

LOW TEMPERATURE PYROTECHNIC SMOKES, **A POTENTIAL LOW COST ALTERNATIVE TO NONPYROTECHNIC SMOKE** **FOR ACCESS DELAY APPLICATIONS**

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ABSTRACT

Smokes are frequently used as visual obscurants in access delay applications. A new generation of low temperature pyrotechnic smokes is being developed. Terephthalic Acid (TPA) smoke was developed by the U.S. Army and Sebacic Acid (SA) smoke is being developed by Thiokol Corp. The advantages these smokes offer over traditional pyrotechnic smokes include; low generation temperature (approximately 450° C), lower toxicity, and lower corrosivity. The low generation temperature reduces smoke layering effects and allows the addition of sensory irritants, such as o-Chlorobenzylidene Malononitrile (CS), to the formulation. Some advantages low temperature pyrotechnic smokes offer over nonpyrotechnic smokes include; low cost, simplicity, compactness, light weight, long storage life, and orientation insensitive operation. Low cost permits distribution of multiple units for reduced vulnerability and refill flexibility. Some disadvantages may include the combustibility of the smoke particulate; however, the published lower explosive limit of the mentioned materials is approximately ten times greater than the concentration required for effective obscuration. The TPA smoke cloud contains small quantities of benzene, formaldehyde, and carbon monoxide; no benzene or formaldehyde was identified during preliminary SA smoke analyses performed by Thiokol Corp. Sandia performed tests and analyses on TPA smoke to determine the smoke cloud composition, the quantity of particulate produced per canister, and the relationship between airborne particulate concentration and measured optical density values. Current activities include characterization of SA smoke.

BACKGROUND

Visual obscurants are effective access delay components especially when used in conjunction with other barriers and/or dispensable materials. Obscurants

provide delay by increasing the time required to perform sight-related tasks, by enhancing the effects of other barriers and entanglement devices, and by restricting attack modes. They may also produce psychological effects and may be used as carriers for physiological agents.

Smokes are frequently used as visual obscurants. Smokes are suspensions, in a gaseous medium, of liquid or solid particles that have low vapor pressures and settle slowly under the influence of gravity. They range in size from approximately 0.01 microns to perhaps 5.0 microns in diameter. Smokes can be disseminated pyrotechnically, i.e., involving combustion, or nonpyrotechnically. Pyrotechnic smokes are available in different colors; however, white smokes are most effective for screening applications.

In the late 1970's, Sandia developed a nonpyrotechnic, or cold, smoke generator. The smoke generator was one component comprising an Igloo Access Denial System. The U.S. Army adopted the system with some modifications and it became known as the Weapon Access Delay System (WADS). Consequently, the non-pyrotechnic smoke generator used in the system was frequently referred to as the WADS smoke generator. Figure 1 shows the WADS smoke generator.

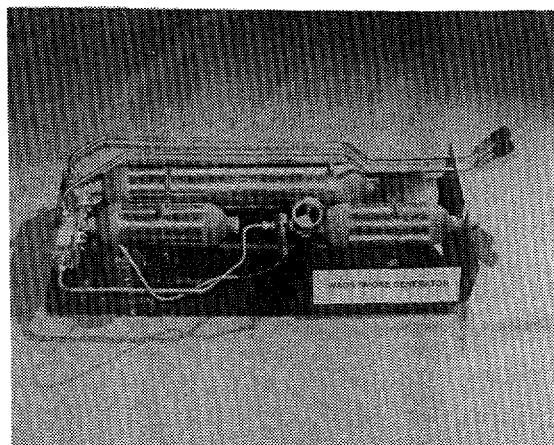


Figure 1. WADS Smoke Generator.

This work was supported by the United States Department of Energy under contract DE-AC04-94AL85000.

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The WADS generator uses ultrahigh purity nitrogen as the propellant to spray titanium tetrachloride and ammonium hydroxide through fine atomizing nozzles into the air where they react to form titanium dioxide and ammonium chloride smoke particles. Water is also produced by the reaction. The smoke particulate is white, noncombustible, low toxicity, and produces a neutral pH to minimize corrosion.

The WADS smoke generator had many advantages over some of the more conventional smoke generators at that time. The WADS smoke generators were volumetrically efficient with an expansion ratio, the ratio of the dispensed volume to the stored volume, of about 50,000:1. After the generator was initiated, it no longer required external power. The WADS smoke generator was available in two models; a booster for rapid fill, and a sustainer that dispensed the smoke for a longer period of time. The smoke generator had a design life of five years. It was relatively simple in principle of operation; however, it required precision machining, scrupulous cleaning and drying processes, special chemical handling and filling procedures, and for compatibility with the stored chemicals, all wetted metals were stainless steel. The design also incorporated many organic seals. Because of the strict processes and construction materials used, the smoke generators were expensive, approximately \$8,000 to \$12,000 each in large quantities and much more in small quantities.

LOW TEMPERATURE PYROTECHNIC SMOKES

In 1990, Sandia began reinvestigating pyrotechnic smokes because of the high cost and limited life of the cold smoke generators. Pyrotechnic smoke devices have other advantages in addition to low cost. They are simple, compact, light weight, and orientation insensitive. These advantages allow the integration of a distributed system which may reduce the time required to fill a volume, and may allow a refill capability which can equate to longer obscuration times. In addition, the low generation temperature allows the addition of sensory irritant materials to the formulation.

TEREPHTHALIC ACID (TPA) SMOKE

The U.S. Army is one of the largest users of smokes and has conducted significant research and development in the area of pyrotechnic smokes. Sandia contacted the U.S. Army's Edgewood Research, Development, and Engineering Center (ERDEC) and was informed that a new low temperature pyrotechnic

smoke, called terephthalic acid (TPA) smoke, was being developed for use as a low-toxicity replacement for hexachloroethane (HC) smoke in field training exercises. Sandia contracted ERDEC to formulate and build grenade size TPA smoke canisters for evaluation for access delay applications.

Figure 2 shows an ERDEC supplied TPA smoke canister. The canisters are a standard M18 grenade configuration measuring approximately 6.35 cm (2.5 in.) in diameter, and 11.94 cm (4.7 in.) long. Each canister contains 340 g of the smoke producing mixture. The smoke mixture is pressed around a tapered mandrel to form the perforated pyrotechnic grain. Five grams of a starter mixture are added to facilitate ignition. The ignition source is located in one end of the canister and the smoke exit port is in the opposite end. The Sandia TPA smoke canisters were supplied with Reynolds Industries Systems Inc. (RISI) SQ-80 igniters installed. The Sandia evaluation units were built at a cost of approximately \$85 each and the SQ-80 igniters were approximately \$15 each.

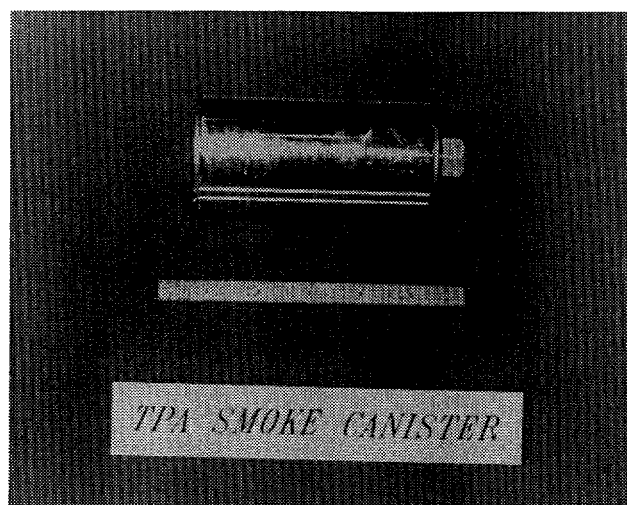


Figure 2 TPA Smoke Canister

Preliminary studies indicate the TPA smoke is low toxicity¹, nonmutagenic², and environmentally acceptable³. ERDEC has recently completed a comprehensive toxicity investigation of TPA smoke⁴ and concluded that it is lower toxicity than HC smoke. Terephthalic acid is a combustible material. Pure TPA has a published lower explosive limit (LEL) of 50 g/m³ and a minimum ignition energy of 20 millijoules.

TPA smoke is formed by a vaporization/condensation process. The burning fuel and oxidizer provides the thermal energy necessary to vaporize the TPA and the gas pressure required to dispense it from the canister.

In the air it condenses to form a white particulate with a mass mean diameter of less than one micron.

SEBACIC ACID (SA) SMOKE

Currently, Sandia is investigating sebacic acid (SA) smoke, a low temperature pyrotechnic smoke developed by Thiokol Corporation. Thiokol provided Sandia ten each SA canisters for a preliminary evaluation. The SA canisters are the same physical size as the ERDEC TPA smoke canisters with two major differences. Instead of a single smoke exit hole, the SA canisters have four smaller holes. The second difference is that the ignition port is located in the same end of the canister as the smoke exit holes. The SA canisters contain approximately 285 g of the sebacic acid smoke mixture. The canisters were provided without initiation devices. A copper oxide/aluminum thermite electric match works well for igniting the starter mix used with the SA smoke mixture. Like TPA, SA particulate is combustible. Pure sebacic acid has a published lower flammability limit of 42 g/m³ and a minimum ignition energy of 5 millijoules.

TESTING AND EVALUATION

Sandia has performed a significant amount of testing with TPA smoke and is currently evaluating SA smoke. Not all of the tests were performed with SA smoke canisters. All tests were conducted in a structure having an approximate volume of 43 m³ (1500 ft³). Temperatures were measured using bare

tipped, stainless steel sheathed, chromel-alumel (type K) thermocouples. Obscurity levels were measured using an instrument designed and built by Sandia National Laboratories called an Optical Densitometer (SLOD). The instrument is calibrated before each test using neutral density filters. Thus, the obscuration data units are neutral or optical density values. The equation for optical density is shown below:

$$\text{Optical Density (OD)} = \log_{10} 1/\text{Transmittance}$$

TPA TEST RESULTS

The TPA smoke canisters are not orientation sensitive; however, the time required to achieve maximum obscuration is dependent on the canister orientation and location and ranges between 45 and 135 seconds. The canister burn time ranges between 47 and 58 seconds. Figure 3 shows a graph of optical density relative to time for single and double canister TPA smoke tests; single canister SA smoke tests; and the small version of the cold smoke generator. The small cold smoke generator contains approximately one-fourth the chemicals of the WADS generator. The data suggest the pyrotechnic smokes are more persistent than the cold smoke and that two grenade-size TPA canisters provide a level of obscuration equal to or greater than the cold smoke generator. Approximate cost of the small cold smoke generator is \$6500, approximate cost of two TPA canisters is \$200. The cost estimates are for the smoke producing hardware alone and do not include the cost of the firesets or the command and control systems.

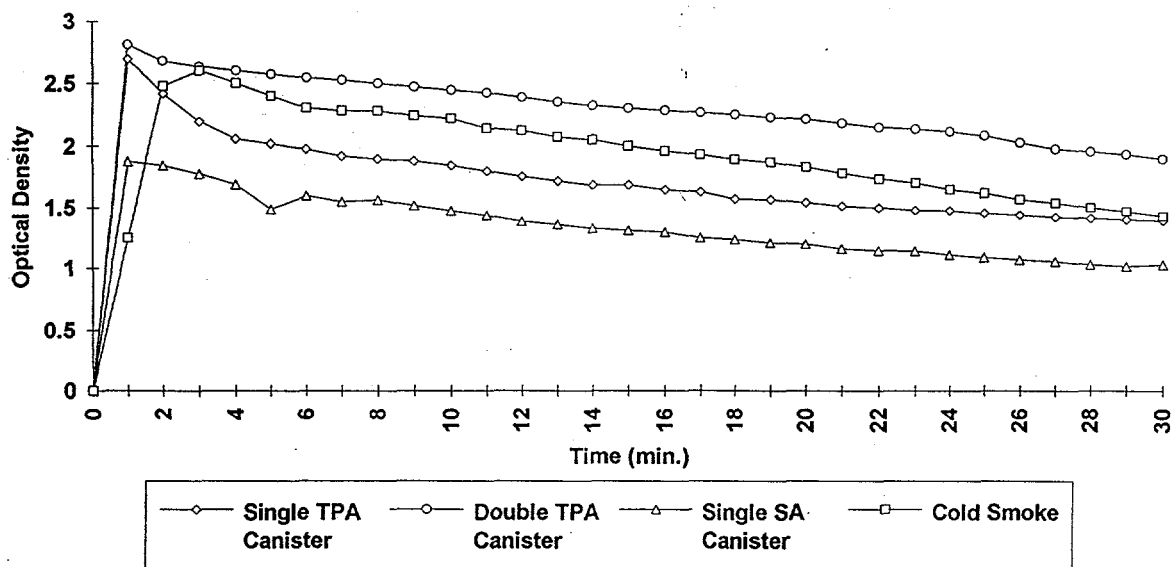


Figure 3. Comparison of Optical Density vs. Time for Single and Double Canister TPA Tests, Single Canister SA Tests, and Cold Smoke.

The TPA canisters produced approximately 130 g of particulate. The Yield Factor, expressed in percent, is the weight of the particulate produced divided by the total weight of smoke mixture. The yield factor for the TPA canister ranges between 35% and 39%. Terephthalic acid was identified as the major component in the smoke particulate, comprising greater than 80% of the particulate. Two or three other organic compounds were observed comprising a few percent each, and the balance of the smoke particulate, approximately 5%, was the inorganic compound potassium chloride. The main constituent of the material remaining in the canister after the burn was potassium chloride.

Gas samples were collected and analyzed. The typical combustion products carbon dioxide, carbon monoxide, and water vapor were identified. Small amounts of benzene and formaldehyde are also generated. The quantity of benzene and formaldehyde produced is proportional to the number of canisters dispensed, and it is uniformly distributed throughout the test chamber. The quantity of benzene measured was approximately 16 ppm per canister in the test chamber or approximately 1.9 g per canister. The quantity of formaldehyde measured was approximately 15 ppm per canister or approximately 0.7 g per canister. The measured quantity of carbon monoxide produced by a single canister was approximately 270 ppm or 11 g per canister.

The quantity of smoke required to effectively obscure a volume is dependent on the level of obscuration and the duration. The test data indicate a total airborne particulate concentration of 4 g/m³ consistently produced an effective level of obscuration. Thus, the effective airborne particulate concentration is 4 g/m³. An initial fill of approximately 5 to 6 g/m³ should provide effective obscuration for 30 minutes inside a closed volume, i.e., with no ventilation.

Results of accelerated corrosion testing indicated that the TPA smoke is mildly to moderately corrosive to aluminum alloys and the 300 series stainless steel alloys.⁵ The TPA corrosion effects were significant on unprotected mild steel and steel armor plate. Armor plate that had a chromate primer applied exhibited localized corrosion in areas where there may have been defects in the coating. In general, the coating provided protection against the corrosive attack. The TPA particulate was slightly soluble in water; it formed a mildly acidic solution with a pH range of 3.3 to 3.4.

Terephthalic acid is a combustible material that, in dust form, has a published lower explosive limit of 50 g/m³ for the pure material. Other combustible solids, vapors, and gases are formed as a result of the pyrotechnic

dissemination process. Sandia performed testing to determine the lower explosive limit of the pyrotechnically disseminated TPA smoke which included all the combustible reaction products. Test results indicated the LEL to be 90 g/m³.

The Occupational Safety and Health Administration (OSHA) limits the concentration of combustible dusts for manned operations to 10% of the LEL⁶. The National Fire Protection Association 69, Standard on Explosion Prevention Systems requires that combustible dust levels in unoccupied areas be maintained at or below 25% of the LEL.

Based on the OSHA regulation for manned areas and the Sandia measured LEL of 90 g/m³, manned operation would be allowed, using proper safety equipment, at 9 g/m³ total particulate concentration. Since an initial concentration of 5 to 6 g/m³ is recommended to provide an effective level of obscuration for 30 minutes in a non-ventilated volume, under these recommended conditions the explosive hazards are not significant. There may be situations; however, when significantly higher concentrations could be achieved resulting from variable volumes, multiple initiations, etc. Therefore, the possibility of achieving higher concentrations should always be considered.

A hazard analysis has been performed to assess the potential health hazards associated with exposure to the byproducts formed by the pyrotechnic dissemination of TPA smoke⁷. These byproducts are benzene, carbon monoxide, and formaldehyde. A benzene exposure limit of 50 ppm-hours, not to exceed 250 ppm regardless of duration, was selected based on the National Research Council's Committee on Toxicology published Emergency Exposure Guidance Levels (EEGL's) for exposure to benzene. A carbon monoxide exposure limit of 900 ppm-hours, not to exceed 3000 ppm regardless of duration, was selected based on the predicted symptoms of headache and nausea. A formaldehyde exposure limit of 25 ppm, regardless of duration and duration not to exceed one hour was selected based on the Emergency Response Planning Guideline values for exposure to formaldehyde published by the American Industrial Hygiene Association.

The health hazard analysis was based on the predicted exposure for three different time periods. These time periods are five, ten, and thirty minutes. The starting point for the exposures is the "design concentration" 5 g/m³. It was again assumed that each canister produced 130 g of particulate, 1.9 g of benzene, 11 g of carbon monoxide, and 0.7 g of formaldehyde. Table 1 summarizes the exposure estimates for the were exceeded.

	EXPOSURE (Ct, C) ESTIMATES			
	Benzene	Carbon Monoxide	Formaldehyde	
Exposure Scenario	Limit = 50 ppm-hr	Limit = 900 ppm-hr	Limit = 25 ppm	Limit(s) Exceeded
t = 5 min. (0.083 hr)	C _{Bt} = 1.7 ppm-hr	C _{CO} = 31 ppm-hr	C _F = 21 ppm	None
t = 10 min. (0.167 hr)	C _{Bt} = 3.8 ppm-hr	C _{CO} = 62 ppm-hr	C _F = 21 ppm	None
t = 30 min. (0.5 hr)	C _{Bt} = 11.5 ppm-hr	C _{CO} = 185 ppm-hr	C _F = 21 ppm	None

Table 1 Exposure Estimates for Three Scenarios

The temperature inside the test chamber typically increased about 6° C (11° F) per canister during the burning process. The maximum canister temperature was 225° C (437° F) and the measured maximum temperature of the burning pyrotechnic mixture was 440° C (824° F).

SA SMOKE TEST RESULTS

To date, we conducted four SA smoke tests. From the data in Figure 3 we see that the optical density values for SA smoke are lower than those for the TPA smoke. This is expected because the TPA canisters contain 340 g of mixture of which 194 g are TPA; whereas, the SA canisters contain 285 g of which 142 g are SA. The persistence of the SA smoke is similar to the TPA smoke as indicated by the parallelism of the two lines. The maximum canister temperature was 338° C (640° F) and the maximum plume temperature measured at 15.24 cm (6 inches) from the smoke exit ports was 204° C (400° F).

The SA canisters produce approximately 75 g of particulate from 285 g of smoke producing mixture

resulting in a yield factor of approximately 26%. At this time there is not sufficient data to determine an effective concentration. Analyses of the smoke particulate and the canister residue are currently being performed to identify and quantify their constituents.

There was no benzene, acrolein, or toluene detected; however, formaldehyde was detected. The concentration measured was approximately the same as for the TPA smoke. Approximately 15 ppm formaldehyde were measured in the test chamber. Results from the analysis to identify other gaseous constituents in the smoke cloud, primarily organic compounds, have not yet been received.

COST COMPARISON

An attempt was made to compare costs of the various types of smokes. This was done by estimating the number of pyrotechnic smoke canisters required to provide the same obscuration as a WADS type cold smoke generator. This comparison was selected because of the number of WADS generators currently in use. Table 2 shows the cost comparison data.

	WADS Smoke Generator	Small Cold Smoke Generator	TPA Smoke Canister	SA Smoke Canister
Performance	1	4	6	8 - 10 ¹
Unit Cost	\$12,000 ²	\$6500 ³	\$100 ⁴	\$100 ⁴

1. Based on limited data.
2. Cost is dependent on number of units built (range \$8,000 to \$16,000).
3. Cost in 1991.
4. Small quantity costs, larger canisters can be built for minimal additional material cost.

Table 2 Cost Comparison Data for Three Types of Obscurant Smoke

Conclusions

Both terephthalic acid smoke and sebacic acid smoke offer some significant advantages over both cold smoke and other pyrotechnic smokes. Some of the advantages when compared to cold smoke include: low cost, simple, compact, light weight, long shelf life, high reliability, no liquid chemicals to leak or to be concerned about seal compatibility. Because both TPA and SA smokes are low temperature, it is believed that sensory irritants may be added to the formulations. The TPA smoke has been determined to be lower toxicity and lower corrosivity than other pyrotechnic smokes frequently used.

Toxicological data on the exposure to TPA particulate concentrations representative of those that are recommended for access delay applications, i.e., 4 to 6 g/m³, are not available. The ERDEC Toxicity Report (ref. 4) evaluates concentrations as high as 2 g/m³. The health hazard assessment suggests that the benzene and carbon monoxide are not a problem from an acute exposure perspective. Furthermore, these substances would allow increases in the "design concentration", i.e., 5 g/m³, up to levels where explosibility would be a factor. The health hazard assessment indicates that formaldehyde may be the limiting agent. The predicted concentration is near the 25 ppm limit. If the formaldehyde estimate is correct, there is no opportunity to increase the "design concentration" beyond the stated 5 g/m³ without incurring unacceptable health effects, by our definition. At this time, there is not sufficient data on SA smoke that would allow us to make a similar statement.

We believe there are applications where TPA and possibly SA smoke may be suitable for use as a low cost obscurant substitute for nonpyrotechnic smoke. Sebacic acid smoke may be more desirable from a toxicological perspective; however, at this time the data are not conclusive.

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