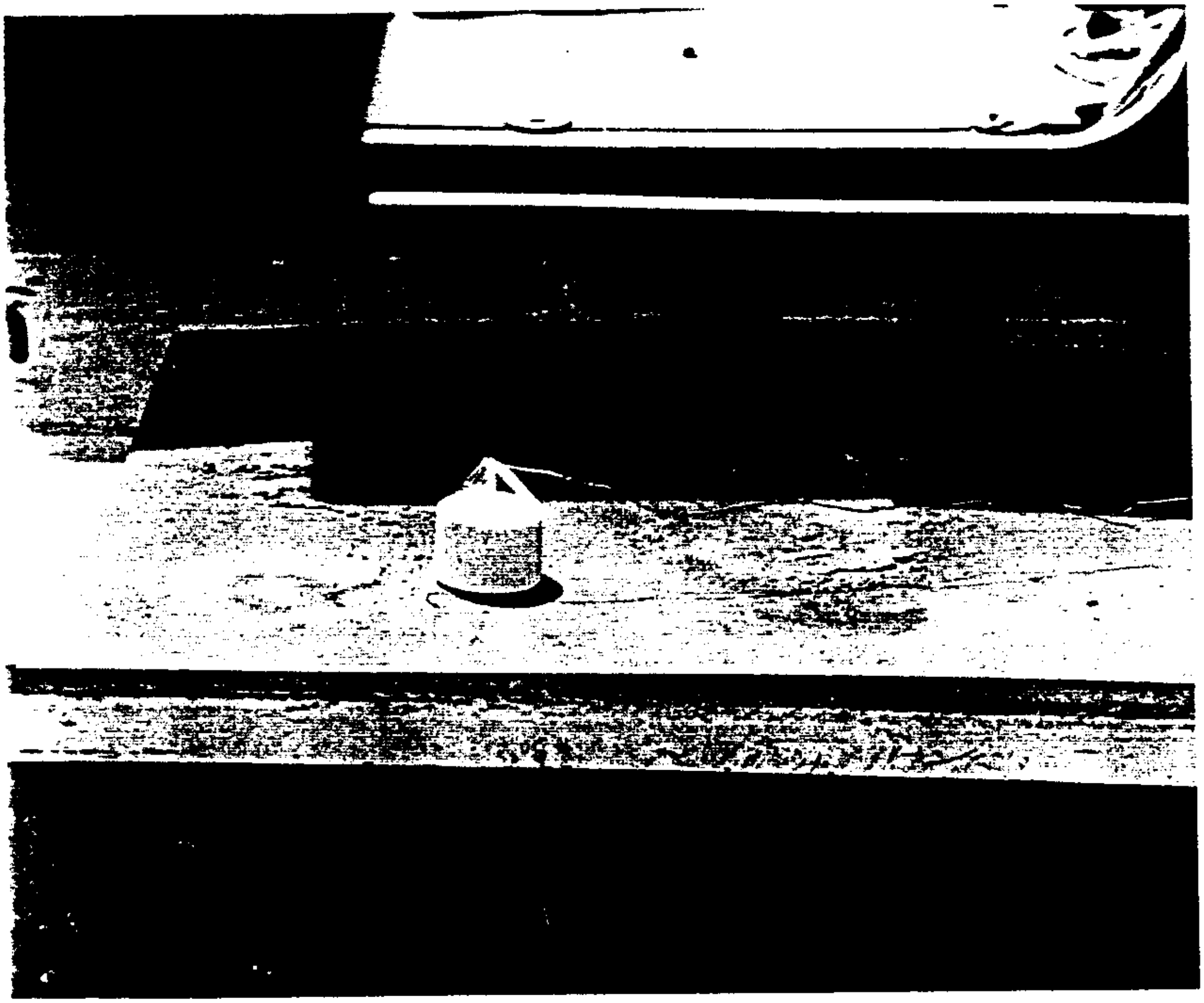

Figure 1 EMAA cylinder wired for ignition.

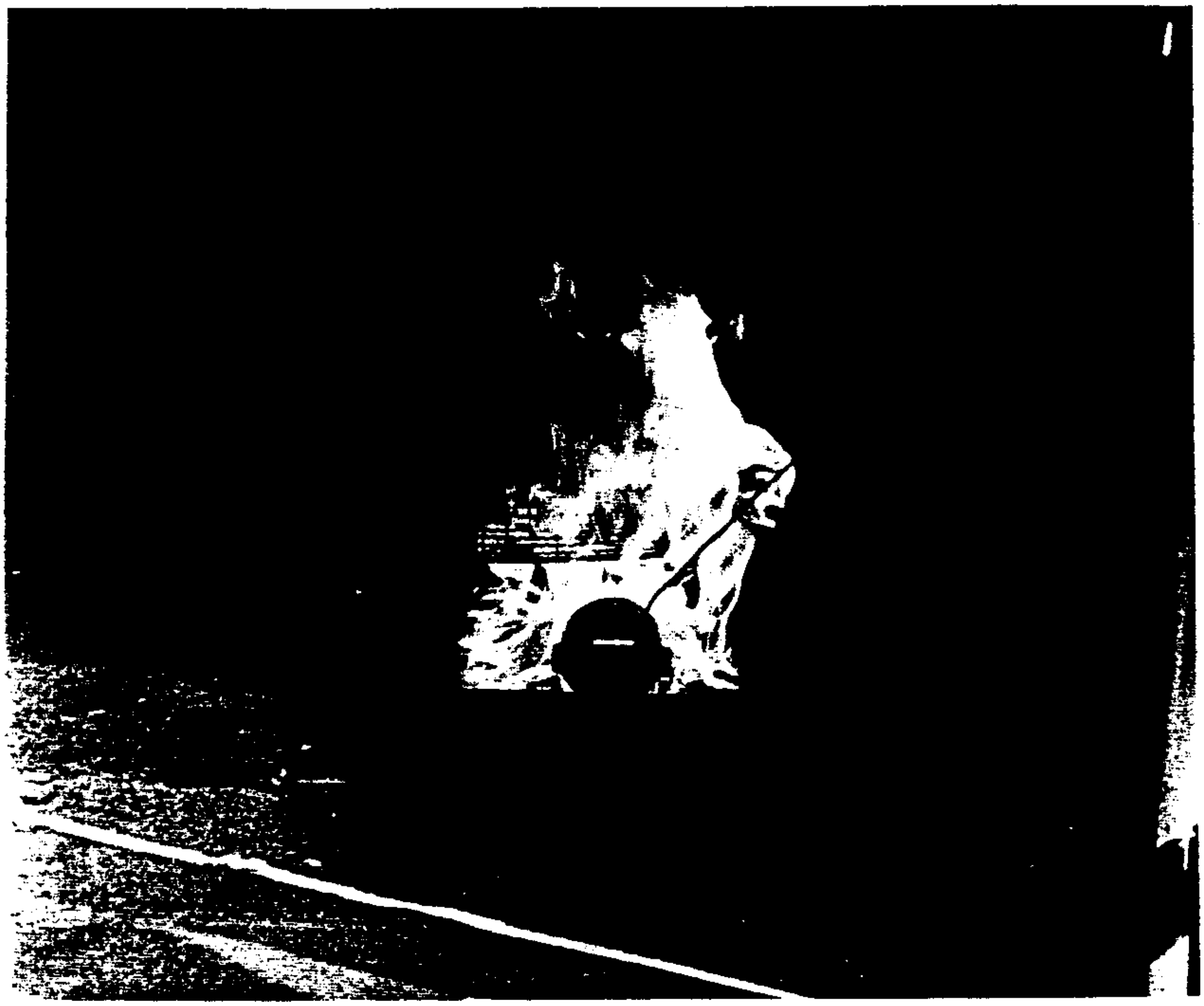

Figure 2 Self-ignition test, EMAA on grid over n-heptane fire.

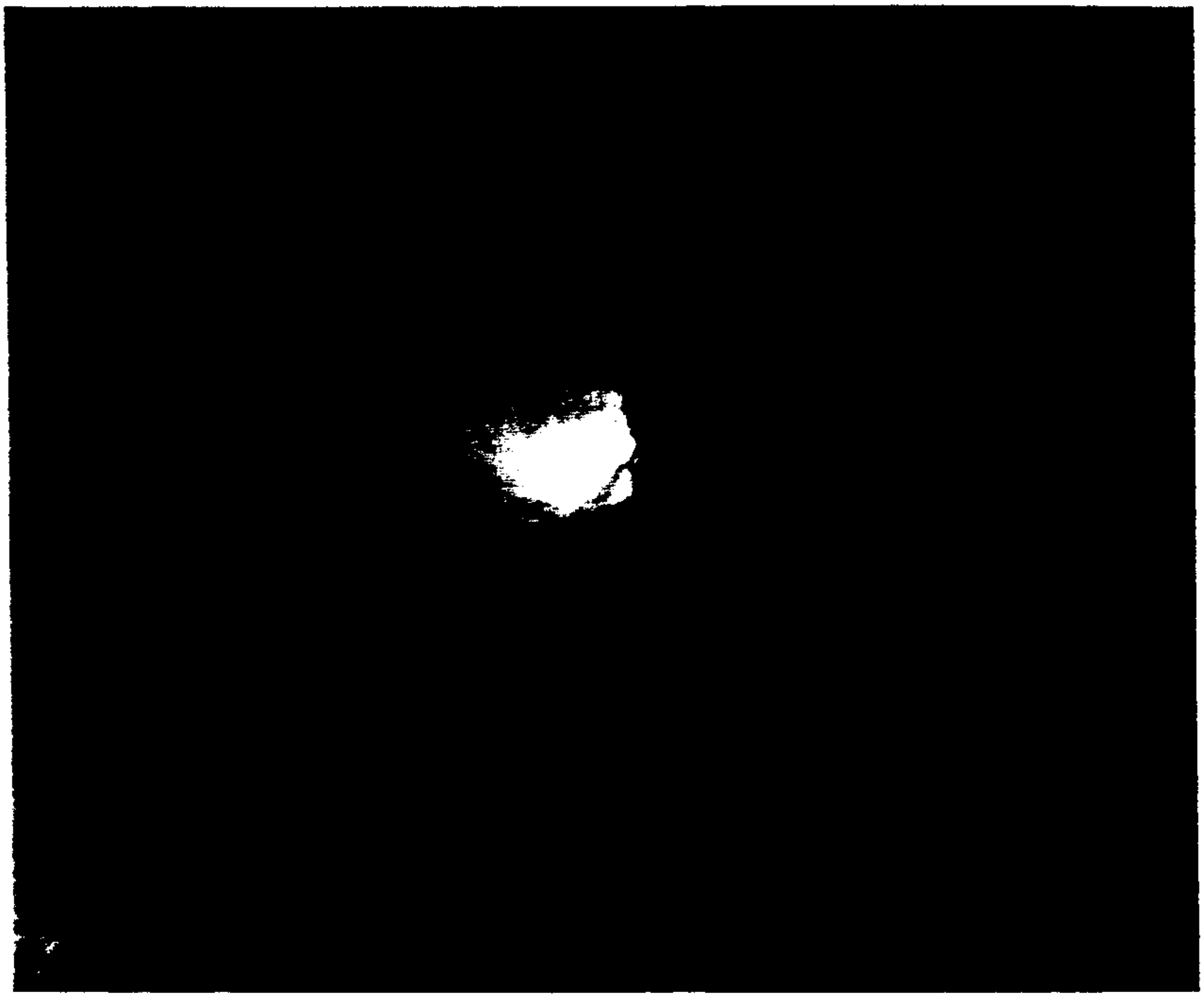

Figure 3 EMAA material in initial stages of burning.

Figure 4 Aerosol smoke generated by EMAA ignition emerging from test chamber

Table 3 Extinguishment Test **Results,** Preliminary Laboratory Tests

Series	Type	Amount, g	Ignition time, s	Burn time, s	Ext. time, s	Reduced Ext time, s
1	A	10.3	5.0	10.0	25.0	20.0
1	B	9.4	8.0	19.0	45.4	35.4
1	C	10.4	7.0	17.0	39.4	32.4
1	B	10.1	4.0	15.0	49.0	45.0
2	A	10.1	6.0	10.7	10.3	4.3
2	B	9.8	4.5	13.9	12.5	8.0
2	C	9.8	4.5	10.3	12.5	8.0
3	A	20.8	4.0	9.0	20.0	16.0
3	B	20.3	5.0	15.0	30.9	25.9
3	C	21.8	5.0	18.0	16.0	11.0
4	A	10.1	6.0	10.0	15.0	9.0
4	B	9.8	4.0	16.0	18.0	14.0
4	C	10.5	4.5	12.0	14.0	9.5
5	A	10.0	3.0	11.0	18.6	15.6
5	B	9.9	4.0	16.0	20.0	16.0
5	C	11.2	4.0	14.0	18.0	14.0

Table 4 Extinguishment times using EMAA fire suppressant, medium to large scale tests.

NO.	Form	Mass, Kg	Test Chamber	Fire Origin	Time, s
1	Tablet	0.125	3 m^3, closed	1 ft^2 n-heptane	24
2	Tablet	0.150	3 m^3, closed	1 ft^2 n-heptane	21
3	Powder	0.150	3 m^3, closed	1 ft^2 n-heptane	19
4	Tablet	0.250	3 m^3, closed	n-heptane+ cables	60
5	Tablet	0.250	3 m^3, closed	n-heptane +plastics	60
6	Tablet	0.500	10 m^3, semi-open	n-heptane spray + pan	30
7	Tablet	0.300	55 gal drum	water/n-heptane*	13
8	Powder	0.250	55 gal drum	water/n-heptane*	4
9	Tablet	6.000	70 m^3, closed	2 x 1 ft^2 n-heptane	62

* EMAA initiated underwater in barrel with 75 mm n-heptane on water.

Table **5** Comparison **of EMAA and** *gaseous* **extinguishants**

PARAMETER	HALON 1301	GASEOUS REPLACEMENT	CO_2	EMAA
1. ODP	High	Low/Zero	Zero	Zero
2. GWP	Mod	Low/High	Zero	**Nil**
3. Toxicity	LOW	LOW	High	Low
4. Conductivity	LOW	LOW	LOW	LOW
5. Corrosivity	Mod	Low/Mod	Low/Mod	Unk
6. Vol. Efficiency	Good	Moderate	LOW	Exc
7. Ext. Concentration	5%	10 - 15%	45%	
8. Ext. Density	$300 g/m^3$	**600-900** g/m^3	**700** g/m^3	$50 g/m^3$
9. Cost,	$150/m^2	>$250/m^2	$150/m^2	$50/m^2
10. Life Cycle Cost,	High	High	High	LOW

a - Includes piping, cylinders, installation, no detection
b - Includes initial cost, maintenance, agent replacement

5. TOXICITY

A full toxicological study of **EMAA** has not yet been conducted. Preliminary analysis of gases from testing has been conducted and the results provide some insights into the safety of EMAA. Samples of the aerosol particles and gases have been processed by various equipment and methods: GC/MS, IR spectrometry, **and** x-ray fluorescence. The constituents of **an** atmosphere after a typical EMAA tablet ignition are indicated below. Cooling of the aerosol may be required in cases where the generation temperatures of the aerosol are out of range for a given application,

Table 6 Constituents **of** sample **EMAA post-ignition** atmosphere

	Without cooling	With cooling
N_2	78-79%	78-79%
O_2	19-20%	**20-21%**
CO_2	**0.2-2%**	**0.1-0.6%**
CO	**0-0.1%**	**0.1-0.5%**
C_nH_{2n+2}	**1-16** ppm	**1-700** ppm

The constituents of a post-fire, n-heptane extinguishing scenario were:

Table 7 Constituents of EMAA post-combustion fire suppression atmosphere

N_2	78-79%
O_2	18-20%
CO_2	0.4-2.3%
CO	0.19-0.56%
C_nH_{2n+2}	1-300 ppm
Hcl	0.001%
KCl	0.082%
M2	0.017%
$MgCl_2$	0.01%
H_2O	0.1%

Hazardous gases such as phosgene, chlorine, and cyanide have not been detected in the testing. It should be noted that the neat components of the solid tablet are non-toxic.

In summary, preliminary efforts at examining the overall toxicology of EMAA in neat and combustion states, including a fire test atmosphere, do not reveal any significant problems due to toxic components.

6. APPLICATIONS

The aerosol generated when an EMAA solid is ignited has several properties that differentiate it from both gaseous agents and dry chemicals. In fact EMAA could be said to be an intermediate agent between these two extremes in fire suppression techniques. Several of the key characteristics and features of EMAA that influence the design of applications are:

a. Similar to a gaseous agent, EMAA can flow around barriers and obstacles, behaving as a gas in its basic transport properties. It can be introduced into ductwork and be delivered to an area via forced convection. Dry chemicals, in contrast, are limited by obstructions.

b. EMAA has excellent fire suppression characteristics, similar to dry chemicals, both of which are 6 times as effective as Halon 1301 per unit mass and up to 10 times as effective as the forecasted replacements for Halon 1301 such as perfluorobutane and HFC-23.

c. EMAA initiation is independent of oxygen supply and can therefore be effective under or within a liquid or at altitudes where oxygen concentrations are low.

d. Initiation of EMAA can be via electrical ignition or self-ignition due to interaction with the fire.

e. The delivery rate of EMAA is a function of its composition, form (solid, powder, gel), and the delivery system. The aerosol is generated via combustion of the EMAA material and variations in the active component, oxidizer, and reducer dramatically affect the bum rate, perhaps up to **2** orders of magnitude in difference.

f. EMAA does not require piping, pressure cylinders, or valves. **A** device for containing the EMAA solid material is all that is normally required. Pressure testing, weighing, pressure/leak detection, and other maintenance and testing of cylinders/pipes/nozzles/valves is not required.

The low weight to extinguishing capability of EMAA provides tremendous performance advantages for weight/space critical applications. **A** CO, cylinder weighing more than 150 Kg can be replaced with about **4** Kg of EMAA.

This excellent performance capability and its add-on ability will enable such applications as trucks and cars, boats and ships, engine compartment protection, fuel tanks, and numerous other applications. Where portability, expandability, simplicity, ruggedness, and cost are factors, it would appear that **an** EMAA system would be a consideration.

The major **unknowns** relative to EMAA at present are its materials compatibility performance, especially corrosion, and its application against deep-seated fires. Testing to assess EMAA performance in both of these areas is ongoing.

7. CONCLUSIONS

The development of aerosol fire suppression systems is a newly emerging discipline that holds great promise in offering an excellent option for consideration for several fire protection roles. An ongoing Air Force research program is examining the basic physics and chemistry of fire suppression aerosols and assessing the employment of aerosol delivery systems for a variety of applications.

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