Inerting and Extinguishment of Aerozine-50 with Water and/or CF_3Br

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Two parts by weight of water per part of Aerozine-50 (A-50) will "inert" a spill of A-50 against ignition in air. In the case of a burning A-50 pool, the fuel evaporation rate is about 0.6 lb/min-ft^2 during most of the duration of burning, and a well-distributed spray of 1.2 lb water/min-ft^2 of liquid surface is sufficient for extinguishment. To inert an A-50 spill against hypergolic ignition with N_2O_4, as much as 10 lb of water are required per lb of fuel, depending on the circumstances of mixing. In situations where use of large amounts of water may not be practical, CF_3Br (Halon 1301) can abate fire hazards; ~7% of CF_3Br in the atmosphere will inert a small spill at room temperature against ignition by spark or pilot flame. The same concentration would extinguish most secondary fires ignited by the hypergolic reaction of A-50 and N_2O_4, but impracticably high concentrations of CF_3Br would be required to extinguish an established A-50 pool fire or to inert the maximum vapor concentrations of A-50 possible in a closed chamber.

Introduction

THE propellant Aerozine-50 (A-50) contains by specification[1] approximately 51 wt % of hydrazine (N_2H_4) and at least 47 wt % unsymmetrical dimethylhydrazine (UDMH). Being a blend of volatile fuel (UDMH) with an endothermic one, A-50 combines the handling hazards of low flash point and wide flammable range. Other special characteristics are hypergolic ignitibility with certain oxidizers, catalytic decomposition by iron oxide, and exothermic behavior with CO_2 and H_2O.

In most circumstances the preferred countermeasure to a spill of A-50 is the application of copious amounts of water, because water's mutual solubility with A-50 results in a strong suppression of the fuel's vapor pressure. If the hazard is a fuel vapor concentration, a water spray may be used to reduce this vapor concentration below the lower flammable limit, which is ~2%. The optimum water delivery is in fine droplets. If the hazard involves a pool of liquid A-50, the addition of water will raise its flash point, but in this application a coarse water spray will bring about the dilution more quickly and safely. In the event of an existing fire above a pool of liquid A-50, water is probably the only effective extinguishant; the optimum drop size depends on the amount of water available and on its delivery rate.

However, A-50 is used under some circumstances wherein a water deluge could be more damaging than the small fire that it was meant to avert. The use of CF_3Br (bromotrifluoromethane or Halon 1301, hereinafter simply called Halon)** as a first-stage inerting or extinguishing agent (to be followed only if necessary by water deluge) has been studied. Halon "inerts" an A-50 vapor/air mixture by raising the lower flammability limit of the fuel vapor, and it inerts a pool of spilled A-50 by raising its fire point. It extinguishes an A-50 vapor/air flame by reducing the burning velocity to a point of flame destabilization; its action in the extinguishment of a burning A-50 pool is more complicated, as will be discussed.

This paper provides some quantitative measurements with which to estimate the water and/or Halon requirements for rendering A-50 spills inert and for extinguishment of A-50 fires. Some attention also is given to extinguishment of secondary fires and to the products of combustion of A-50 in a Halon-containing atmosphere.

Evaporation of A-50

When an isoteniscope containing A-50 is evacuated, there is a rapid loss of vapor pressure p_v as dissolved gases†† are pumped off. After about 0.5% of the sample weight has been removed, p_v becomes relatively stable as shown by points

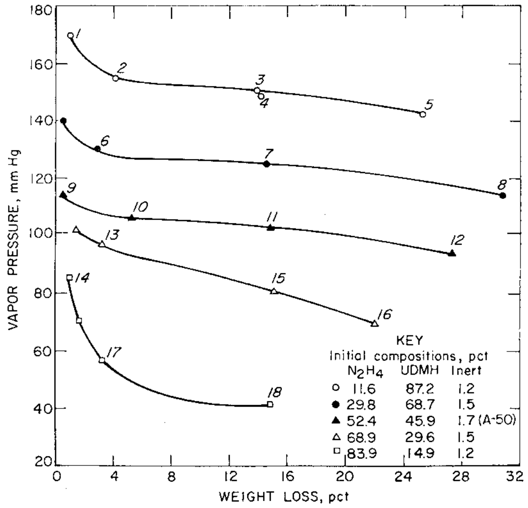

Fig. 1 Vapor pressures of hydrazine-UDMH mixtures vs evaporative weight loss at 77°F.

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** Reference to trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

†† Gas chromatographic analyses of these gases identify hydrogen, nitrogen, methane, ammonia, methylamine, and dimethylamine, the relative quantities of which may be a function of the age of the A-50 sample.

Table 1 Liquid and vapor compositions during evaporation of A-50 from trays

Liquid comp, g				Vapor comp, mol %		Evaporation rate, lb/ft² min
Total	N_2H_4	UDMH	Other	N_2H_4	UDMH	
a) 2.5 fps air flow at 72°F						
100	52.4	46.0	1.6			0.0155
				16.1	83.9	
87	51.6	33.2	2.2			...
				20.6	79.4	
60	48.5	9.5	2.0			0.0091
b) Natural wind (0–5 fps) at 45°F						
100	54.2	43.0	2.8			0.0078
				...	100	
94	54.2	35.8	3.7			...
				7	93	
87	54.0	30.0	3.0			0.0031
				20	80	
77	52.7	19.6	4.4			...
				34	66	
65	50.0	10.0	4.9			0.0019

9–12 of Fig. 1. By titrating the residual liquid for N_2H_4 and UDMH[1] at each numbered point of Fig. 1, one obtains the liquid compositions to be plotted at appropriate p_v's in Fig. 2; by difference between successive liquid analyses one can estimate, with admittedly lower precision, the vapor compositions given in Fig. 2. The liquid-vapor equilibrium curves in Fig. 2 were derived by extrapolation from 100°–200°F of the distillation data of Mignotte.[2] Thus, it appears that the p_v's and compositions related to A-50 are adequately predictable, if one is willing to neglect the first 0.5% or so of material evaporated. In particular, the vapor concentration above A-50 at 77°F is ~90 mole % UDMH and the total p_v is 113 mm Hg. During the early stages of evaporation of A-50, the vapor concentration stays above 80 mole % UDMH until the liquid composition has changed roughly to point 14 in Fig. 2, with ~$\frac{1}{3}$ of the liquid evaporated. But now Fig. 1 shows that further evaporation will involve a drastic decrease of p_v.

The evaporation rate (V_e, lb/ft²-min) in still air from a flush circular area of radius r is given by[3]

$$V_e = (4\rho D/\pi r) \ln(p - p_d/p - p_s) \qquad (1)$$

where ρ is the vapor density, D is the diffusion coefficient into air, p is atmospheric pressure, p_s the saturation vapor pressure, and p_d the partial pressure of the vapor at some distance from the surface.

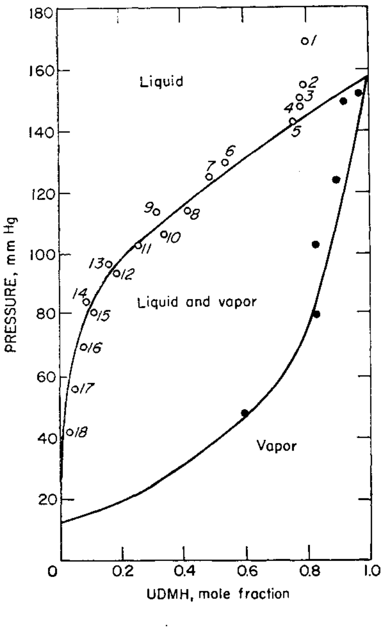

Fig. 2 Vapor-liquid equilibrium, N_2H_4/UDMH solutions, 77°F.

For evaporation into fresh air ($p_d = 0$) at p_s appropriate to A-50 at room temperature, Eq. (1) may be approximated by

$$V_e = Kp_s/p \qquad (2)$$

where K is a constant. From Fig. 2, it appears that the initial rapidly evolved vapors from a spill must be largely UDMH; flammable limits and burning velocities will be essentially those of UDMH. By the time the vapors have become predominately N_2H_4 (and may exhibit the decompositional burning that is characteristic of N_2H_4 vapors‡‡), p_s and V_e are both lower by a factor of 3.

Table 1 refers to pools of A-50 that were evaporated in air streams. Weighings provided a measure of V_e, and samplings provided information as to liquid and vapor composition. In a 72°F air stream, V_e drops by nearly 50% whereas 40% of the pool weight is lost. At 45°F there is a 75% decrease in evaporation rate during a 35% weight loss.

Effects of Convection on Evaporation Rate

In an attempt to evaluate D in Eq. (1), 1-pint samples of A-50 were evaporated from a 14-in.-diam aluminum tray located centrally on the floor of a 4 × 4 × 4 ft plywood box. The lowest of several V_e's measured was 0.0010 lb/ft²-min, giving a D of at least twice the expected value.§§ This discrepancy is presumed to result from convective (layering) currents that are particularly characteristic of A-50 because of the high density of fuel vapors. At air speeds $U_a \leq 5$ mph, the initial V_e's varied by

$$V_e = 0.002 + 0.006\,(U_a, \text{mph})^{1/2} \qquad (3)$$

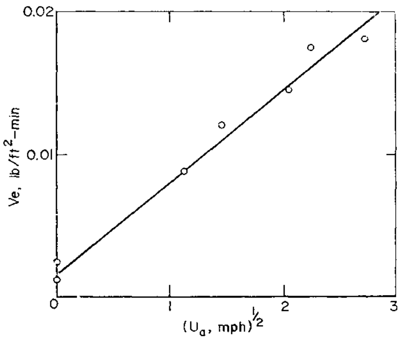

Fig. 3 Evaporation rate of A-50 from shallow pools.

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‡‡ According to Ref. 2, this occurs at less than 46 mole % UDMH.

§§ The diffusion coefficient for 90 UDMH-10 N_2H_4 into air should be about 0.1 cm²/sec.

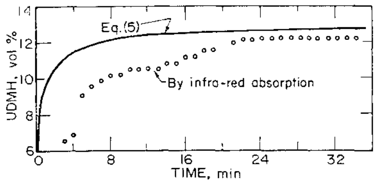


Fig. 4 Time history of UDMH concentration 0.5 in. above a pool of A-50 at 72°F.

as shown in Fig. 3. Since the dilution of a fuel vapor presumably depends on the first power of U_a, Eq. (3) implies that the condition most conducive to forming flammable mixtures is minimum U_a, i.e., near the intercept of Fig. 3.

Another approximate empirical equation is[3]

$$V_e = K_2/R^{1/2} \tag{4}$$

where R is pool radius. Accordingly our evaporation rates from 14-in.-diam trays were about twice the values found elsewhere from 4-ft-square trays.[4]

Vapor Concentrations above a Pool

If a liquid spill occupies the entire cross section of the enclosure and there is no convection, the initial V_e is given by Eq. (1) and the instantaneous fuel concentration is given by

$$C = C_{\text{eq}}[1 - \text{erf}\; h/2(Dt)^{1/2}] \tag{5}$$

where C_{eq} is the equilibrium fuel concentration; erf, the error function; h, the height above the liquid level; D, the diffusion coefficient; and t, time.[5] Equation (5) was used to calculate $C(t)$ at $h = 0.5$ in. above a pool of A-50 at 72°F. The resulting curve in Fig. 4 is compared with experimental values obtained with the 14-in.-diam tray in the 4 × 4 × 4 ft box. As much as 3 min of the rather long delay in reaching any expected UDMH concentration may represent the delay times of sampling and instrument response,¶¶ but the major part of the discrepancy is caused by a layering current that carries UDMH concentrations laterally across the floor of the enclosure. The existence of this current was confirmed repeatedly by igniting the system at some horizontal distance from the tray.

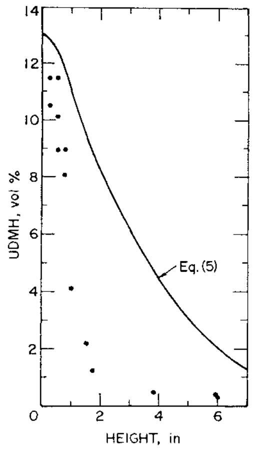
Figure 5 gives a comparable picture of $C(h)$ at $t = 10$ min. Whereas the "theoretical" curve indicates a 6-in.-thick flammable zone, the experimental values show flammability extending only to $h \simeq 1.5$ in. Now remembering that Figs. 4 and 5 refer to an artificially quiet atmosphere above the liquid, it is evident that the flammable zone in any real situation of natural or forced convection must be very thin. This correlates with the experimental finding (discussed later) that ignition of an A-50 pool at 77°F can be prevented by only 7% of Halon.

Although layering decreases the thickness of the flammable zone immediately above a spill, it poses the likelihood of vapor trails and flammable mixtures at some appreciable distance from the spill. Since the equilibrium concentration of UDMH and N_2H_4 in air is about 14% heavier than air, layering is particularly dangerous when the liquid leaks down a sidewall or onto some such configuration as the rungs of a ladder. In this connection, Halon looks particularly attractive as inerting agent; a 20/80 Halon air mixture is almost exactly as dense as the vapors evolving from A-50.

Vapor Reduction by Application of Water

The gas saturation method was used to determine the composition of vapors above various A-50/water mixtures at 77°F (Fig. 6). Dry helium was used as the carrier gas. Three glacial-acetic-acid scrubbers were used in series to

Fig. 5 Concentration of UDMH vs height above an A-50 spill after 10 min.



absorb the vapors; N_2H_4 and UDMH were obtained by titration, and water vapor by difference from the weight loss of the A-50/water mixture. Figure 6 indicates that 50 wt % water reduces the total pressure of fuel vapors to about 16 mmHg, that is, to the lower flammable limit at 77°F.

In an experiment similar to that of Fig. 4, UDMH concentration was monitored at a point 11 in. from the edge of the 14-in.-diam tray and ½ in. above floor level. One pint (427 gm) of A-50 was poured into the tray, and when the UDMH vapors had attained a 5–6% level (see Fig. 7a), 1040 g of water was discharged into the chamber as a coarse spray; most of this water fell into the liquid fuel. The UDMH concentration was abruptly lowered to ~1% and stayed indefinitely below 2%. Figures 7b and 7c show the results of similar experiments employing 800 and 240 g of water, respectively. In Fig. 7b, where the water dilution was somewhat less than 2:1, the expected final UDMH concentration (from Fig. 6) should have been ~1%; it is indeed below the lower limit of flammability. In Fig. 7c, the water dilution was somewhat more than 1:2, so that a final UDMH concentration of ~6% was expected. Although these last two water additions were made with fog nozzles,*** it is quite clear that droplet size was not involved here except as it may have affected the water fallout and therefore the ultimate dilution ratio.

The most direct specification of safe water dilution ratios is a plot of flash point vs water concentration; one then dilutes the fuel to a flash point above the highest temperature of

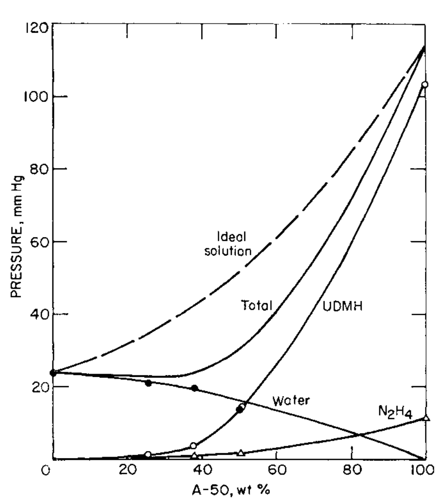


Fig. 6 Partial pressures of water, UDMH, and hydrazine in the vapor phase above A-50 water mixtures at 77°F and 1 atm.

¶¶ A sampling flow of 100 cm³/min was drawn through an infrared absorption cell and sample line with total volume of 65 cm³.

*** Bete Fog Nozzle Inc., 322 Wells Street, Greenfield. Mass,

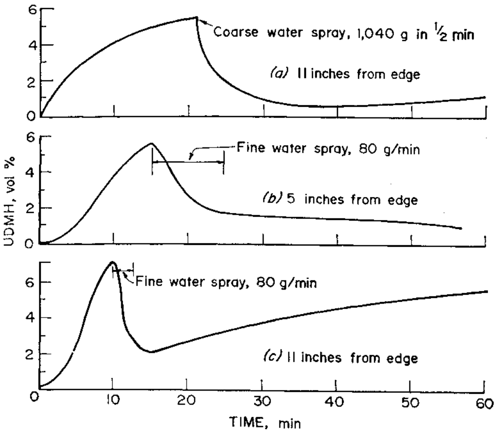


Fig. 7 UDMH concentrations in vicinity of A-50 pool as affected by water spray.

possible interest. Measured flash points for A-50/water mixtures are shown as circles in Fig. 8. If the liquid temperature is not to exceed 77°F, then 42% by weight of water is required. However, in the practical situation of water addition to an A-50 spill, the heat of solution may raise the A-50/H_2O mixture to a temperature above its flash point. The triangles of Fig. 8 represent temperatures attained by mixing A-50 and water in an insulated cup. The intersection of the heating curve and the flash-point curve provides the minimum safe dilution with water, ~64% if all of the heat of solution is retained.†††

It might still conceivably be possible to ignite a 64% water-diluted A-50 if the solution came in contact with an ignition source such as an electrical short that heated the solution above the temperatures of Fig. 8. For this reason, various UDMH/N_2H_4/H_2O mixtures (points 1–5, Fig. 9) were allowed to burn to self-extinguishment, after which their unburned residues were analyzed for UDMH and N_2H_4. Such residues do not provide flammable vapors at their boiling points, and their compositions are shown as points 1′–5′ in Fig. 9. The best curve separating flammable from nonflammable zones appears to cross the A-50/water line at ~65% water, in good agreement with Fig. 8.

If both fuel (A-50) and oxidizer (e.g., N_2O_4) spills occur, either propellant, or both, may be diluted with water to prevent ignition. Three situations were considered: 1) N_2O_4 contacts water-diluted fuel, in which case about 10 parts water per part of fuel are necessary to prevent ignition; 2) fuel contacts water-diluted N_2O_4, the minimum safe dilution being about 2 parts water per part of N_2O_4; and 3) water-diluted fuel contacts equally diluted N_2O_4, in which case equal weights of water and of propellant prevent hypergolic ignition. These dilution ratios are not so contradictory if one considers that the optimum (stoichiometric) oxidant/fuel ratio is more than 2:1.

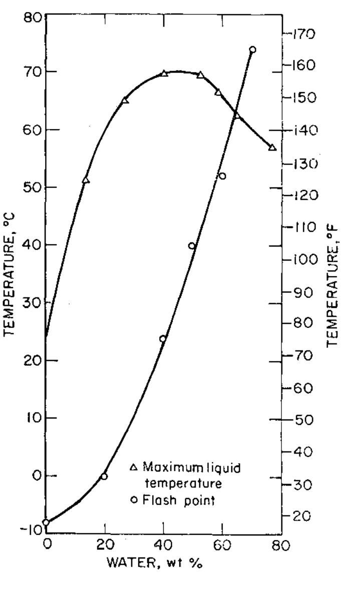


Fig. 8 Flash points of A-50/water mixtures (circles) and maximum temperatures attained by mixing A-50 and water at initial 24°C (triangles).

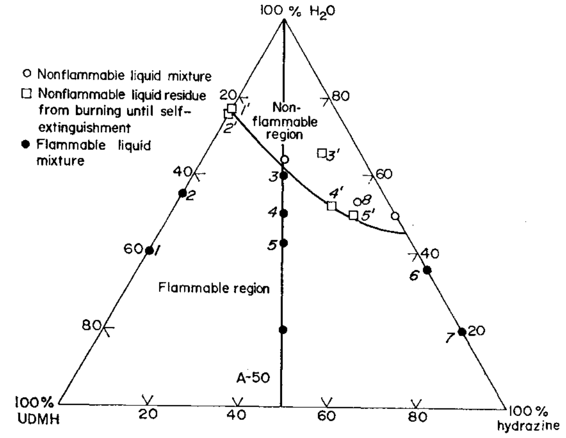


Fig. 9 Combustion properties of UDMH-hydrazine-water mixtures in air at ambient temperatures.

The results of 65 ignition tests are condensed in Fig. 10, which may be read as follows: An arrow from the N_2O_4 vertex to the A-50/water line indicates that N_2O_4 is poured into the diluted fuel; the arrow is also the approximate boundary of the hypergolic ignition zone, such that ignition occurs to the left (water reduction) side of an arrow; each of the other five arrows has the same significance. The broken line labelled "Hot" was obtained by pouring A-50/water while it was still hot from mixing into an equally diluted N_2O_4/water mixture; this conservation of the heat of dilution widens the hypergolic range.

Extinguishment of A-50 Fires by Water

Water decreases the burning rate of a UDMH or N_2H_4 fire, whereas the gases N_2, CO_2, and Halon have no apparent effect short of extinguishment (see for example Fig. 11 and columns 2 and 3 of Table 2). Three procedures by which one might extinguish an A-50 fire with water are:

1) Add sufficient water to the liquid fuel so that it concentrates with continued burning, and the mixture eventually

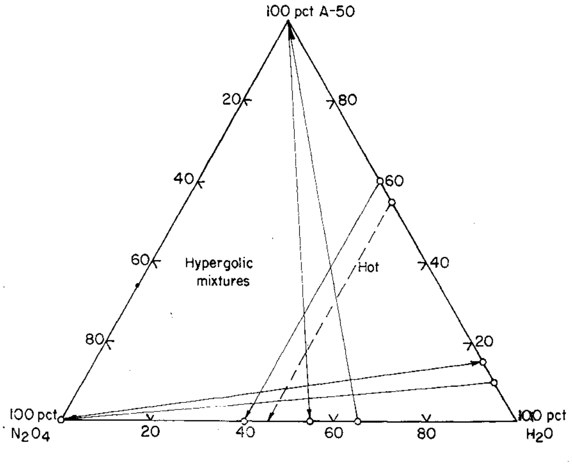


Fig. 10 Critical hypergolic A-50/water-N_2O_4 mixtures at ambient temperatures.

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††† Flash point measurements were made by J. Cooper, Chemist, Safety Research Center, for analysis of collected products.

Table 2 Burning rates and minimum percentages of Halon 1301 for extinguishment of 6-in.-diam water-diluted pool fires

Fuel	Water added, wt %	Burning rate, lb/ft²-min	Halon 1301 needed, vol %
A-50	0	0.35	48
	20	0.21	16
	50	0.11	2.5
	64	0	...
MMH	0	0.3	40
	20	0.15	14
	40	0.11	2.5
	70	0	...
Hydrazine	0	2.7	>50
	20	0.43	18
	40	0.13	2.5
	50	0	...

distills itself into the nonflammable zone of Fig. 9. Mixtures shown as points 3–5 of Fig. 9 burn to eventually nonflammable residues represented by points 3′–5′; a serious disadvantage is the long duration of burning by which the fire achieves its own lingering end. Test 10 of Table 3 also illustrates the method; 10 lb of A-50 was ignited in a 22-in.-diam tray and given 15 sec to preburn, whereupon water was added at 12 lb/min in a stream that mixed with the A-50. It required 1¾ min (21 lb of water) to extinguish the 10 lb of A-50.

2) Add water vapor to the distilled fuel vapors at such a flow rate as to place the vapors outside flammable limits. In the 22-in.-diam tray, the burning rate V_f is about 0.6 lb/ft²-min during the early stage of fuel consumption. In tests 11–14 of Table 3, a water fog was added at a weight ratio of about 2:1, and extinguishment occurred rather quickly in each of 3 tests with water rates V_w upwards of 1.3 lb/ft²-min. However, in test 13 with V_w = 1.1 lb/ft²-min, the fire burned to completion. The 2:1 weight ratio here is only accidentally the same as the weight ratio for inerting liquid A-50.

3) Reduce V_f (= V_e) by applying water, thereby making the fire more susceptible to extinguishment by a chemical agent. The final column of Table 2 shows that much less Halon is needed to extinguish fires of water-diluted fuels. Moreover, it should be possible to dilute the burning vapors with water in the presence of Halon, and this is the sense of Table 4. In tests 3 and 5 with no Halon, $V_w \simeq 0.4$ lb/ft²-min sufficed to build up nonflammable concentrations only after ~1.5 min of burning; with ~5% of Halon, tests 2 and 4, true extinguishment occurred at about the same V_w; with the same nominal Halon concentration, a spray of 0.14 lb/ft²-min was ineffective, but a 0.6 lb/ft²-min spray gave fast extinguishment.

Effects of Halon 1301 on A-50 Vapor/Air Flames

Three representative fuel vapors in air were investigated: UDMH in concentrations from 0 to 20%; 80 UDMH-20 N_2H_4, from 0 to 27%; and 50 UDMH-50 N_2H_4 from 0 to 13%. These were metered as liquids through motor-driven syringes and were completely vaporized at slightly elevated temperature, typically 100°F, into a metered gas stream of air and Halon.

Table 3 Extinguishment of 10 lb of A-50 after 15-sec preburn in 22-in.-diam tray

Test	Water rate, lb/ft²-min	Spray	Time to extinguishment, sec
10	4.6	Coarse	105
11	1.44	Fine	15
12	1.37	Fine	17
13	1.14	Fine	No extinguishment
14	1.37	Fine	21

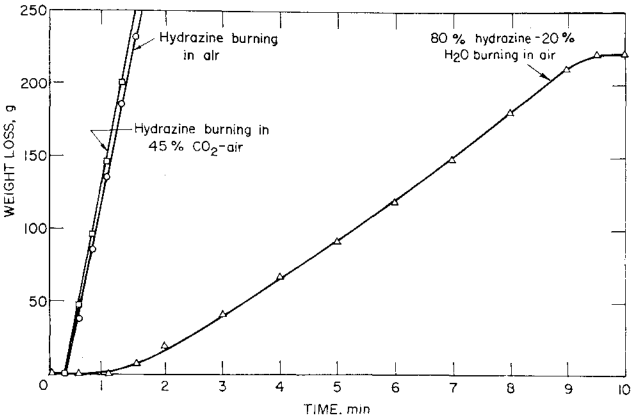

Fig. 11 Hydrazine burning rates with diluents.

Limit-of-flammability experiments were conducted in the Bureau of Mines F-11 apparatus,[6] which is a flow-type unit contained in a temperature-controlled chamber. Previous work with this unit had shown that inerting requirements at 100°F are not significantly different from those at 72°F. The vertical flammability tube is 40 in. long and 4 in. in diameter and is fitted with platinum electrodes connected across a 15-kv, 60-ma luminous tube transformer for generating an ignition spark. Premixed fuel vapor/air/Halon mixtures were introduced at the bottom of the tube at velocities below 0.2 fps. After the tube was flushed at least three times, the ignition source was energized; the test mixture was considered flammable if flame propagated over 1.7 ft or more of length. The laboratory was darkened to facilitate observation of the weakly luminous flames; flame propagation was also confirmed by the temperature rise of a 40-gage Chromel-Alumel thermocouple.

Figure 12 shows the limit curves as determined by some 70 trials; the experimental points are omitted for clarity. A curve for 80 UDMH-20 N_2H_4/air/N_2 is included for comparison. The solid portions of the curves are terminated where the fuel vapor concentration reaches its equilibrium value at 77°F. Arrows indicate the concentrations for stoichiometric combustion to CO_2, H_2O, and N_2.

The greater effectiveness of Halon as compared to N_2 appears more significant if one considers that the most probable

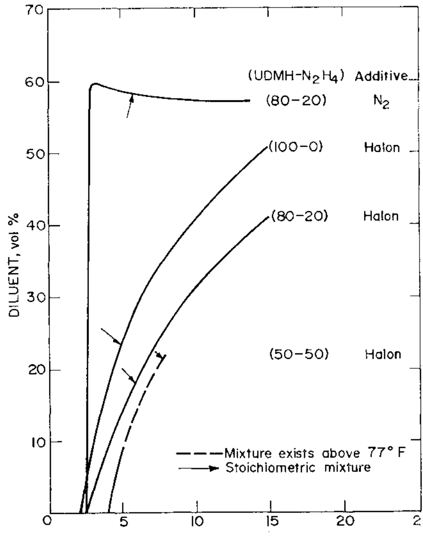

Fig. 12 Effect of diluents on flammable limits of A-50 vapors in air at 100°F, 1 atm.

Table 4 Times to extinguishment (t_{ext}) by water and Halon 1301 of A-50 burning in 14-in.-diam tray

Test	Nozzle (Bete)	Water		Halon 1301 in air, %	Preburn time, sec	t_{ext}, sec
		psi	lb/ft²-min			
1	P-54	60	0.57	5.6	8	12
2	P-28	30	0.38	4.8	7	16
3	P-28	30	0.38	0	10	83
4	P-28	30	0.43	5	26	37
5	P-28	30	0.43	0	30	64
6	P-10	90	0.14	5.5	15	108

Table 5 Marginal Halon 1301 concentrations to prevent ignition of A-50 pools

Series	Tray diam, in.	Tray depth, in.	Liquid temp., °F	Vapor pressure,[a] psi	Halon in air,[b] %
1 (spark)	4	0.38	57	1.6	4.9–7.5
2 (spark)	4	2	57	1.6	5.5–8.2
3 (spark)	4	0.38	84	3.0	9.3–11.8
4[c] (spark)	14	5	86	3.2	5.7–12.5
(fuse)					12.5
5[d] (flame)	6	0.38	72	22	6.3
			76	2.5	6.3

[a] From Ref. 12.
[b] Ignition occurs below this range; no ignition above it.
[c] The several tests of this series were carried out in a 12-ft-diam sphere using 1 pint (473 ml) of A-50.
[d] Using 250 ml of A-50.

mixtures at any distance from a spill will be lean mixtures. Nearly 60% of N_2 is required to inert even a very lean (80 UDMH-20 N_2H_4)/air mixture; almost the same figure has also been found for UDMH/air.[7] On the other hand, the required concentration of added Halon rises much less steeply to about 20% at the respective concentrations for stoichiometric burning. A disappointing feature of inhibition by Halon is the continued rise in requirement as the mixtures become progressively richer than stoichiometric.

The vapors from A-50 spill become easier to inert with Halon as the liquid evaporates; this follows both from the curves of Fig. 12 and from the decreasing p_v as UDMH is depleted in the liquid.

Premixed vapor/air/extinguishant streams also were ignited above a 1-cm-diam Pyrex burner. Flame size was determined from a direct photograph, judging by the inside edge of the blue reaction zone, and average burning velocity U_f was calculated by the total area method.[8] The U_f's of uninhibited UDMH/air and 80 UDMH-20 N_2H_4/air are shown in Fig. 13. The peak U_f, ~36 cm/sec, is comparable to those of saturated hydrocarbon/air mixtures. The addition of 20% of N_2H_4 to the UDMH has little effect on U_f other than a shift of pertinent concentrations.

When Halon is added to the fuel/air mixtures, U_f decreases linearly with additive concentration to the point of flame destabilization; this is shown in Fig. 14 for lean and rich 80 UDMH-20 N_2H_4/air/Halon systems. The results of Rosser et al.,[9] who used Halon in lean and rich methane/air, are reproduced on the same scale. The effectiveness of extinguishant may be expressed as the slope, $\Delta U_f/C_x$ (burning velocity reduction in cm/sec divided by additive concentration in percent). Our slopes are smaller than those for CH_4/air flames in Fig. 14 and for NH_3/O_2/air flames as reported by Rosser et al.[9] Halon is several times more effective than N_2, and the effectiveness of either falls off badly with rich mixtures.

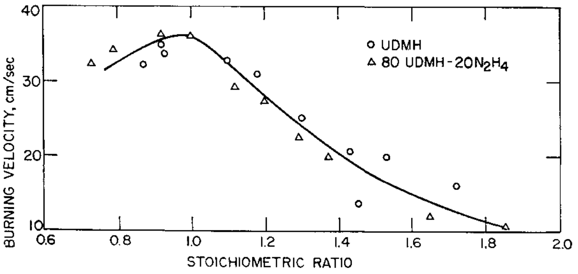

Fig. 13 Laminar burning velocities of two premixed fuel vapor-air systems at 77°F.

To simulate more closely the extinguishment of a pool fire, N_2, CO_2, and Halon were added to a secondary air stream around a rich (8.2%) flame of 80 UDMH-20 N_2H_4/air. It was found that the ambient air can be entirely replaced with N_2 without effect, but 41% of Halon leads to a 5% decrease in U_f; 48%, to a 40% reduction in U_f, and 50%, to blowoff. As shown later, this is close to the amount of Halon required to extinguish an A-50 pool fire.

Inerting of A-50 Pools by Halon 1301

The preliminary tests of "inerting" and extinguishment were carried out in the 2-ft-diam by 4-ft-high chamber (Fig. 15). The desired ambient atmosphere was obtained by a constant throughput of ~6.2 ft³/min of air plus extinguishant, which entered the chamber through the diffuser coil and pebble bed at

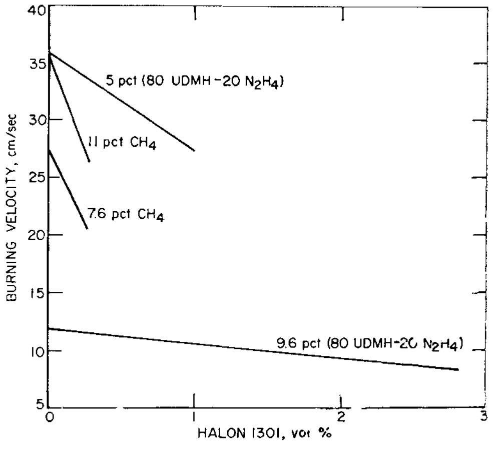

Fig. 14 Reduction of burning velocity by Halon 1301.

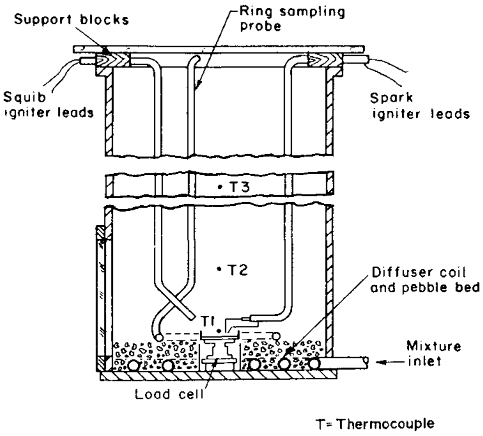

Fig. 15 Vessel used for extinguishing and igniting trials (2-ft diam, 4 ft high).

the bottom. Windows (for photographic coverage), thermocouples (for flame sensing) and a ring probe (for gas sampling) were provided. The liquid sample, initially 50 ml of A-50, was contained in a 4-in.-diam by $\frac{3}{8}$-in.-deep crystallizing dish seated on a load cell for recording of weight loss. Ignition was effected by a spark 0.25 in. above the liquid surface. With no Halon in the atmosphere at room temperature, ignition was effected reliably with each spark. Upon addition of Halon, the vapors above the liquid continued to flash with each spark but pool ignition became erratic; at 6–7% of Halon, the pool failed to ignite even with repeated sparks.

Figure 12 showed that 7% of Halon raises the lower flammability limit of UDMH only from 2.0 to 2.7%. In view of this small change of flammability, the inerting by 6 to 7% of Halon was at first taken to be an artifact of the pool and igniter geometry. Accordingly, the work was expanded as shown in Table 5 to investigate the effects of several system parameters. Series 1 and 2 of Table 5 show that the depth of dish is relatively unimportant, whereas series 3 and 4 show the very minor effect of dish diameter. All data show that the required concentration of Halon is roughly proportional to the p_v of A-50. Series 5 shows essentially the same concentration threshold, 6.3% of Halon at 72°–76°F, when the igniter is a methane/oxygen torch (170 cal/sec) sweeping across the liquid surface. This is included along the base of the triangular flammability diagram of Fig. 16. Note that less Halon is needed here (dashed curve) than for the extinguishment of an established A-50 fire (solid curve). In search of some general explanation, the same experiments were conducted with CO_2; however, the CO_2 concentration required for inerting was 29–33%, which is comparable to the 35% required for fire extinguishment.

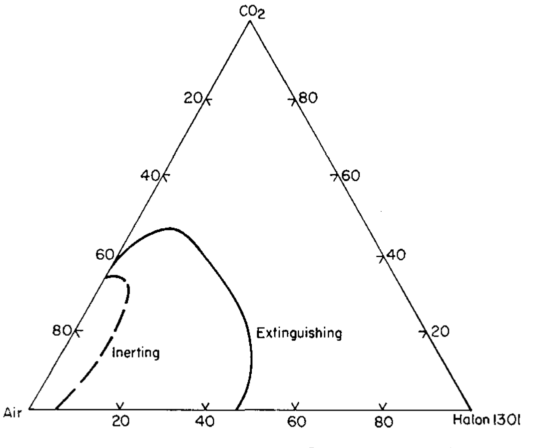

Fig. 16 Inerting and extinguishment requirements of A-50 in air with CO_2 and Halon 1301.

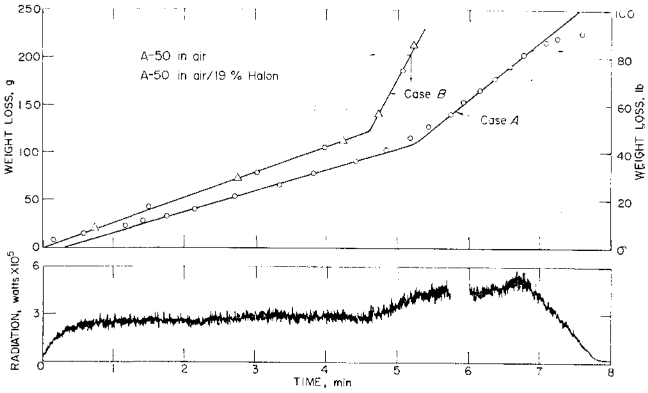

Fig. 17 Case A: burning of 90 lb of A-50 from a 4-ft-diam aluminum tray in air; case B: burning in 6-in-diam glass tray.

Extinguishment of A-50 Pool Fires with Halon 1301

The burning of liquid A-50 is typical of liquid hydrocarbon fuels except for the endothermic nature of the propellants. Figure 17 shows the radiation level (assuming spherical symmetry) and the weight loss vs time of 90 lb of A-50 burning in a 48-in.-diam aluminum tray (case A). There are clearly two stages: the first resembling pool burning of UDMH[10] and during which the first half of the weight loss occurs, followed by the second in which there is faster burning accompanied by vigorous agitation of the liquid. We assume that the explanation of this behavior is provided by Mignotte[2] who reports that a decomposition flame of hydrazine vapor is extinguished by 46 mole % UDMH. Such a UDMH concentration is exceeded in the fuel vapors until the liquid is about half distilled. No effective countermeasure was found for the second stage of burning except for dilution with water. However, the fire can be extinguished during the first stage by large concentrations of CO_2 or Halon.

Burning rates were determined from the slopes of the lines for the two stages as in Fig. 17, for tray diameters (d) from $2\frac{1}{2}$ to 48 in. Figure 18 shows that the initial low rates vary with d in the same way as do the burning rates of pure UDMH.[10] The higher second-stage rates are seen to be lower than the burning rates of pure hydrazine[11] in these shallow pools and seem to reach a limiting value at $d \simeq 2$ ft. The various symbols used in Fig. 18 pertain to experiments with glass, steel, and aluminum trays, among which there were no obvious differences in the initial burning rates.

For burning of a deep pool in a steel tray, the rate of fuel consumption increased continually rather than in the stepwise

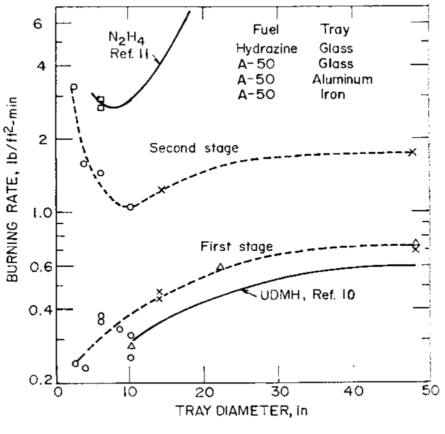

Fig. 18 Burning rates of A-50 as function of tray diameter.

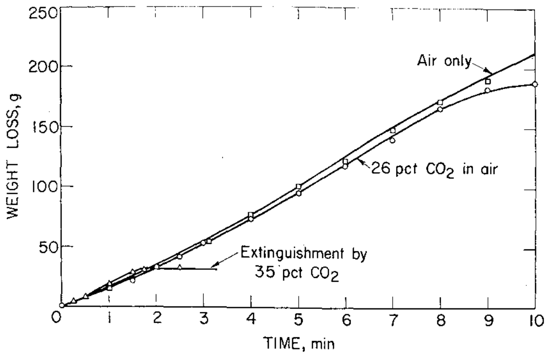

Fig. 19 UDMH burning in air-CO_2 mixtures.

fashion of Fig. 17. Some 114 lb of A-50 were burned in a 22-in.-diam steel tray; V_f increased from 0.6 lb/ft^2-min at the start to about 6 lb/ft^2-min at the end; these numbers are in fair agreement with the UDMH and hydrazine curves of Fig. 18.

The addition of CO_2 to the ambient air has almost no effect on V_f until, at 35% of CO_2, a UDMH or (first stage) A-50 flame abruptly blows off (Fig. 19). The effect of adding Halon is more complicated. At some concentration in the range of 5–15% of Halon, the luminous diffusion flame disappears and the Halon then reacts directly with the hot vapors above the liquid surface, generating a dense white smoke. In the meantime, the weight loss rate is unaffected as shown in Fig. 17, case B, and burning proceeds into the usual second stage. The concentration of Halon required to extinguish completely an A-50 fire is a strong function of tray diameter; thus, 36% of Halon suffices for a 4-in. tray, but 48% was required by a 6-in.-diam pool. Since even 36% is an impracticable quantity of extinguishant, the work was not pursued with larger pool diameters or depths.

In experiments similar to those on the extinguishment of A-50, conventional liquid fuels were ignited in 6-in.-diam trays, allowed a minute of burning, and then extinguished with Halon. The required concentrations of Halon were 5% to extinguish burning hexane and 9% to extinguish methanol. The similarity of these numbers to the 6.3% required to inert an A-50 pool and to the 5–15% required to extinguish the visible flame of A-50 leads us to the following speculation: In both early and later stages of A-50 burning there is a decomposition flame close to the liquid surface with CH_4, H_2, and NH_3 as major products followed by an air-supported diffusion flame that burns these products to CO_2, H_2O, and N_2; and the decomposition flame (at least in the early stages) is only initiated by the diffusion flame. Therefore, the inerting of an A-50 pool is comparable to the inerting of other liquid fuels; but once ignited, the A-50 fire is nearly independent of its ambient atmosphere and becomes more self-sufficient as the fuel becomes richer in N_2H_4.

Table 6 Analyses of smokes from initial and final stages of burning of A-50 pool fires in contact with various percentages of Halon 1301

Burning stage	1	1	1	1	2
Halon 1301, %	14.9	25.4	25.4	33.8	14.9
Fuel composition, wt %:					
Carbon	0.21	0.05	0.06	0.17	0.10
Hydrogen	3.93	3.94	4.06	(5.08)	3.86
Nitrogen	14.0	14.0	14.0	14.0	14.0
Fluorine	0.29	0.22	0.31	0.40	1.78
Bromine	73.2	73.5	67.7	72.2	66.0
Fuel consumption, mg/sec	44	51	...	50	...
NH_4Br production, mg/sec	3.5	6.4	...	7.2	...

Product Analysis‡‡‡

Several small (3-cm-diam) dishfuls of A-50 were allowed to burn within a glass chamber so as to permit total collection of products. The smokes generated in Halon/air atmospheres were caught on glass cloth filters and submitted to analysis for C, H, N, F, and Br (Table 6). The numbers have been normalized to 14.01 for nitrogen so as to show at a glance the degree to which the smoke is represented by its major constituent, NH_4Br. The first four columns of data refer to the early stages of A-50 burning in which the major fuel constituent was UDMH. The average empirical formula of product is $NH_{3.98}Br_{0.90}C_{0.01}F_{0.02}$. X-ray diffraction showed the samples to be impure ammonium bromide which became quite pure NH_4Br on a single recrystallization from ethyl alcohol. The final column represents a late stage of burning in which the fuel would have been primarily N_2H_4. A substantial amount of fluoride appears in the smoke analysis.

The table also includes the production rates of smoke in several experiments. Smoke outputs were roughly proportional to Halon concentration. About 3 to 6% of the nitrogen from the burned fuel and about the same proportion of bromine from the Halon appear in the NH_4Br. No appreciable smoke was found in premixed vapor/air/Halon flames or in pool burnings wherein the luminous reaction zone had not been eliminated. High densities of smoke appeared during attempted spark ignitions of A-50 pools inerted by Halon.

The gaseous products of the small pool fires were submitted to gas chromatography in which, unfortunately, no peak representing a fluorine compound could be identified. Table 7 shows identifiable gaseous products. In the absence of Halon (col. 2) the only gases are air, H_2O, CO_2, and excess N_2. In the Halon experiments, H_2 and hydrocarbons appear in the UDMH stage of burning (col. 3), whereas NH_3 and additional H_2 appear in the N_2H_4 burning stage (col. 6). Note particularly that the same products appear at 0.6 cm (cols. 4 and 5) from the liquid surface as 15 cm downstream. Now consider that V_f from Fig. 17, case B, is completely independent of the presence of 19% of Halon. Thus, it appears that the V_f in *each* stage of burning is independent of the diffusional flame that converts intermediate products to CO_2 and H_2O. In the N_2H_4 stage (cols. 5 and 6), such intermediate products as NH_3 and H_2 are sufficiently exothermic relative to N_2H_4 to maintain a decomposition flame, but in the UDMH stage (cols. 3 and 4), much of the exothermicity depends on a small amount of H_2O that is formed near the liquid surface. Presumably this is the burning that can be inhibited by a large concentration of Halon.

Table 7 Gaseous products above 3-cm-diam A-50 pool

Burning stage	1	2	1	1	2
Halon 1301, %	0	25	25	25	15
Height above liquid, cm	15	15	0.6	0.6	15
Gaseous products					
H_2	0.1	3.5	8.8	18.8	12.4
O_2	17.5	16.7	13.4	3.7	8.5
N_2	80.1	66.2	61.1	41.9	48.3
CH_4	...	4.1	5.2	8.5	0.2
CO	...	0.2	0.4	0.3	...
CO_2	1.8	0.1	0.1	0.0	...
C_2H_4	...	0.2	0.3	0.3	...
C_2H_6	...	0.3	0.3	0.4	...
H_2O	0.5	1.2	1.4	0.4	0.3
HN_3	...	...	0.8	17.6	27.0
Halon 1301	...	6.9	7.7	6.1	2.3
Unidentified	...	0.6	0,4	2.0	0.9

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‡‡‡ The authors are indebted to T. Christos, Chemist, Safety Research Center, for analysis of collected products.

Table 8 Flame spread rates of several materials ignited in Halon 1301/air mixtures at 1 atm (24-in.-diam sphere)

Material	Burning angle	Igniter[a]	Halon 1301, vol %	Flame spread rate, in./sec
Velostat #1701 (0.008 in. thick)	45°	A	11.1	NP[b]
			4.9	NP
			3.3	NP
			2.3	NP
			1.1	0.3
			0.0	0.6
	Vertical	A	2.1	NP
		B	2.2	<6″ propagation
Polyurethane foam (⅛-in. sheet)	45°	A	4.0	NP
			1.9	NP
			1.4	NP
			1.0	NP
			0.0	0.3
			0.0	0.5
	Vertical	B	2.0	NP
Cotton sheeting	45°	A	2.2	NP
	Vertical	B	2.2	1.0[c]
Kimwipe	Vertical	A	1.9	NP
Sanidrape	Vertical	A	2.0	NP
		B	2.0	<6″ propagation
			2.3	do

[a] A, glowing Nichrome coil with ⅛-in. hardwood core; B, glowing Nichrome coil + four safety match heads.
[b] NP, flame did not propagate more than 1 in. beyond igniter coil.
[c] Material consumption not beyond 6 in.

Extinguishment of Secondary Fires

If the A-50 spill is small, the chief hazard may be the ignition by a small A-50 fire of other combustibles in the vicinity; Halon may provide important protection against such a secondary fire. Flame spread determinations (Table 8) were conducted in various Halon/air atmospheres within a 2-ft-diam sphere using five materials: Velostat No. 1701 (0.008 in. thick; a carbon-filled polyethylene sheet), polyurethane foam (⅛-in. sheet), cotton sheeting, kimwipe paper, and Sanidrape paper sheeting. The material was mounted on a rack so as to burn with upward propagation in either a vertical position or inclined at a 45° angle. The Halon/air atmospheres were prepared by the partial pressure method with subsequent mixing by a fan. Two types of igniter were used: igniter A comprised an electrically heated Nichrome coil enclosing a hardwood core, and igniter B comprised four safety match heads in contact with the Nichrome coil and with the combustible material. The match heads gave a more positive source of ignition, as the Halon often suppressed the flame from the burning wood. Even though the match head ignition in the vertical position is the most drastic test, none of the materials could be made to burn completely in an air atmosphere containing 2.2% of Halon.

Samples comprising five layers of 0.3-mil aluminized Mylar were ignited in air and in a 2.2% Halon/air mixture. They were mounted at both a 45° angle and in a vertical position, with upward propagation. Because of the difficulty in obtaining sustained combustion of this thin material, a slow-burning propellant was used with the Nichrome coil to effect ignition; 2 g of an aluminum-ammonium perchlorate base propellant was used. With this means of ignition, a flame could be sustained for 2 to 3 sec. The flame spread rate in air was 1.6 in./sec when ignited at a 45° angle and 3.3 in./sec with vertical burning. When an atmosphere containing 2.2% Halon was used, the flame did not propagate 3 in. beyond the igniter source. Also, a crumpled 2-in.-diam × 6-in.-long mass of Mylar was mounted vertically and ignited by the slow-burning propellant in a 2.2% Halon/air atmosphere. Again, less than 3 in. of burning resulted.

Table 9 summarizes the results of the various inerting and extinguishment tests with Halon.

Table 9 Summary of Halon 1301 requirements

Function	% Halon 1301 needed
Extinguish A-50 pool fire	~48[a]
Inert richest possible vapor-air mixture at 72°F	40–50
Inert stoichiometric vapor-air	~20
Insert A-50 pool (4–14 in. diam):	
At 85°F	9.3–11.8
At 72°F	~7
At 57°F	5.5–7.5
Destabilize at premixed (Bunsen) flame	~3
Extinguish secondary fires:	
Methyl alcohol	9
Hexane	5
Fabrics and mylar	2

[a] First stage; probably impossible to extinguish second stage.

Summary and Conclusions

A mixture of 2 parts by weight of water per part of A-50 is not flammable at its boiling point. Therefore, A-50 leaks and spills can be rendered nonflammable with twice their weight of water even though their heat of dilution is conserved; established fires on A-50 pools can be extinguished by such water applications.

Several mitigating circumstances can reduce the required quantity of water. In the case of an evaporating spill, the vapor pressure drops rapidly after the first 30–40% (by weight) of the fuel has evaporated. Very little water is then required to render the residual high-boiling fraction inert. In the case of a fire, one can ignore the liquid phase and render the vapors nonflammable by addition of about 1.2 lb/ft^2-min of a fine water spray. One can also slow down the burning of A-50 with water to achieve extinguishment by modest concentrations of Halon.

In the special case of simultaneous spills of A-50 and N_2O_4, as much as 10 parts by weight of water are needed to prevent the violent hypergolic reaction.

A practicable concentration of Halon 1301 (e.g., 10%) can provide a large measure of protection against A-50/air fires. Such a concentration will "inert" a small spill of A-50 against ordinary ignition sources and will also prevent flame propagation in the lean vapor/air mixtures which might be found at any appreciable distance from a small leak.

Ten percent of Halon 1301 will not extinguish an established A-50 pool fire or a flame propagating through a rich vapor/air mixture such as might occur in unventilated compartment. However, it will extinguish secondary fires ignited by such events.

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Refined Measurements of Exhaust-Plume-Induced Radar Amplitude and Phase Noise

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A new facility for measuring plume-induced radar attenuation and noise is described. Three solid-propellant motor firings were conducted and measurements of *X*- band attenuation and *X*-band AM and PM noise are reported. Influences of sideband frequency and plume position on noise levels are shown. Peak attenuation level for this highly aluminized propellant was approximately 12–15 db. Maximum noise levels, like attenuation, occurred in the afterburning regions of the plume and showed a strong dependence on plume position. Near the nozzle exit plane, the amplitude noise in a 500-Hz bandwidth, 1 kHz from the CW, *X*-band carrier was about 37 dbc. At aft regions of the plume, the attenuation and amplitude noise levels increased about 3 and 10 db, respectively. Phase noise levels were comparable to the amplitude noise levels. Results of this test series were compared with data reported previously for nearly identical propellant/motor systems. Attenuation and AM noise measurements agreed well with earlier tests, but PM noise measurements were higher than those previously reported. These new data are considered more accurate because of the careful attention given to facility calibration and to elimination of acoustically induced noise.

Introduction

In a previous publication, Smoot and Seliga[1] reported amplitude- (AM) and phase-modulated (PM) noise levels that were induced on an *X*-band radar signal that traversed a rocket exhaust plume. These data were the first measurements of this type that were known to have been published in the open literature. Reported levels of AM noise were substantially higher than those for PM noise. However, PM noise levels showed wide excursions during each test firing. The authors noted: "It is doubtful that the PM levels shown were significant, except for the 18% aluminized propellant."

This paper describes a new facility for measuring plume-induced radar attenuation and noise. Three motor firings have been conducted using one of the propellant formulations, the same hardware, and essentially the same conditions as the previous tests. These newer attenuation and AM noise measurements agree well with earlier measurements, but PM noise data are substantially different.

Experimental Program Plan

Microphonic interference caused by the severe acoustic environment on the modified *X*-band circuitry was investigated during the first firing. In the second and third firings, exhaust plume induced *X*-band attenuation and *X*-band AM

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