# FIRE SUPPRESSION EFFICIENCY OF BROMOALKENE/NITROGEN GAS MIXTURES AS TOTAGFLOODING AGENTS

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## ABSTRACT

The fire suppression efficiencies of I-bromo-I-propene / nitrogen and 2-bromo-3,3,3 trifluoro-1-propene / nitrogen gas mixtures as total-flooding agents were studied by a cup-burner method. It was shown that addition of small amounts of I-bromo-I-propene and 2-bromo-3,3,3 trifluoro-I-propene to nitrogen can improve the suppression effectiveness of the inert gas by 34 and 64% respectively. An arrangement for mixing organic compounds with inert gases before application to fire was proposed.

## INTRODUCTION

The international ban on the production of ozone-depleting halons has forced scientists to search for environmentally benign fire suppressants. A wide variety of chemical groups have been considered for possible use as halon replacements during the last decade. Metal compounds, sulfur compounds, bromoalkenes, and bromoethers are among the new classes of compounds that have been identified as having high fire suppression efficiency and low environmental impact [1-4]. Halon 1301 is a highly effective total-flooding agent because of its ability to inhibit flames at low concentrations. It is a nonconductive and clean agent with low boiling point and low toxicity. Most of the new compounds considered as halon replacements have high boiling points and are liquid at room temperature, and therefore cannot be used as total-flooding agents. However, mixtures of these compounds in an inert gas such as nitrogen can produce a gaseous agent suitable as Halon 1301 replacement. The purpose of this project was to investigate the effectiveness of mixtures of bromoalkenes/nitrogen as total-flooding fire suppressants.

Inert gases extinguish fire by reducing the oxygen concentration to between 10 to **14%.** They are nontoxic, electrically nonconductive and clean fire suppressants. The main problem of inert gases is that they are not very effective. Large volumes of these agents are needed to extinguish a fire. Storage volumes required for inert gases are 11 to 13 times larger than for Halon 1301. Addition of an effective fire suppressant to inert gases can increase their extinguishing concentrations and thus reduce storage volume requirements. The maximum concentration of a vapor (such as bromoalkenes) in a gas depends on its vapor pressure and the total pressure. The partial pressure of a vapor in a mixture is given by:

$$p_V = P\,y_V \tag{1}$$

Where $p_V$ is partial pressure of vapor, $y_V$ is mole fraction of vapor, and P is the total pressure. As long as the partial pressure of vapor in the mixture is less than its vapor pressure (at the system temperature), it will not condense, and the mixture can be used as a clean fire suppressant. Inert gases are usually stored at pressures over 2000 psia. At such high pressures, maximum concentration of vapor in the gas is very small. Therefore, the organic compound should be stored in the liquid form in the gas cylinder or in a separate container. It should be vaporized and mixed with the inert gas before it is applied to the fire.

## EXPERIMENTAL SECTION

**Materials and Reagents.** In this study, two bromoalkenes, namely 2-bromo-3,3,3 trifluoropropene and 1-bromo-I-propene from Lancaster Synthesis, Ltd., were studied. Representative characteristics of the two bromoalkenes are reported in Table 1. n-Heptane (HPLC Grade) was from Fisher Scientific, Inc. The air and nitrogen were all from Air Products and Chemicals, Inc.

TABLE 1. CHEMICAL AND PHYSICAL PROPERTIES OF TWO BROMOALKENES.

| Property | I-Bromo-I-Propene | 2-Bromo-3,3,3-trifluoro-1-propene |
|---|---|---|
| CAS Number | 590-14-7 | 1514-82-5 |
| Purity | 98% | 97% |
| Molecular Formula | $CH_3$-CH=CHBr | $CH_2$=CBr$CF_3$ |
| Molecular Weight | 120.98 | 174.95 |
| Appearance | Colorless to yellow liquid | Colorless liquid |
| Boiling Point | 58-62 °C | 33-33.5 °C |
| Density | 1.415 g/ml | 1.79 g/ml |
| Solubility in Water | Immiscible | Immiscible |

## APPARATUS AND PROCEDURE

**Apparatus.** A schematic diagram of the experimental apparatus for measuring the extinguishing concentration is shown in Figure 1. It has four major parts: a cup burner (I); a liquid fuel feeder with a fuel level control device (K& M); a Tedlar Bag provided chemical/ inert (such as bromoalkenes/nitrogen) gaseous mixtures (E); and the gaseous mixture-air mixture supply unit (A & G). The burner (made of quartz) is constructed based on the specifications given in ISO 14520 (determination of the flame extinguishing concentration of gaseous extinguishants by the cup-burner method). The dimensions of the burner are 30 mm OD of the cup and 85 mm ID ofthe chimney.

**Procedure.** Experiments for measuring **of** the extinguishing concentrations were carried out **as** follows:

(1) A small amount of organic compound (1-5 **ml)** was injected into the Tedlar Bag.

(2) A specific volume of nitrogen (3-8 liter) was also introduced into the Tedlar Bag immediately, then the Tedlar Bag was closed and kept in the pressure vessel (F) until the liquid chemical was completely vaporized (8-12 hrs).

(3) Vessel (F) was closed and connected to a compressed nitrogen gas cylinder to keep its pressure constant at 11 psig.

(4) n-heptane was introduced into the cup burner and the fuel level in the cup is adjusted to within 5-10 **mm** of the top of the cup.

(5) The air with a flow rate of 10 L/min by mass-flow controlled (A) is passed through the burner. The fuel is then ignited and allowed to burn for a period of at least 2 min.

(6) The flow of the flooding agent is then started at a constant pressure (–11 psig). The flow rate by the Digital flow meter controlled is increased in increments until flame is extinguished.

(7) A waiting period of about 30 sec is allowed between each successive increase in the flowrate of the agent so that the new proportion of air and agent in the manifold reaches the cup position. The flowrate of the flooding agent at extinction is found from the Digital flow meter. Each experimental result was repeated three times to verify data reproducibility.

## RESULTS AND DISCUSSIONS

The concentration of suppressant in volume percent was calculated as follows:

$$C = \frac{V_{sup}}{V_{air} + V_{sup}} \times 100\% \qquad (2)$$

Where C =extinguishing concentration in %v/v

$V_{air}$ = volumetric flow rate of air, L/min
$V_{sup}$ =volumetric flow rate of suppressant, L/min.

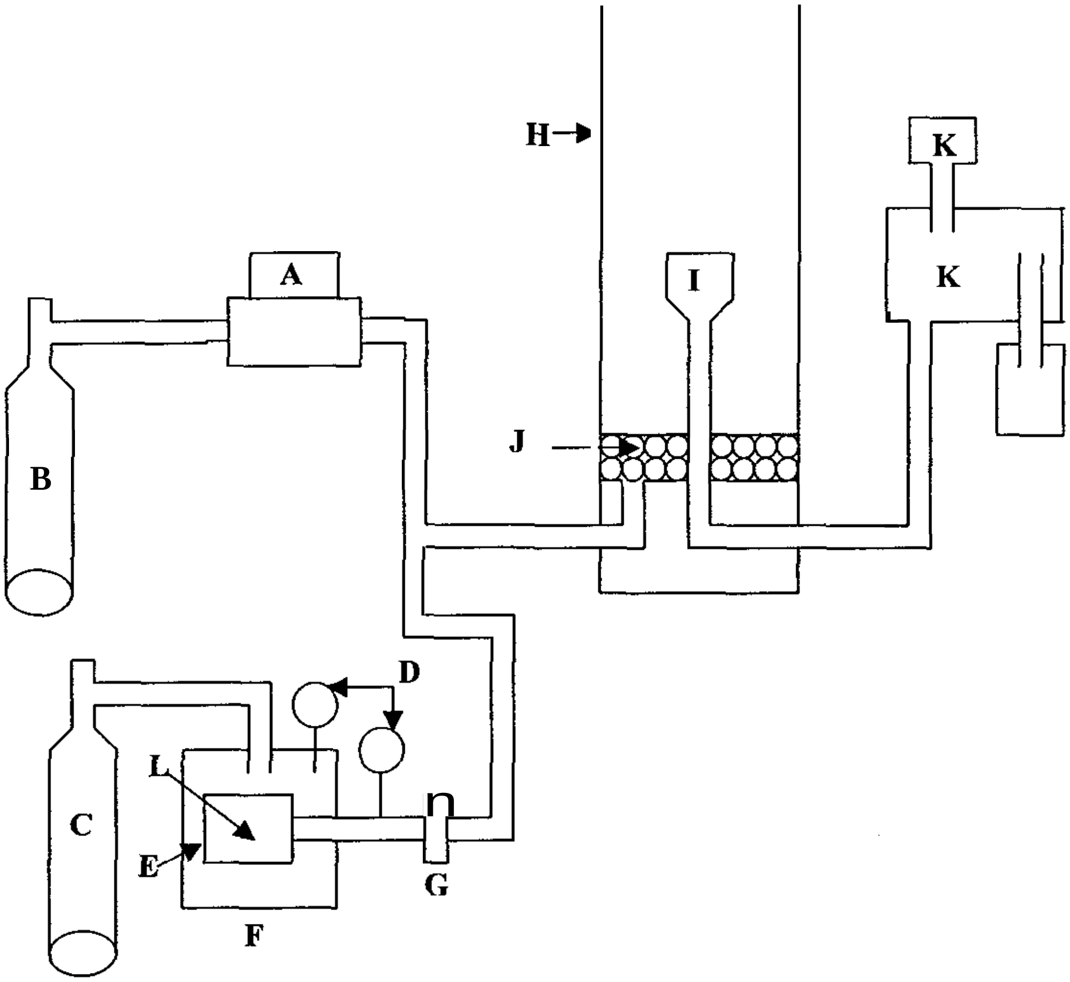

Figure 1. Schematic diagram of the experimental apparatus for measuring extinguishing concentration of bromoalkene/nitrogen. A: Mass flow controller; B: Air; C: Nitrogen; D: Pressure meters; E: Tedlar bag; F: Container (steel bottle); G: Digital flow meter; H: Chimney; I: Cup burner; J: Glass beads; K Fuel (*n*-Heptane); L Bromoalkene/nitrogen mixed gas.

The extinguishing concentrations of the pure agents are given in Table 2. The suppressant effectiveness of the two bromoalkenes is very close to that of Halon **1301.** However, the main difference between these compounds and Halon **1301** is their boiling points. The bromoalkenes are liquid at room temperature and cannot be used as a total-flooding agent. The results of cup-burner experiments for the mixtures of the two alkenes in nitrogen are given in Figures 2 and 3. The extinguishing concentration for both bromoalkene / nitrogen mixtures decreased with increasing concentration of organic compound. Mixtures of two agents with different extinguishing concentrations might be expected to exhibit extinguishment performances that change linearly with composition. An extinguishment concentration of a mixture that is lower than predicted from a linear dependence is an example of synergism. The mixtures of both bromoalkenes with nitrogen show synergism.

As it can be seen from Figure 2, addition of small quantities of I-bromo-I-propene to nitrogen improves its extinguishing capabilities considerably. A 4.5% (volume) mixture of the bromoalkene in nitrogen has an extinguishing concentration **of 22%,** compared to **33.6%** for pure nitrogen, for a reduction of 34%. Further addition of the organic compound will improve the fire suppressant effectiveness of nitrogen only slightly; e.g., a 15.9% I-bromo-I-propene mixture has an extinguishing concentration of about **18%.**

TABLE 2. THE EXTINGUISHING CONCENTRATION OF PURE COMPOUNDS.

| Compound | Extinguishing Conc.Vol.% |
|---|---|
| $N_2$ | 33.6 |
| $CH_3$-CH=CHBr | 3.0[*] |
| $CH_2$=CBr$CF_3$ | 3.5[*] |
| $CF_3$Br | 3.8 |

[*] From Nyden *et al.* [4] after accounting for differences in the dispersion of **a** liquid and a gas.

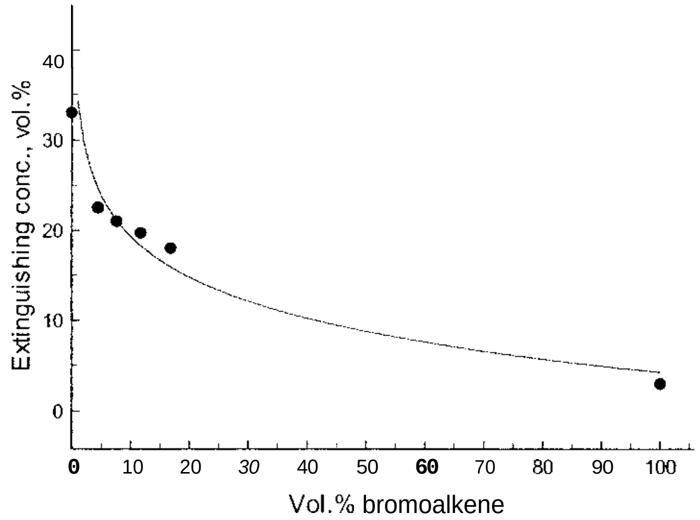

Figure 2. Extinguishing concentrations of I-bromo- I-propene / nitrogen mixtures,

The extinguishing concentrations of 2-bromo-3,3,3-trifluoro-1-propene / nitrogen mixtures are shown in Figure 3. The suppressant effectiveness of the mixture improves steadily as the concentration of bromoalkene is increased. For a 32% mixture of organic compound in nitrogen, the extinguishing concentration is about 12%, for a 64% improvement in the effectiveness of nitrogen.

Inert gases are usually stored in cylinders at pressures over 2000 psia. Due to condensation, high concentrations of organic compound vapors in inert gases cannot be stored at elevated pressures. The organic compound, therefore, should be stored in liquid form, converted to vapor, and mixed with the inert gas when needed. Two arrangements are possible: (I) the organic compound is stored as liquid in the inert gas cylinder at high pressure; and (2) the liquid is stored in a separate container. In the former, the organic compound (such as bromoalkenes) is stored at high pressure in the gas cylinder. During application, as the gas is released, pressure in the cylinder drops and the liquid vaporizes, thus providing a continuous flow of the gaseous mixture. Due to the high pressure in the cylinder, however, the concentration of the vapor **will** not reach high values until a good portion of the gas has been released, which means that the fire will be essentially extinguished with the inert gas initially. Another problem with this arrangement is that there may not be enough time for the liquid to vaporize. The latter is a better arrangement, i.e., to store the liquid in a separate container. During application, the liquid is sprayed into the inert gas as it leaves the high-pressure cylinder. The gas carries the droplets to the fire. If the droplets are vaporized before the stream reaches the fire, a clean agent with suppressant effectiveness **far** better than the inert gas has been produced. The time required to vaporize the liquid droplets completely is calculated from the following theoretical method.

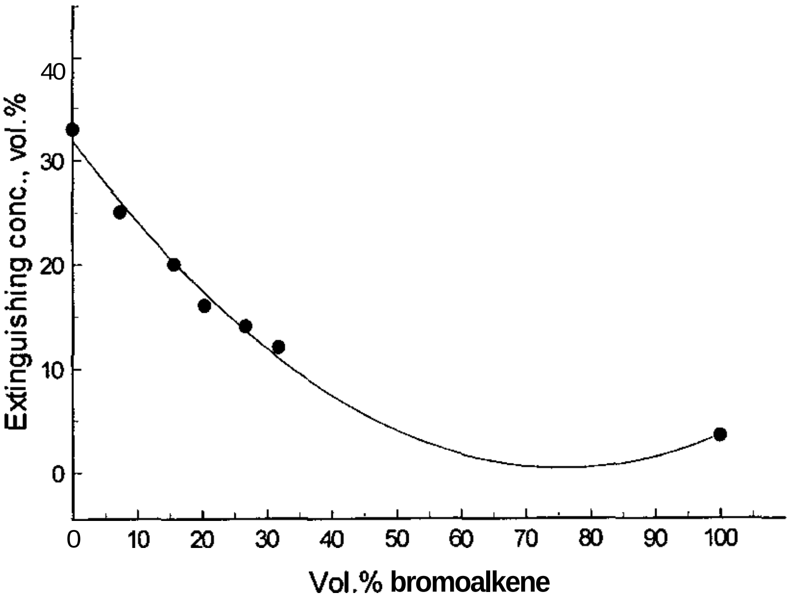

Figure **3.** Extinguishing concentrations of **2-bromo-3,3,3-trifluoro-1-propene** / nitrogen mixtures.

The rate of decrease in particle size during evaporation is given by [5]

$$\frac{d(d_p)}{dt} = \frac{4\,D\,M}{R\,\rho_p\,d_p}\left(\frac{p_v}{T} - \frac{p^*}{T^0}\right)\left[\frac{2\,\lambda + d_p}{d,, + 5.33\left(\frac{\lambda^2}{d_p}\right) + 3.42\,\lambda}\right] \tag{3}$$

Where:

M = Molecular weight, g/gmole
R = Gasconstant
$\rho_p$ = Particle density
$d_p$ = Particle diameter
D = Diffusion coefficient
$P_v$ = Partial pressure of vapor in the gas

P* = Vapor pressure *of* liquid
λ = Mean free path
T = Temperature of gas
$T^0$ = Temperature of droplets
T = Time

For droplets larger than **2 μm,** the last bracket in Eq. **(3)** can be neglected.

$$\frac{d(d_p)}{dt} = \frac{4\,D\,M}{R\,\rho_p\,d_p}\left(\frac{p_v}{T} - \frac{p^*}{T^0}\right) \tag{4}$$

Integration of Eq. (4) from the initial size of the droplet to zero, gives droplet lifetimes:

$$t = \frac{R\,\rho_p\,d_p^2}{8\,D\,M\left(\frac{p^*}{T^0} - \frac{p_v}{T}\right)} \tag{5}$$

If the temperature of the gas (T) is assumed to be equal to the temperature of the droplets, Eq. *(5)* is reduced **to:**

$$t = \frac{R\,T\,\rho_p\,d_p^2}{8\,D\,M\left(p^* - p_v\right)} \tag{6}$$

The partial pressure of the vapor in the gas can be written in terms of the relative humidity $(a)$:

$$\alpha = \frac{p_v}{p^*} \tag{7}$$

Substitution of Eq. (7) into **(6)** yields:

$$t = \frac{R\,T\,\rho_p\,d_p^2}{8\,D\,M\,p^*\,(1 - a)} \tag{8}$$

To use Eq. (8) to calculate drying time for droplets of the organic compounds, vapor pressure ($p^*$) and diffusion coefficient of organic vapor in the inert gas (D) are needed. These properties are not available for the two bromoalkenes studied here. They can be estimated from correlations available in the literature. Myrdal et al. **[6]** developed an equation for the vapor pressure of complex organic molecules. This equation, which requires only the knowledge of boiling point and molecular structure, has been shown to be fairly accurate for a wide variety of compounds and over a wide range of temperatures. The results of calculations for 1-bromo-1-propene and 2-bromo-3,3,3 trifluoro-1-propene are given in Table 3. The diffusion coefficient of a binary mixture can be estimated from the Wilke–Lee modification [7] of the Hirschfelder–Bird–Spotz method [8]. This correlation requires the knowledge of the boiling point and density of liquid. The results of calculations for diffusion coefficient of the two bromoalkenes in nitrogen at 25 °C are given in Table 4.

TABLE 3. RELATIONS FOR VAPOR PRESSURE OF BROMOALKENES

| Compound | Vapor Pressure Equation (T is in °K, P* is in atm) |
|---|---|
| $CH_3\text{-}CH{=}CHBr$ | $\log P^* = 36.27 - \frac{3051}{T} - 4.667 \ln T$ |
| $CH_2{=}CBrCF_3$ | $\log P^* = 35.88 - \frac{2804}{T} - 4.667 \ln T$ |

TABLE 4. DIFFUSION COEFFICIENT OF BROMOALKENES IN NITROGEN AT 25 °C.

| Compound | Diffusion Coefficient, $m^2/s$ |
|---|---|
| $CH_3\text{-}CH{=}CHBr$ | $9.704 \times 10^{-6}$ |
| $CH_2{=}CBrCF_3$ | $8.99 \times 10^{-6}$ |

Eq. (8) gives the time needed to vaporize completely a droplet of size $d_p$ in terms of temperature and the amount of vapor in the gas (relative humidity). The results of calculations for drying times of droplets of 1-bromo-1-propene and 2-bromo-3,3,3-trifluoro-1-propene in nitrogen at 25 °C are given in Figures 4 and 5, respectively. The drying time for 1-bromo-1-propene is about three times larger than for 2-bromo-3,3,3-trifluoro-1-propene, because 1-bromo-1-propene has a lower vapor pressure. It takes about $5\times10^{-3}$ sec for a 10 µm droplet of 1-bromo-1-propene (at 80% relative humidity) to vaporize completely. For a 100 µm droplet, drying time is about 0.8 sec. The results clearly show that the drying time is very short and **all** the droplets of the organic compound will be vaporized before the mixture reaches a fire.

## CONCLUSIONS

The fire extinguishing concentrations of 1-bromo-1-propene / nitrogen and 2-bromo-3,3,3 trifluoro-1-propene / nitrogen gas mixtures at various concentrations of 1-bromo-1-propene and 2-bromo-3,3,3 trifluoro-1-propene were determined by a cup-burner method. The extinguishing concentration for both

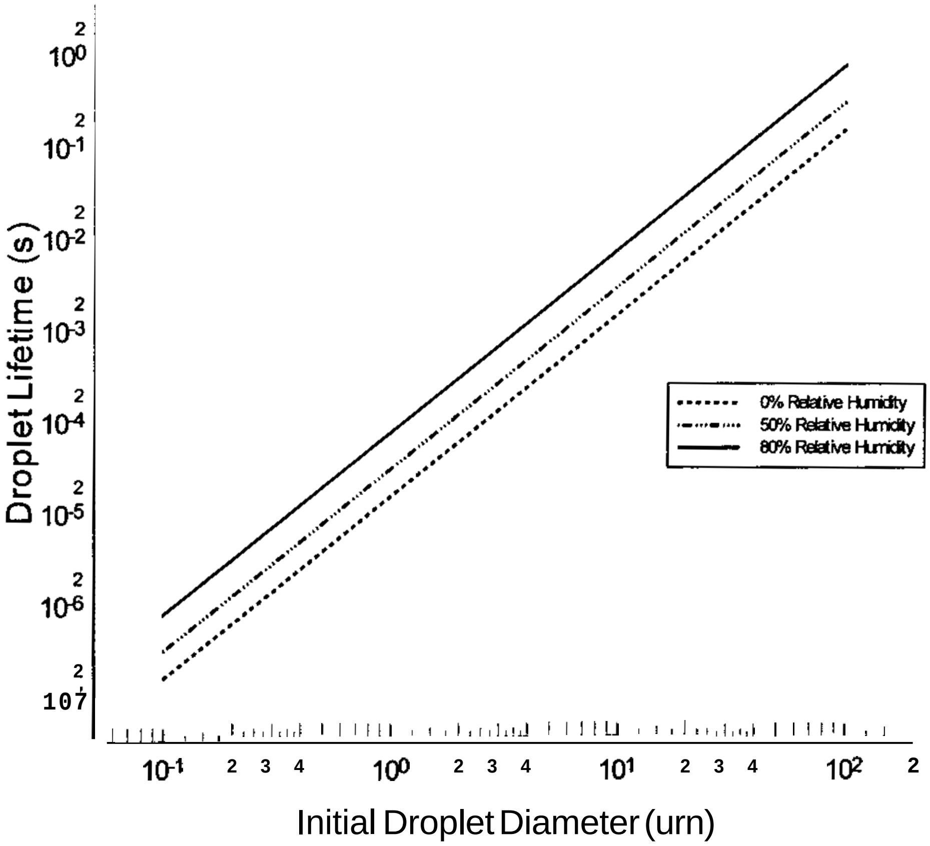

**Figure 4. Drying time** for **1-bromo-I-propene droplets at 25 "C.**

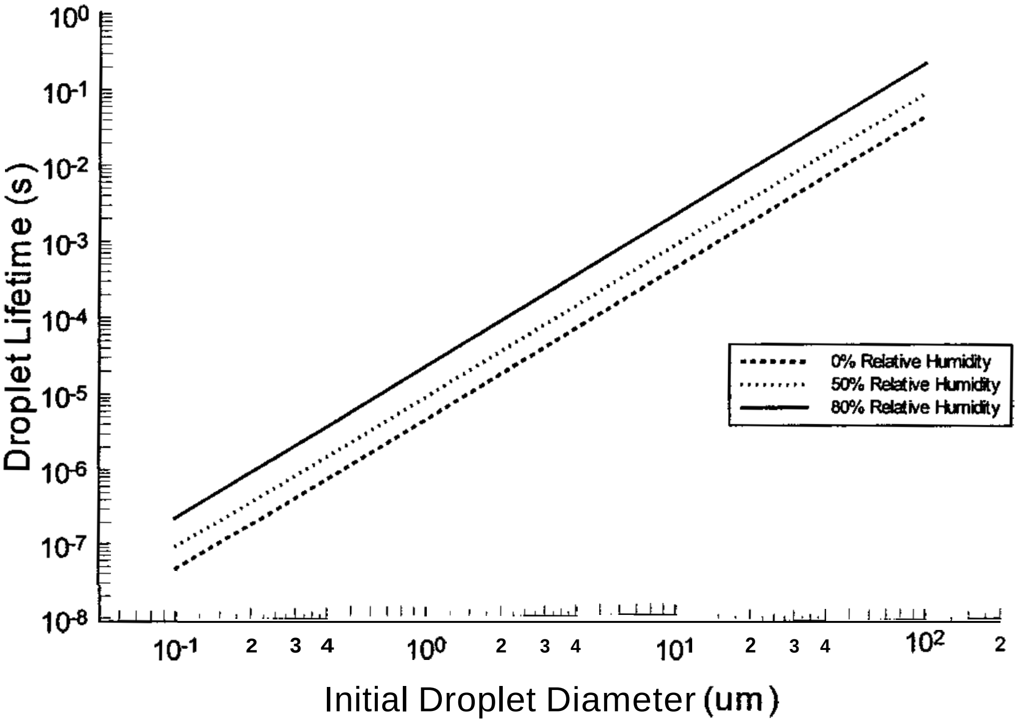

**Figure 5. Drying time for** 2-bromo-3,3,3 **trifluoro-I-propene droplets at 25 "C.**

bromoalkene /nitrogen mixtures decreased with increasing concentration of the organic compound. The mixtures of both bromoalkenes with nitrogen showed synergism.

A mechanism for mixing organic compounds with inert gases before application to fire was proposed. In this arrangement, the organic compound is stored in a separate container and is sprayed into the inert gas as it leaves the high-pressure cylinder. Theoretical study showed that droplets of the two bromoalkenes with diameters as large as 100 µm will be vaporized in less than a second, and a completely dry gas will be produced.

## ACKNOWLEDGMENTS

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