

# SCREENING OF CANDIDATE FIRE SUPPRESSANTS

by

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## ABSTRACT

Exploratory research has indicated that the following chemical families are likely to contain chemicals possessing both a high degree of fire suppression efficiency and low environmental impact: the bromoalkenes, bromoethers, and phosphorus-containing compounds, including the alkyl phosphates, phosphites, and phosphonates. Candidate suppressants were selected from these chemical families on the basis of their volatility and existing toxicity data. The relative performance of these compounds as fire suppressants was assessed by comparison of the results obtained from the NIST Dispersed Liquid Agent Fire Suppression Screen Apparatus.

## INTRODUCTION

The search for alternatives to halon fire extinguishants, has to date not produced any candidates that meet all the criteria for next generation fire suppressants. Exploratory research has, however, indicated that the following chemical families are likely to contain chemicals possessing both a high degree of fire suppression efficiency and low environmental impact: the bromoalkenes, bromoethers, and phosphorus-containing compounds, including the alkyl phosphates, phosphites, and phosphonates [1-3]. The purpose of our investigation is, therefore, to screen promising candidates from these chemical families for critical properties with the expectation that these results will point to a more optimal solution for fire suppression in the highly space- and weight-constrained environments of current weapons systems. The screening methods implemented in this study were advanced in a recent report [4] sponsored by the Next Generation Fire Suppression Technology Program (NGP).

Candidate suppressants were selected from the aforementioned chemical families on the basis of existing toxicity data [1] and the results from quantitative structure activity relationships (QSAR) for compound volatility [5]. Their relative performance as fire suppressants was assessed by comparing results obtained on the Dispersed Liquid Agent Fire Suppression Screen (DLAFSS) apparatus [6] with cup-burner extinction values reported in previous investigations [1]. Depending on whether the major concern was determined to be atmospheric lifetime or ground water pollution, assessments of the environmental impact of these candidates were made either on the basis of their reactivity with OH radical or QSARs for aquatic toxicity based on octanol-water partition coefficients, respectively.

## COMPUTATIONAL AND EXPERIMENTAL PROCEDURES

The fire suppression effectiveness of dimethyl methylphosphonate (DMMP) and some liquid bromoalkenes was examined using the NIST Dispersed Liquid Agent Fire Suppression Screen Apparatus. A detailed description of the apparatus and the experimental procedure were reported by Yang et al. [6]. Briefly described, the apparatus consists of a small vertical wind tunnel, a porous cylindrical burner located at the test section, and a small nebulizer located in the settling chamber of the tunnel (Figure 1). The nebulizer is used to generate a small spray of liquid droplets. The experiments were conducted by increasing the air flow through the tunnel with a fixed liquid delivery rate to the nebulizer. The droplets are entrained by the air flow and transported to the test section. The velocity at which the flame at the forward stagnation region of the burner is

blown-off was used as an indicator for comparing the fire suppression efficiencies of various candidate suppressants.

If the droplets are not uniformly dispersed, the calculated agent mass fraction will be underestimated. Depending on the effective coverage area, a difference of a factor of between 2 and 3 in the calculated liquid mass fraction can result. This effect was examined by placing a filter paper over the exit of the test section while atomizing water containing a dye [6]. The circular pattern on the filter paper indicated that mist from the nebulizer completely covers the burner and its vicinity. This coverage area is estimated to be approximately 40% of the total cross-sectional area of the test section and is assumed to be independent of the agent being screened.

Since the delivery rate of the agent affects the velocity of the air flow at blow-off, and since this delivery rate is adjusted to compensate for many factors, a reference is needed to compare and interpret the data in a consistent and meaningful way. In response to this, Yang et al. developed a test protocol based on the observed cup-burner extinction value for nitrogen gas [6]. This involves a linear extrapolation of the blow-off velocities, obtained at various application rates, to a reference velocity corresponding to the velocity at blow-off for N<sub>2</sub> in a cup burner. The uncertainties in the corresponding concentrations (at flame blow-off) are determined from the standard deviations of the slope and intercept ( $1\sigma$ ) obtained from linear regression of the velocity at flame blow-off vs. delivery rate data [7].

## RESULTS

### BROMOALKENES

This chemical family, comprised of compounds with molecular structures containing both a carbon-carbon double bond and a bromine atom, was advanced by several authors in a series of papers and reports [1,8,9]. The justification for their further consideration as halon replacements is the expectation that they will have short atmospheric lifetimes due to the propensity of alkenes to undergo addition reactions with OH radical at the site of the double bond. At the same time, the presence of a Br atom suggests that these compounds will also have a high degree of fire suppression efficiency.

Cup-burner extinction measurements have been reported for 2 to 6 carbon bromoalkenes with various substitution patterns [1,10]. The results are generally consistent with our expectations except for the performance of the 2 carbon analogues (bromoethenes), which were significantly worse than what was observed for the other members of this chemical family. The extinction concentrations (for *n*-heptane fuel) range from about 0.025 mole fraction, obtained for CH<sub>2</sub>=CBrCF<sub>3</sub>, to 0.063 mole fraction for CF<sub>2</sub>=CFBr. The relative effectiveness of these compounds as fire suppressants may be judged by comparing these values to the extinction concentration of 0.031 mole fraction measured for CF<sub>3</sub>Br [10]. On the basis of our previous experience with cup-burner extinction measurements [10] and by comparing values measured in this laboratory with values obtained on identical compounds measured in other laboratories [1], we estimate that the relative uncertainties in these extinction concentrations are on the order of  $\pm 0.003$  mole fraction.

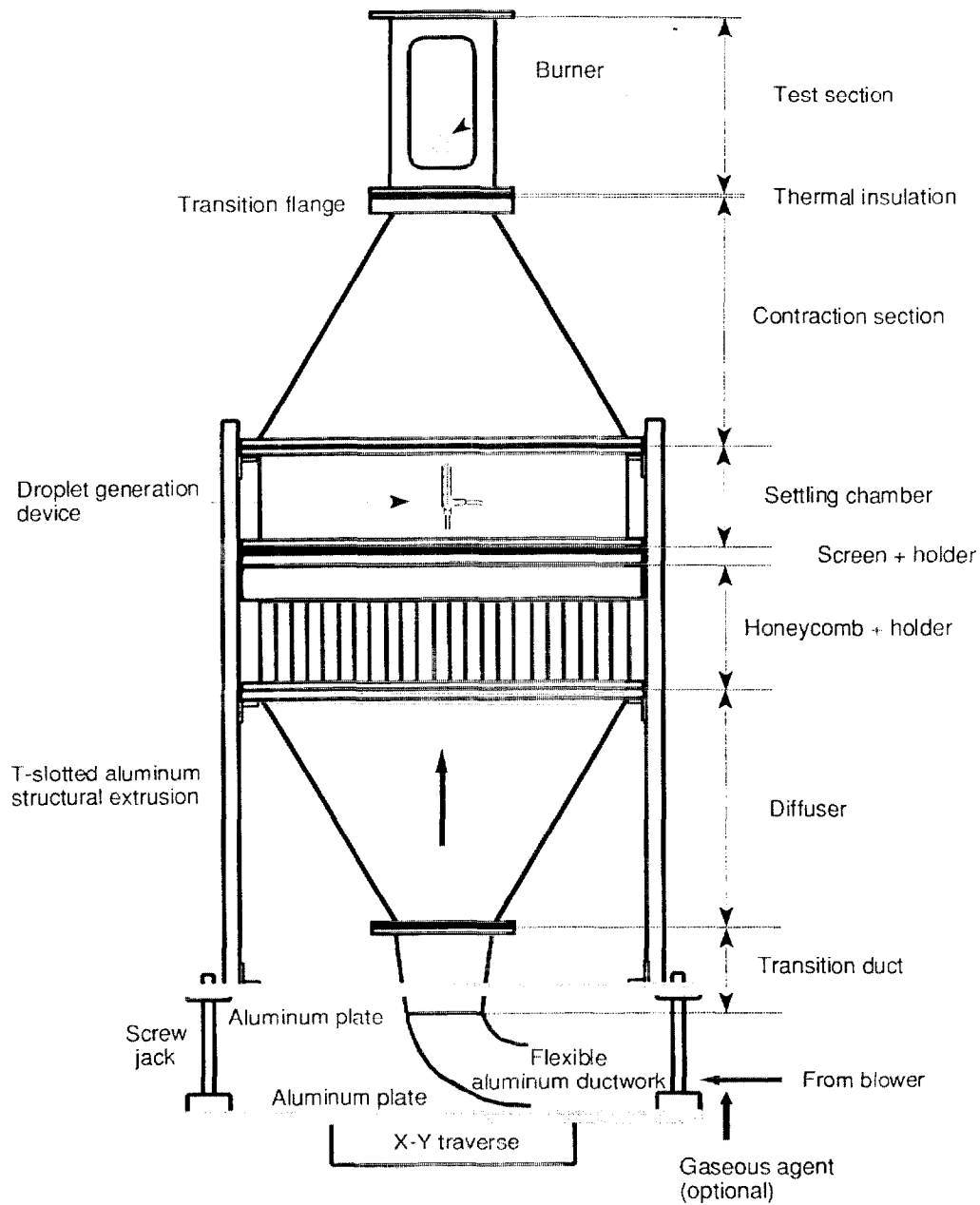


Figure 1. Diagram illustrating the components that comprise the Dispersed Liquid Agent Fire Suppression Screen Apparatus.

The inhalation toxicity of selected bromoalkenes was also determined. Limit tests, where 10 rats were exposed to 0.05 mole fraction of the agent for 30 min, were performed on eight candidates from this chemical family [1]. Lethality and/or lung tissue damage was observed in rats exposed to five of these compounds. While no lethality or lung damage was observed for  $\text{CHBr}=\text{CHCF}_3$ , clinical signs of shaking (a possible neural behavior effect) or shivering were noted during exposure to this agent. In summary, no identifiable toxic effects, other than mild anesthesia, were observed for  $\text{CH}_2=\text{CBrCF}_3$ ,  $\text{CHBr}=\text{CHCF}_3$ , and  $\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$ . These three compounds are the subjects of ongoing toxicity evaluation tests, the results of which will be reviewed in greater detail in other presentations at this conference.

On the basis of the data obtained in cup burner and inhalation toxicity tests,  $\text{CH}_2=\text{CBrCF}_3$ ,  $\text{CHBr}=\text{CHCF}_3$ , and  $\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$ , appear to be the most promising candidates from this family of chemicals. Since we are most interested in agents that have the potential for use in total-flooding applications, we have focused our attention on 2-bromo 3,3,3 trifluoropropene ( $\text{CH}_2=\text{CBrCF}_3$ ), which has the lowest boiling point of the three candidates and is commercially available. This compound boils at 34 °C, whereas 1-bromo 3,3,3 trifluoropropene ( $\text{CHBr}=\text{CHCF}_3$ ) and 4-bromo-3,3,4,4-tetrafluorobutene ( $\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$ ) have boiling points of 42 °C and 54 °C, respectively. Unfortunately, the brominated ethenes, which would otherwise be more attractive candidates for total-flooding applications (since they are gases at room temperature), are less effective suppressants than these higher molecular weight compounds. Indeed,  $\text{CH}_2=\text{CHBr}$  is flammable and was observed to create a new flame zone when it was tested in a cup burner, while  $\text{CF}_2=\text{CFBr}$  and  $\text{CF}_2=\text{CHBr}$  were found to be considerably less effective than Halon 1301 (requiring about twice as much agent on a molar basis) [11]. Toxicity may also be a concern for these compounds. This is certainly true for bromotrifluoroethene [12]. The possibility that other compounds from this chemical family might be sufficiently volatile to be used for total flooding was explored using a computer program that correlates properties, in this case boiling point, with molecular structure [5]. These calculations indicated that the bromoalkenes with 4 or more carbons have higher boiling points (by at least 20 °C) than  $\text{CH}_2=\text{CBrCF}_3$ . While we recognize that this observation is not, by itself, sufficient to exclude the higher molecular weight bromoalkenes from further consideration, there do not seem to be any compelling reasons to suspect that these compounds will provide any advantages over the compounds already considered. Thus, we conclude that the bromopropenes are the best prospects from this chemical family for use as total-flooding agents, with  $\text{CH}_2=\text{CBrCF}_3$  being the most attractive alternative. The other promising candidate, 4-bromo-3,3,4,4-tetrafluorobutane, is less volatile and consequently, may have more value as a streaming rather than a total-flooding agent.

The environmental impact of  $\text{CH}_2=\text{CBrCF}_3$  is also under investigation. Since it is volatile, we are more interested in its behavior in the atmosphere than in its effect on ground waters [4]. Preliminary measurements\* using the flash photolysis/resonance fluorescence technique indicate that the rate constant for the reaction of this compound with OH radical at 25 °C is  $k_{\text{OH}} = (3.75 \pm 0.062) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (where the uncertainty is based on a coverage of  $2\sigma$ ). This is in the range of the values obtained in previous measurements on fluorinated alkenes [13] and suggests a tropospheric lifetime in the vicinity of 4 days [14]. Based on these results, we anticipate that this compound will have acceptable ozone depletion and global warming potentials [15]. The validity of this assessment, however, may be challenged on the grounds that the products

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\* Louis, F., personal communication, April 2000.

formed by the addition of the OH radical to an alkene are not likely to undergo the same tropospheric degradation pathways as the alkyl radicals formed by the abstraction of a H from an alkane [16]. Thus, a definitive pronouncement must be deferred until the atmospheric fate of these compounds has been elucidated. We have recently undertaken a study using quantum mechanical calculations to explore the reaction surface. Our preliminary results on bromoethene indicate that the OH• adds to the carbon that is bonded to the Br. This is followed by a beta-scission of the C-Br bond, thereby liberating the Br in the process of forming the enol, which subsequently tautomerizes to the ketone.

The concentrations at flame blow-off for various liquid flame suppressants based on measurements made on the DLAFSS apparatus are presented in Table 1. The actual values have been extrapolated in accord with the test protocol developed by Yang et al. [6] to facilitate comparison with previous data obtained from cup burner measurements on gas phase agents. On this basis, we have also included a value for Halon 1301 (CF<sub>3</sub>Br). The discrepancy between the value listed in Table 1 and the accepted cup-burner extinction concentration of 0.031 mole fraction reflects the fact that it is based on data obtained from a different burner using heptane, rather than propane, as the fuel [17]. Nevertheless, we feel that it provides a useful reference point for the assessment of the fire suppression efficiencies of liquid agents, such as the bromoalkenes, based on the results of extinction measurements made on the DLAFSS apparatus. It is of considerable interest to note that ordinary water is considerably more effective than CF<sub>3</sub>Br when judged on a per unit mass basis and about equally effective on a molar basis. This is a consequence of the fact that water can be extremely effective in removing heat from the flame as a consequence of its large enthalpy of vaporization. Unfortunately, compounds with large enthalpies of vaporization will also have high boiling points so that dispersion and transport into the flame are likely to present a problem. Thus, there is a trade-off between fire suppression efficiency and compound volatility that must be considered when evaluating the performance of candidates.

TABLE 1. AGENT CONCENTRATIONS AT FLAME BLOW-OFF.

Molecule	Boiling Point (°C)	Mass Fraction†	Mole Fraction‡
H <sub>2</sub> O	100	$(2.27 \pm 0.1) \times 10^{-2}$	$(3.60 \pm 0.1) \times 10^{-2}$
CF <sub>3</sub> Br*	-58	$(1.70 \pm 0.1) \times 10^{-1}$	$(3.80 \pm 0.2) \times 10^{-2}$
CHBr=CHCH <sub>3</sub>	60	$(4.94 \pm 0.5) \times 10^{-2}$	$(1.20 \pm 0.1) \times 10^{-2}$
CH <sub>2</sub> =CBrCF <sub>3</sub>	33	$(7.83 \pm 1.0) \times 10^{-2}$	$(1.39 \pm 0.2) \times 10^{-2}$
CF <sub>2</sub> BrCF <sub>2</sub> CF <sub>2</sub> CF <sub>2</sub> Br	97	$(4.26 \pm 1.3) \times 10^{-2}$	$(3.57 \pm 1.2) \times 10^{-3}$
CH <sub>3</sub> P=O(OCH <sub>3</sub> ) <sub>2</sub>	181	$(1.46 \pm 0.1) \times 10^{-2}$	$(3.40 \pm 0.2) \times 10^{-3}$

\* Concentrations obtained using a different opposed flow burner and fuel [11, 17].

† Uncertainties based on a coverage of 2σ.

The data in Table 1 clearly show that CH<sub>2</sub>=CBrCF<sub>3</sub> is a potent flame suppressant. Indeed, the listed value suggests that it is almost three times as effective as CF<sub>3</sub>Br in destabilizing the flame in the DLAFSS apparatus. This is misleading because it does not account for differences in the dispersion of a liquid and a gas. Thus, when the blow-off concentration of CH<sub>2</sub>=CBrCF<sub>3</sub> (and the other liquid agents) is scaled by 2.5, which is the ratio of the observed coverage factors for a liquid (only about 40% of the cross-sectional area) and that of a gas (which completely covers the cross-sectional), the result is comparable to the cup-burner extinction concentration for CF<sub>3</sub>Br.

Although this scale factor is admittedly based on a crude estimate of the dispersion of liquid agents, it appears to be informative in that it is consistent with the intuitive notion that there should be reasonable conformity in the fire suppression efficiencies of bromine-containing agents. On the other hand, the observation that  $\text{CF}_2\text{BrCF}_2\text{CF}_2\text{CF}_2\text{Br}$  destabilizes the flame at a concentration of only about 25% of what is required for  $\text{CH}_2=\text{CBrCF}_3$  (rather than 50% which is what we might predict on the basis of the number of Br's in the molecular structure) indicates that other factors, apart from the presence of bromine, are also contributing to the fire suppression efficiencies of these compounds. The fact that  $\text{CF}_2\text{BrCF}_2\text{CF}_2\text{CF}_2\text{Br}$  is a larger molecule with a much higher boiling point suggests that the following properties may also be important considerations: enthalpy of vaporization (since heat will be removed when a liquid agent evaporates in the flame), heat capacity (which increases in proportion to the number of atoms in the molecule) and flammability (which enhances combustion).

## PHOSPHORUS-CONTAINING COMPOUNDS

Compounds in which a phosphorus atom is bonded directly to a carbon and/or oxygen appear to have some properties that make them suitable for use as fire extinguishants. At this point, only one of these candidates, dimethyl methylphosphonate ( $\text{CH}_3\text{PO}(\text{OCH}_3)_2$ ), has been studied in detail. Since HFC-125 is available and already in use, a minimum criterion for the next generation of halon replacements is that they be more effective suppressants than this agent [4]. This is certainly the case for DMMP, which has been shown to possess a high degree of fire suppression efficiency by Fisher and coworkers [3]. Indeed, our measurements on the DLAFFSS apparatus (Table 1) indicate that this compound is effective in destabilizing the flame at concentrations that are less than 25% (after scaling by 2.5) of the value observed for Halon 1301.

A literature search was performed on DMMP, which is widely used as a flame retardant in halogenated polyester resins and rigid polyurethane foams, to obtain information about the physical and chemical properties of this candidate. Weil [18], described DMMP as a low viscosity, water-white liquid with a boiling point of 181 °C. The relatively high boiling point of this compound suggests that its most significant environmental impact will be in the soil and ground waters, rather than the atmosphere. The screening protocol calls for the evaluation of octanol-water partition coefficients ( $K_{\text{OW}}$ ) for compounds such as DMMP, which contain both hydrophilic ( $\text{P}=\text{O}$ ) and hydrophobic (hydrocarbon) functionalities [4]. Molecules having this characteristic are likely to pose the biggest threat to wildlife because they are sufficiently hydrophobic to penetrate cell-barriers, but not so much so that they remain dissolved in the first fat layer encountered, without ever reaching the most vulnerable tissue [19].

This compound was screened for environmental toxicity, as measured by its effect on fish, aquatic invertebrates, and algae, using the computer program ECOSAR. (Note: Certain commercial equipment, instruments, materials or companies are identified in this paper in order to specify the experimental procedure adequately. This in no way implies endorsement or recommendation by NIST.) This program, which is distributed by the US Environmental Protection Agency [20], estimates toxicity limits from structure activity relationships based on the presumption of a linear relationship between toxicity and the logarithm of  $K_{\text{OW}}$  [21]. The values of the slope and intercept have been determined previously by fitting experimentally determined  $\text{LC}_{50}$  and  $\text{EC}_{50}$  data for specific classes of compounds. The results listed in Table 2 were obtained using  $\log K_{\text{OW}} = -0.52$  which is appropriate for methyl phosphate esters [21]. In an effort to provide a perspective for the interpretation of these results, we have also included the

TABLE 2. ENVIRONMENTAL TOXICITY OF DMMP.

SMILES:	CP(=O)(OC)OC	MOL WT:	124.08	
CHEM:	Dimethyl methylphosphonate	Log Kow:	-0.52 (User entered)	
CAS Num:	756-79-6	Wat Sol:	2.052E+005 mg/L (calculated)	
MOL FOR:	C3 H9 O3 P1			
ECOSAR Class	Organism	Predicted Duration	End Point	mg/L (ppm)
Neutral Organic SAR	Fish	14-day	LC <sub>50</sub>	26098.307 (6233.249)
		(Baseline Toxicity)		
Neutral Organics	Fish	96-h	LC <sub>50</sub>	21502.666 (4959.232)
Neutral Organics	Fish	14-day	LC <sub>50</sub>	26098.307 (6233.249)
Neutral Organics	Daphnid	48-h	LC <sub>50</sub>	19359.422 (4533.300)
Neutral Organics	Green Algae	96-h	EC <sub>50</sub>	10468.688 (2482.644)
Neutral Organics	Fish	30-day	ChV	1845.408 (440.976)
Neutral Organics	Daphnid	16-day	EC <sub>50</sub>	329.680 (84.999)
Neutral Organics	Green Algae	96-h	ChV	243.990 (65.707)
Neutral Organics	Fish (SW)	96-h	LC <sub>50</sub>	1456.439 (373.607)
Neutral Organics	Mysid Shrimp	96-h	LC <sub>50</sub>	37470.746 (7386.088)
Neutral Organics	Earthworm	14-day	LC <sub>50</sub>	4558.818 (1448.153)

values obtained for ethanol (listed in parentheses) using this program. On the basis of this comparison, DMMP appears to be relatively benign.

On the other hand, the terrestrial lifetime of this compound may be an issue even if the LC<sub>50</sub> data are not cause for alarm. The predominant decomposition pathway for this compound in the environment is hydrolysis via the base catalyzed cleavage of the P-O bond to produce methanol and methyl methylphosphonate (the mono ester of methylphosphonic acid). The data in reference [22] indicate that the lifetime due to (non-enzymatic) hydrolysis at pH 7 and 25 °C is close to 88 years. However, this is probably an overestimate of the actual terrestrial lifetime of DMMP. This compound, like all members of this chemical family, is susceptible to enzymatic hydrolysis by phosphatases, which are present in all living organisms [18]—ubiquitous in the environment.

The toxicological properties of this compound are summarized in Table 3, which was taken from Lewis [23]. The hazard rating (HR) of 2, which is based on an appraisal of a large number of studies, means “medium” hazard on a scale of 1, 2, or 3. Further examination of the toxicity data indicates that the acute toxicity of this compound is actually quite mild. Indeed, the LD<sub>50</sub> in rats from oral administration is 8210 mg/kg. This value is considerably higher than the LD<sub>50</sub> for rats given common table salt (sodium chloride), which is reported as 3,000 mg/kg [24].

Unfortunately, the safety profile for DMMP also points to evidence of mutagenic and/or carcinogenic activity from long-term exposures. More specifically, we were able to find literature



appears to meet the criteria required for total-flooding applications; although at 34 °C its boiling point may be a little too high for some applications in military aircraft. Although other bromopropenes have not been ruled out, they have somewhat higher boiling points than  $\text{CH}_2=\text{CBrCF}_3$  which may impart additional limitations on their use. The brominated ethenes, which are gases at room temperature, have poor fire suppression efficiencies, while bromoalkenes containing more than three carbons are not sufficiently volatile for total-flooding applications. At least one of these higher molecular weight compounds,  $\text{CH}_2=\text{CHCF}_2\text{CBrF}_2$ , does appear to be suitable as a streaming agent.

Only one phosphorus-containing compound,  $\text{CH}_3\text{PO}(\text{OCH}_3)_2$ , has been studied in detail. Although it possesses exceptional fire suppression efficiency, its high boiling point (181 °C) makes it unsuitable for total-flooding applications. It may have uses as a streaming agent, but evidence of mutagenic and/or carcinogenic activity from long-term exposures to this compound will have to be countered before it can be recommended. We are actively considering other structural variations containing phosphorus that might result in a more volatile and less toxic compound.

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