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## INTERMEDIATE SCALE FIRE EXTINGUISHMENT BY PYROGENIC SOLID AEROSOL

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### BACKGROUND

In addition to the 'halon-like' gaseous candidates evaluated as part of the Naval Research Laboratory (NRL) halon 1301 total flooding extinguishant replacement program, conducted for the Naval Sea Systems Command,<sup>1</sup> we have also had programs evaluating fine water mists<sup>4</sup> and fine dry chemical powders.<sup>5,6</sup> This paper discusses studies on pyrotechnic generated solid aerosol particles as a total flooding fire suppression agent in our 56 m<sup>3</sup> (2000 ft<sup>3</sup>) 4.0 x 3.4 x 4.3 m (13 x 11 x 14 ft) compartment at our Chesapeake Bay Detachment (CBD), as well as some information on CIS (formerly USSR) efforts. Much of the CBD work was presented at the 1993 CFC & HALON Alternatives Conference<sup>7</sup> on October **20-22**, 1993, in Washington, DC. As this is a working conference with a much more focused objective, we are including our previous results for discussion.

Solid, dry chemical extinguishant efficacy has been widely observed. The very large increase in suppression efficiency with decreasing particle size and absolute effectiveness was documented by Ewing, *et al.*<sup>5,6</sup> We also studied dry chemical suppressants as contained in thixotropic media. Burning propellant was demonstrated<sup>8</sup> as possessing fire extinguishant capabilities. The use of pyrogenic extinguishants was shown by Russian studies to have tremendous versatility. Spectronix, Ltd., an Israeli company, purchased the technology and further developed it. It is the Spectronix Fire Extinguishant products, called S.F.E., which we have tested. They were obtained through the U.S. subsidiary Spectrex, Inc.

The thrust for halon replacements has focused on clean gaseous agents, but there are applications where a solid phase aerosol agent provides advantages. Self generating aerosols do not require distribution piping. They may be more easily introduced as modular retrofit systems in

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operational facilities. They leave a residue, but do not generate HF acid as do HFC and PFC candidates.<sup>3</sup> Pyrogenic aerosol agent is based on mixed phase propellant combustion. The agent is activated by igniting a propellant in a suitable generator. The combustion products intended for fire suppression applications include at least one solid phase chemical released as an aerosol cloud. Efficiency is greatly enhanced by the micron range aerosol particle size. If the particulate concentration engulfing the fire is sufficiently high, extinction will occur.

Areas of concern in applying this technology include fire suppression effectiveness, energy generation, the procedure for aerosol release into the enclosure, distribution homogeneity, non-clean agent residue, compatibility with equipment and operations, reliability, system size and weight, and agent toxicity and corrosiveness.

## EXPERIMENTAL

Initial Navy evaluation at the Spectronix Israeli site in August 1992 confirmed that the buoyancy of exothermically produced aerosol is a significant distribution problem in employing S.F.E. as a total flooding agent in large spaces. (A partial description of the Spectronix tests and initial small scale tests at NMERI are given in reference 9). Consequently we have evaluated two Spectronix water cooled aerosol generators and an uncooled generator at CBD.

The Spectronix Fire Extinguishing (S.F.E.) materials consist of a heterogeneous (fuel + oxidant) propellant. Propellant forms include powder, pellet, gel, etc. Initial tests were conducted with small pellets; intermediate scale tests were conducted with multiple 1 kg propellant charges cast into steel containers. We considered two different composition formulations, A and B, as well as conducting limited laboratory testing of C. The components of S.F.E. remain proprietary.

Preliminary experiments were performed to measure the temperature and pressure evolved during aerosol generation in a 34 L (35 cm i.d. x 35 cm height) steel aviation fuel transportation drum. The drum had a removable lid sealed with a rubber gasket. Pressure rise in the container was measured with an externally mounted Validyne pressure transducer, model P24. Two K-type exposed junction thermocouples were positioned inside the container approximately 7 cm from the side and 10 cm and 20 cm from the bottom. The thermocouples had a response time of approximately 2 seconds. Pressure transducer and thermocouple signals were acquired by a computer using Lab-Notebook software/interface and subsequently analyzed using Lotus 1-2-3. The agent pellet was suspended in the container with Nichrome wire (AWG 26) threaded through drilled holes. A Variac transformer was used to resistance heat the wire and ignite the S.F.E.

### Aerosol Generators

Spectronix manufactured several different types of generators for use in the Navy tests. The three types tested are the hot, passive water bath, and water spray generators. The hot generator consists of a steel combustion chamber with a removable door and two exhaust pipes, and an electrical activation system. At least 1 kg of S.F.E. can be used in it. The outside dimensions of the hot generator excluding its exhaust arms are 22 x 20 x 61 cm (8.75 x 8 x 24 in). The two horizontal 8.3 cm (3.25 in) diameter exhaust arms are centered 52 cm (20.5 in) above the floor. The empty generator weighs 14.5 kg (32 lb).

The water bath generator consists of a 42.5 cm (16.75 in) diameter, 32.4 cm (12.75 in) high open top outer container, and an internal chamber with a water tight cover containing 16 "exhaust" tubes that bend downward below the water level. Approximately 20 L of cooling water is placed in the annular volume between the inner and outer containers. Cooling is effected by bubbling S.F.E. combustion products through the water. The generator weighs 16.6 kg (36.7 lb) dry, and 36.6 kg (80.8 lb) with water, not including the up to 1 kg S.F.E. charge.

The third type of generator actively cools the aerosol. The unit is 26.7 x 58.4 x 30.5 cm (10.5 x 23 x 12 in) and weighs 16 kg (35.3 lb). The reservoir can contain 3 L of water. A single pump is used to spray the water from four nozzles directly into the S.F.E. products along the length of their exhaust outlet tube. The water flow is initiated prior to ignition, and maintained until the propellant is consumed. A charge of 1 kg of S.F.E. can be used in it.

The electrical activation system for all generators uses an electric match igniter which is imbedded in the S.F.E. charge. It is then connected to a feed-through receptacle allowing contact on the outside of the generator. These in turn, are wired to control modules for simultaneously activating multiple generators. External power supplies are used to ignite the propellant, and to power the water pumps in the water spray generators.

## Fire Tests

Fire threats employed were n-heptane pool fires 0.8 x 0.3 m (2.5 x 1 feet) and 1.05 x 1.05 m (3.45 x 3.45 feet), with spark ignition reflash attempts on an n-heptane spray fire. Roof vents and a door were employed to ensure proper preburn ventilation.<sup>1,3</sup> However, significant oxygen depletion with the large pool fire could not be avoided. The fuel area (ft<sup>2</sup>) to compartment volume (ft<sup>3</sup>/1000) ratio for the large pool is 6; the ratio is 1.25 for the smaller pool.

The 56 m<sup>3</sup> (2000 ft<sup>3</sup>) 4.0 x 3.4 x 4.3 m (13 x 11 x 14 ft) compartment was instrumented with thermocouple arrays, radiometers, calorimeters, and infrared and standard video recorders. Infrared video capability was essential for monitoring the fire when visible wavelength light was obstructed by the high aerosol concentrations achieved. In addition to the pool fire location, kerosine lanterns were distributed at different heights and under an obstacle to monitor fire extinction. The lanterns were equipped with thermocouples so flame extinction times could be computer recorded, along with the other data.

Optical densities were measured at three different heights, 0.5, 2.0, and 4.1 m (1.7, 6.7, and 13.5 ft). The optical transmissivity probes used infrared light emitting diode sources and photodiode detectors with peak sensitivities at about 0.9 μm. The photodiodes were used with filters to eliminate radiation below 0.7 μm. The path length distance was set at 7.6 cm for the high concentrations generated by the S.F.E. Output was calibrated before and after each test.

Because solid concentrations could not be measured by gas analysis techniques, two types of grab samples were employed. We measured the amounts of agent pulled into pre-evacuated vessels, or trapped in a water bubbler chain.

A typical test was run by charging the aerosol generator(s), fueling the fire pan with n-heptane and starting video and computer data acquisition. All command and data recording was done remotely from our control trailer. The pool fire was ignited after verification of proper instrument functioning. Ventilating door and roof vents were closed 45 seconds after ignition. The generators were activated one minute after ignition, and fire intensity monitored. Grab gas samples were taken to monitor oxygen concentration at extinguishment. Periodically after extinguishment, the n-heptane spray was activated and spark ignition attempted.

## RESULTS

Experiments were performed with small quantities of S.F.E. to observe pressure and temperature increases upon ignition. There are errors in accuracy due to time response and other experimental factors. A 9.85 g pellet of Formulation A in the 34 L drum gave a maximum pressure rise of 17.3 psig approximately 5 seconds after ignition. Temperature maxima at approximately 6 seconds were 270 °C and 327 °C for the lower and upper thermocouples, respectively. The metal drum itself increased in temperature by 14-17 °C over one minute. A similar test with a 2.0 g piece gave a maximum pressure rise of 5.9 psig approximately 4 seconds after ignition. Gas temperature maxima at approximately five seconds were 98 °C and 67 °C for the upper and lower thermocouples, respectively. The drum thermocouples measured a temperature increase of 4 °C.

A 10.8 g pellet of Formulation B gave a maximum pressure rise of 13.6 psig 7 seconds after ignition. The temperatures reached 257 °C and 239 °C for the lower and upper thermocouples, respectively. A 1.85 g piece gave a maximum pressure rise of 5.1 psig 5 seconds after ignition. A significant difference in the temperature maximum was measured by the internal thermocouple. The upper thermocouple reached approximately 99 °C in seven seconds and the drum temperature increased approximately 6 °C.

Other tests were done in a laboratory apparatus with a metal container immersed in an ice bath. This allowed for rapid temperature equilibration and condensation of water produced in propellant combustion. Tests on 2 g pieces of Formulation A in vacuum and in air showed oxygen from the air is required for complete S.F.E. combustion. Preliminary results are that 1/4 to 1/3 of the S.F.E. weight becomes aerosol, and over 200 L of carbon dioxide are produced per 1 kg of S.F.E. (analysis by gas chromatography). Gas chromatography analysis of S.F.E. product gases are given below for the equivalent of 50 g/m<sup>3</sup> loading (Argon by calculation).

S.F.E. at Design Concentration (50 g/m <sup>3</sup> ) Final Gas Concentrations					
Formulation	O <sub>2</sub> %	N <sub>2</sub> %	CO <sub>2</sub> %	CO %	Ar %
A	20.4	76.6	1.8	0.0	0.9
B	20.3	76.9	1.5	0.0	0.9
C	20.2	77.1	0.8	0.8	0.8

Formulation C (B is a combination of A and C) generates an inert product gas which lowers oxygen concentration, resulting in higher CO concentrations from reduced CO oxidation.

### Aerosol Generation and Distribution

There is considerable energy given off during the combustion of S.F.E. propellant. Visible 'flame' plumes 30 cm long exited from the two arms of the hot generator immediately after activation. The hot solid aerosol - gaseous products mixture exited horizontally approximately 30 cm from flow momentum, but then quickly rose almost vertically due to buoyancy forces. Figure 1 shows the optical transmission in the 56 m<sup>3</sup> compartment when 1 kg of S.F.E. is ignited in a hot generator. The highest optical probe (15 cm from the ceiling) was engulfed at 15 seconds; the middle height probe was engulfed at 20 seconds. Not until almost 90 seconds did the aerosol cloud descend to within 0.5 m of the floor. The S.F.E. itself burned for slightly over 35 seconds. Only after over 4 minutes did the transmittances at the three heights equilibrate. The near-uniform concentration then maintained itself.

There was little visible residue once the aerosol cloud was exhausted from the compartment except on surfaces in the vicinity of the exhaust arms. A 1 kg container of S.F.E. was ignited in the open (not in a generator). An intense flame and white plume were emitted, and the metal container became red hot. The S.F.E. formed a ceiling layer that gradually descended. While Formulation A gave neutral pH product, Formulation B was basic (pH > 11).

The passive water bath cooled generators were first tested to observe and characterize the plume and cloud. The generator was installed at approximately 1.5 m (60 in) height and actuated with a 1 kg S.F.E. charge. There was a delay of a few seconds after actuation before the aerosol cloud began being emitted. The cloud from the open top spilled over the sides and sank towards the floor. A buoyant plume also was emitted after about 15 seconds. The plume rose while the "cooled" cloud fell to the floor.

Figure 2 shows the optical transmission from 1 kg S.F.E. ignited in a cooled generator in the 56 m<sup>3</sup> compartment. The buoyant central plume rose slowly forming a ceiling layer that gradually descended down the enclosure walls. After approximately two minutes, the ground level cloud and the descending ceiling layer from the buoyant plume began to merge, obscuring visibility throughout the enclosure. The transmittance began to decrease at the highest detector only after 45 seconds, about 60 sec earlier than it began falling at the lowest elevation. Transmittance at the middle elevation began decreasing only after two minutes. After approximately 5 minutes, steady-state near-uniform transmittance was observed. However, the transmittance levels in the water bath generator test were significantly higher than the corresponding value in the hot generator test. Aerosol depletion in the water bath by solubility and particle trapping (to one fourth the compartment concentration resulting from the hot generator) was attested to by solids observed in the residual water.

Approximately 14 of the initial 20 L of water remained in the annular volume between the inner and outer chambers after the test. Three liters of water siphoned into the inner chamber because of the partial vacuum formed during cool-down, and another 3 L were evaporated, or were carried out as mist. The water bath maximum temperature increased 45 °C. The maximum

rate-of-rise was about 0.5 °C/sec. Water pH readings in the generator outer chamber and inner chamber following the test were approximately 10 and 11, respectively. The observed alkalinity is consistent with the nature of the propellant combustion products.

The "active" water spray generators dispense agent horizontally which remains horizontal for over a meter. However, the aerosol is not cooled sufficiently by the water injection and exits the generator at close to 1000 °C. The horizontal thrust is largely due to pressure differential driven momentum upon escape from a confined higher pressure combustion chamber. Subsequent mixing with ambient air does occur with significant cooling. Buoyancy forces still dominate dispersion once momentum is dissipated. See Figure 3. Due to the different water spray generator configuration, the S.F.E. charge is formed into a smaller surface area configuration than for the other two generators. A 1 kg water spray generator charge burns for about 1 minute, during which time approximately 1.6 L of water are sprayed into the aerosol.

### Fire Extinguishment

Pan fires **0.23 m<sup>2</sup>** in area were extinguished using the hot generators in 115 seconds with 3 kg S.F.E., and in 45 seconds with **4 kg** S.F.E. The latter is equivalent to 71 g of S.F.E. per m<sup>3</sup>. The water bath cooled generators with 3 kg could not extinguish the fires, 5 kg extinguished the fires in over 115 seconds (89 g/m<sup>3</sup>). Even though more agent was used with the water bath generators with a large fraction directed downward to the fire area, the aerosol **loss** in the water bath was overriding. The generation time was approximately **35-40** seconds for these generators. These extinguishment times are long.

The water spray cooled generators (**60-65** second generation time) were more efficient for low location fires. A **0.23 m<sup>2</sup>** pool fire was extinguished in **65** seconds using **3 kg** S.F.E. (**54 g/m<sup>3</sup>**). A combination of **4** water spray generators and **2** hot generators, with 1 kg charges each, extinguished the fire in 45 seconds.

The 1.1 m<sup>2</sup> pan fires were extinguished within **25-27** seconds using the water spray generators with **2** or 3 kg, as little as **36 g/m<sup>3</sup>**. The actual effective amount of S.F.E. **was** less than 15 g/m<sup>3</sup>, as less than half of the **2 kg** charge had been consumed before extinguishment.

### DISCUSSION

Aerosol generation took significant lengths of time. Extinguishment cannot be expected until sufficient aerosol concentration is achieved. Much faster agent burning rates are possible such as with powder S.F.E. media. However, the increased energy release rates complicate pressure and temperature limitation requirements, as well as require greatly improved aerosol cooling mechanisms to obtain uniform distributions. Any one agent need not perform well in all threat cases. It is Navy protocol to simultaneously employ AFFF (foam) to extinguish fuel pool bilge fires in large machinery spaces together with total flooding halon 1301 systems.

The location, type, and size of the fire threat must be considered. Large fires deplete oxygen and reduce air density. The 1.1 m<sup>2</sup> partially self inhibited large pan fires were comparatively much easier to extinguish than the **0.23 m<sup>2</sup>** fires. The different test conditions and fire threats

employed must be considered when comparing various evaluation results.'

S.F.E. is a fuel-rich weak propellant. Oxygen from the surrounding air is required for complete combustion. Indeed, moderate size pieces of Formulation C ignited in the open still generated some soot. If insufficient air is available this will result in increased carbon monoxide as well as less energy to drive the reaction and vaporize the material forming the aerosol. Propellant in a confining generator, and/or with other inert gases being produced (or added for cooling), will have less oxygen available. Available oxygen will change, i.e., decrease, during the charge combustion. Solid agent size and shape will affect surface to volume ratio and heat loss. This will affect combustion efficiency and aerosol generation efficiency. These factors must be considered when characterizing energy release, aerosol temperature, particle size, generation efficiency, residue quantity, and other specie formation and concentrations.

Dry chemical extinguishant behaves very similarly to water. Large water droplets, streams in the extreme, are very inefficient. They penetrate the flame zone largely intact without interacting. Very fine water mist cannot get to the fire, being swept away by fire generated convection currents. But it is the fine droplets that are most effective if sufficient concentrations are injected into the flame zone, by momentum or by drag forces from larger droplets. Ewing, *et al.*,<sup>5,6</sup> have shown that fine dry chemical particles under 20-30  $\mu\text{m}$  have greatly increased effectiveness. Large particles are known to fall out and coat surfaces. We have observed that fine aerosol S.F.E. particles, 0.5-4  $\mu\text{m}$ , when propelled at a fire, will also be swept away by fire generated convection currents. Just as our fine water mist studies show, sufficient concentration must be built up surrounding the base of the fire for extinguishment to occur.

Hertzberg, *et al.*,<sup>10</sup> reported values for minimum dry chemical concentrations to inert a stoichiometric methane-air mixture. The required concentration for inerting a stoichiometric hydrocarbon-air mixture is at least five times as large as the required concentration for extinguishing a pool fire. This can explain why some S.F.E. tests successfully extinguished pool fires but did not prevent some heptane spray fires from igniting.

The small particle size and high concentration aerosol cloud causes concern if used in an occupied enclosure. Particles with diameters less than 5  $\mu\text{m}$  can penetrate deep into the lung and can interfere with pulmonary functions. It is possible for particles of this size to physically clog the small pulmonary air paths. It is therefore important to evacuate the enclosure. A concern for Formulations B and C are the caustic nature of the aerosol propellant residue and the moist aerosol itself. The high alkalinity levels and hygroscopic nature of the aerosol residue may lead to physiological and corrosion problems. Formulation A can also cause corrosion over time. Post-use cleanup is necessary. Some of the aerosol formulations being pursued in the CIS, while possibly more efficient fire extinguishants, may generate more toxic and abrasive products. A previous presentation in this session discussed Navy toxicological evaluation of S.F.E. Formulation A.

US Navy efforts continue with Spectrix, Inc. designing different generators for cooling the generated aerosol. There is a related Spectrix presentation at this meeting entitled "Cooling Particulate Aerosols by Dry Extinguishing Powders." Other efforts are underway in England and the USA. Research in the former Soviet Union also continues, although there are not many

specific details. "VNIPO" completed a study of nine different types of pyrotechnic generated aerosol units from "GABAR," "GRANIT," "PERM," "SOWS," and "Technolog," in October, 1993. This included tests with 5A and 13B challenges in a 64 m<sup>3</sup> volume, monitoring fire temperature by thermocouple, and for "reignition" after ventilation as a measure of effectiveness against smoldering materials. Aerosol production was from one to six generators with approximately 6 kg or less total agent. Only the two GABAR single units succeeded in extinguishing both test fires (burning simultaneously) and preventing reignition.<sup>11</sup> Dr. Baratov claims his GABAR company units have addressed the concerns of ignition of combustibles by hot propellant exhaust, cooled aerosol generation for better total volume distribution, and effectiveness on smoldering combustion. The weights of the heat abstracting units can be considerably more than the pyrotechnic charge weights. Still, total system weight is low compared to the pressure vessels and piping of halon-like systems.

The mechanisms of aerosol fire extinguishment, including heat capacity, vaporization, crystal decrepitation, decomposition, surface mediated reaction, and other chemical pathways, are topics of investigation,<sup>12</sup> and will be dealt with elsewhere. Additional results from further studies, the various manufacturers, and other Air Force, Army, Navy, and FAA facilities, will be hopefully released as completed and as appropriate to the proprietary nature of the material.

## CONCLUSIONS

The considerations raised previously<sup>1</sup> on proper testing and result interpretation hold for aerosol evaluation. An agent can 'prove' to be highly successful against a particular fire threat, in a specific scenario, and not perform nearly as well under different conditions. Simple answers do not exist in the quest for halon alternatives or replacements. Intelligent evaluation of the perceived threat and both product applicability and implementation are absolute requirements.

Fine aerosol fire extinguishing materials have enhanced effectiveness due to their small particle size. Micron size particles also allow for gas-like properties, and the use of aerosols as total flooding fire extinguishing agents. Pyrogenic aerosol, like the S.F.E. investigated, is produced with considerable exoergicity. The resulting increased temperatures work against rapid uniform distribution in volumes of great height. Small rooms, enclosures, and cabinets, do not present the same difficulties. This also holds if very rapid fire extinguishment is not required. While there are several such potential drawback considerations, the flexibility of the technology keeps this approach in the stable of suppressant candidates.

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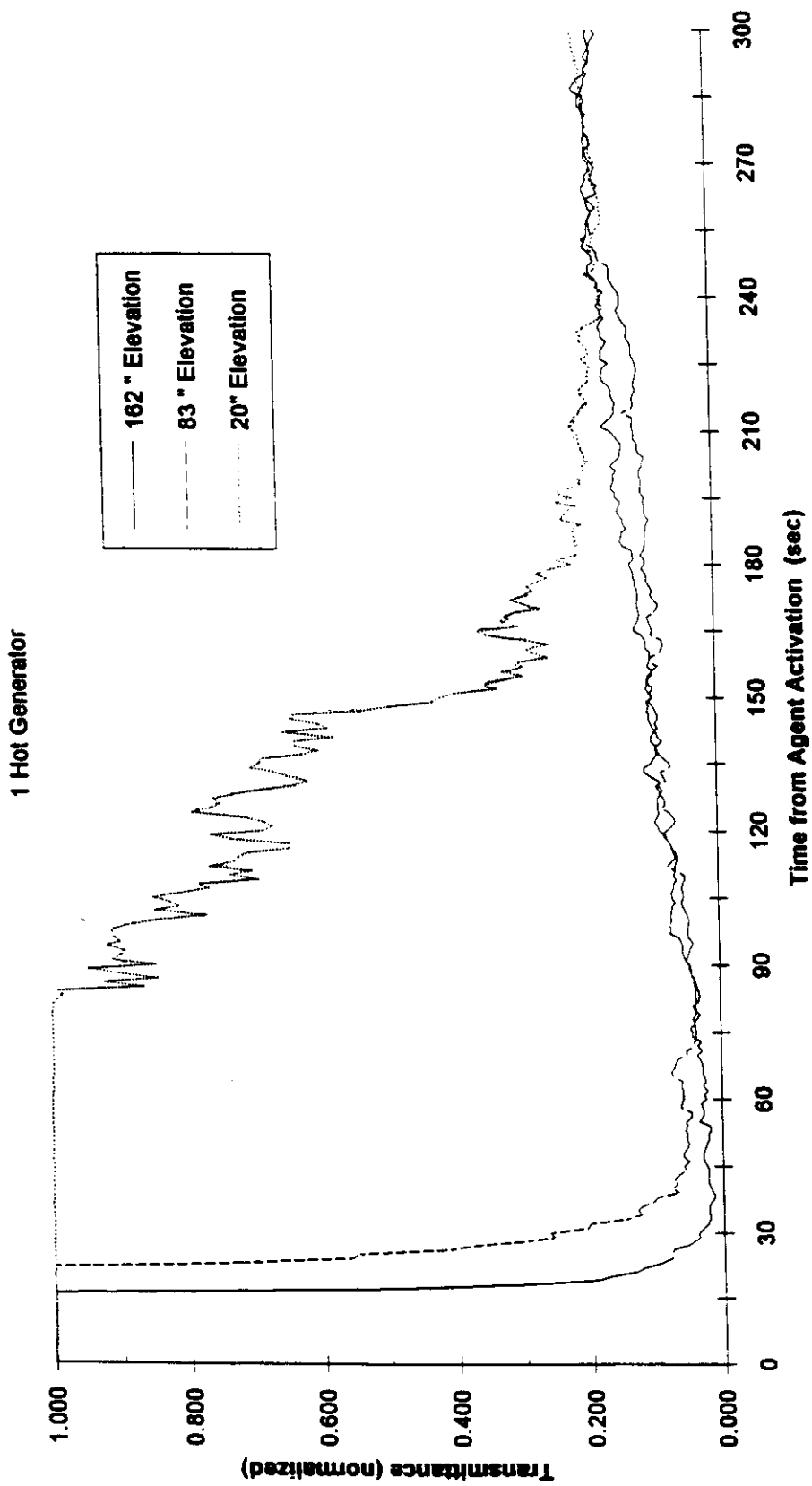


FIGURE 1. OPTICAL TRANSMITTANCE WITH 1 KG IN HOT GENERATOR

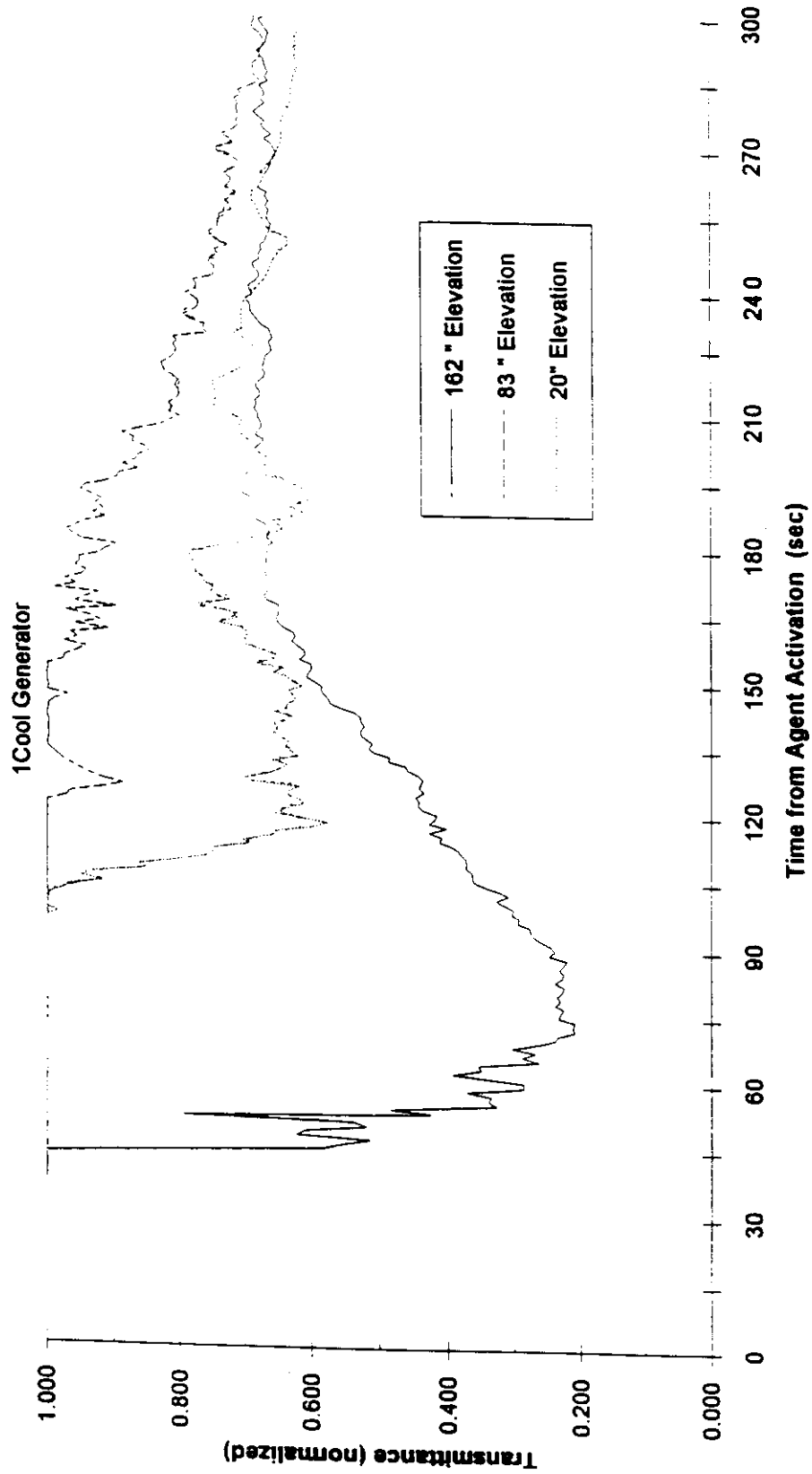


FIGURE 2. OPTICAL TRANSMITTANCE WITH 1 KG IN WATER BATH COOLED GENERATOR

1 Spray Cooled Generator

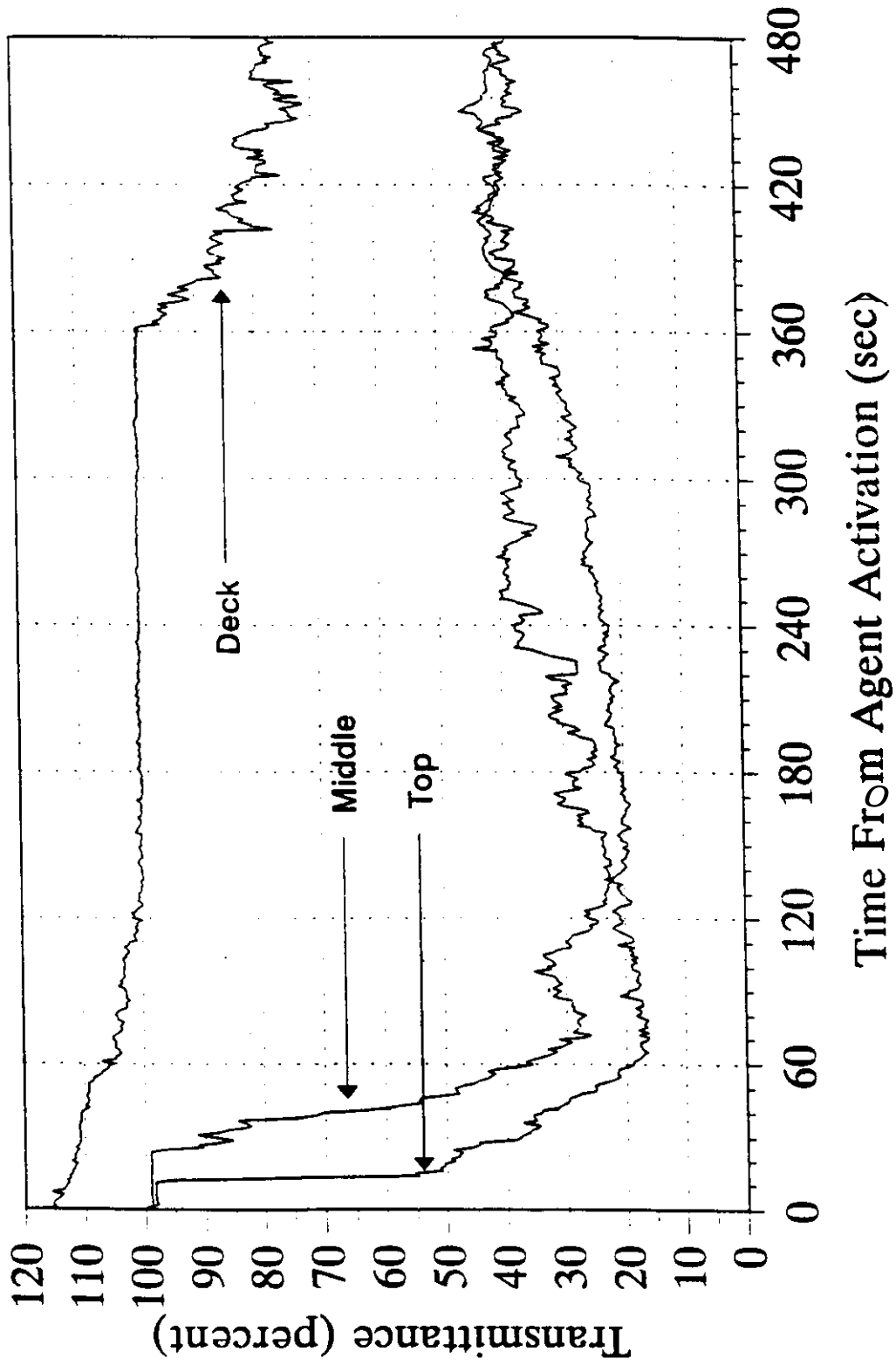


FIGURE 3. OPTICAL TRANSMITTANCE WITH 1 K $\epsilon$  IN WATER SPRAY COOLED GENERATOR