

# LABORATORY TESTING OF SOME PHOSPHORUS-CONTAINING COMPOUNDS AS FLAME SUPPRESSANTS

James Riches, Ken Grant, and Linda Knutsen  
Defence Evaluation and Research Agency (DERA)  
Chemical and Biological Defence Sector  
Haslar, Gosport, Hampshire PO12 2AG, UNITED KINGDOM

## INTRODUCTION

The aim of this work was to evaluate the flame suppression potential of some novel phosphorus-containing compounds (PCC). PCCs have been used for many years as fire retardant chemicals in plastics and in dry chemical (powder) fire extinguishers. Laboratory studies of gas phase flame inhibition by PCCs have been reviewed and studied recently by Fisher et al. [1]. The compounds dimethyl methylphosphonate (DMMP) and trimethyl phosphate (TMP) were shown to be two to four times more effective than Halon 1301 in counter-flow diffusion flame inhibition studies. Korobeinichev et al. [2,3] had previously demonstrated inhibition of low pressure pre-mixed hydrogen/air flames by the same compounds. Direct evidence that PCCs affect radical levels in flames has also been demonstrated [4,5]. Recently PCCs have been proposed as a family of chemicals with potential as halon replacements for streaming applications [6]. Amongst the compounds considered were phosphazenes and phosphites: examples of which have been shown to have low cup-burner values.

In this work the flame suppression behaviour of a number of novel and commonly available PCCs has been studied. Full details of the synthetic procedures and characterisation of the novel compounds has been reported [7]. The structures of the compounds used are shown in Figure 1. The compounds were selected in order to investigate the effect of structural features on flame suppression behaviour. Fluorination was expected to minimise the flammability and promote volatility. Compounds containing direct phosphorus to fluorine bonds are generally neurotoxic by skin contact and/or inhalation and were discounted.

## EXPERIMENTAL

The heat removed from a premixed methane/air flame was measured as a function of agent concentration. This flame suppression measurement method has been developed extensively at the New Mexico Engineering Research Institute [8]. Measurement of the heat removed from a methane/air flame was achieved by measuring the temperature of a cooling liquid pumped through a tube welded to the rim of a Bunsen burner. The temperature was measured using thermocouples that were positioned in the coolant stream and logged every 5 sec. The temperature difference recorded was converted to a measure of the heat removed by the burner (HRBB) by calculation using the known heat capacity and flow rate of the coolant (ethylene glycol). A schematic diagram of the apparatus is shown in Figure 2. The scale of the burner is somewhat smaller than the NMERI Sapphire apparatus. The burner diameter was 22 mm and the total fuel/

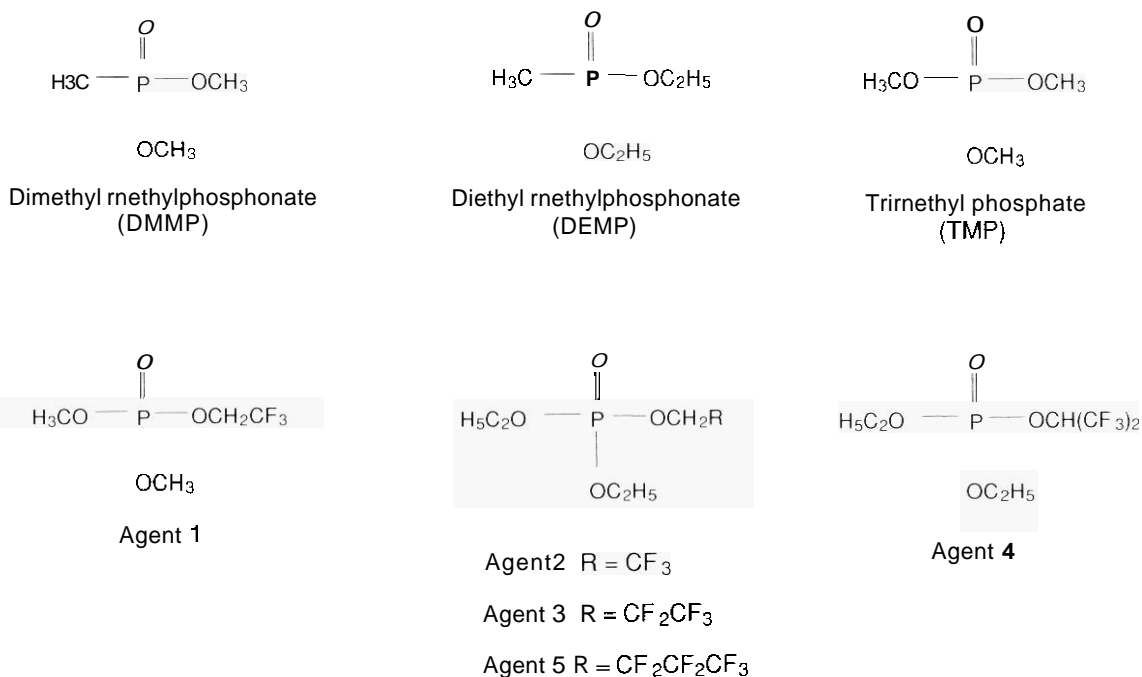


Figure 1. Structures of the phosphorus-containing compounds used in this work

air flow used was 1100 ml min<sup>-1</sup>. A fuel to air equivalence ratio of 1 was used unless otherwise stated. The heat removed by the burner for unsuppressed flames was approximately 80 cal min<sup>-1</sup>.

For experiments involving agents that were liquids at room temperature, these were injected into the pre-mixed gas stream using a syringe and needle driven by a calibrated syringe driving pump. The pre-mixed gas stream was heated to ensure vapourisation of the agents and the burner was also heated to prevent condensation of the agents before the flame.

The combustion gases were transferred to a Perkin Elmer GX System Fourier transform infrared spectrometer through a heated gas line maintained at 200 °C. The spectrometer was fitted with a 5 m variable path length heated gas cell (200 °C) with calcium fluoride windows. The spectral range studied was 4500–1000 cm<sup>-1</sup>. Spectra were recorded continuously at a resolution of 4 cm<sup>-1</sup>.

## RESULTS

The shape of the relationship between HRBB and agent concentration in experiments of this type has been used to give an insight into flame extinguishing mechanisms [8]: linear relationships being indicative of a physical, flame cooling mechanism, and nonlinear relationships of a catalytic mechanism. Addition of all the PCCs tested resulted in a change from the flat blue methane/air flame to an orange cone-shaped flame. This change occurred for very small additions (< 0.1%) of agent. After this initial change in flame shape, there was little further change except for a deepening of the orange colour, and for the non-fluorinated agents, the emission of small quantities of smoke near extinguishment. Extinguishment was not accompanied by a stretching and lifting of the flame from the surface of the burner, as is the case for Halon

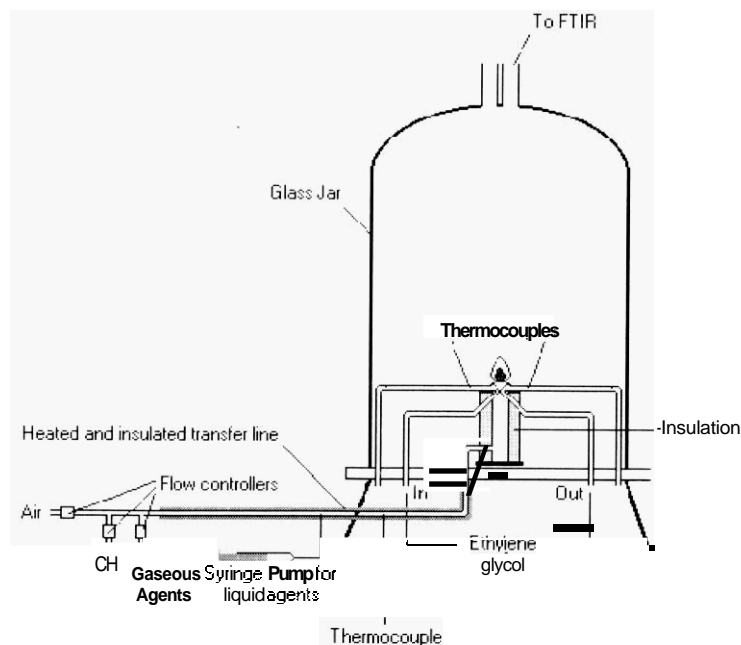


Figure 2. Schematic diagram of flame suppression measurement apparatus.

1301, but by a flickering flame that disappeared suddenly leaving a cloud of vapor. A build-up of “oily” liquid deposits and carbon was noticed on the burner surface when flames were doped with PCCs. Plots of HRBB against agent concentration for Agent 1 and Halon 1301 are shown in Figure 3. The nature of these plots is characteristic of the flame shape and its height above the burner observed throughout the experiment. For example, the value of HRBB at extinguishment is higher for the PCCs because there was no lift-off of the flame from the burner surface. Flame lift-off was a feature of flame suppression with halons, perfluorocarbons, and inert gases in our apparatus.

The curves obtained for the PCCs were also compared with water, which should act physically, and some structurally similar compounds that were known fuels: ethyl acetate, which has a structure similar to DEMP but lacking a phosphorus atom and an -OEt group; and iso-octane, a hydrocarbon fuel with a branched structure. Plots of HRBB against agent concentration for these compounds are shown in Figure 4. The change in the HRBB on addition of the fuels is expected since any additive that alters the flame shape will have an effect on the HRBB; however, these data show that for Halon 1301 and the PCCs there is a large effect on the HRBB at very low agent concentrations indicating a catalytic flame suppression mechanism.

The extinguishing concentrations for all PCCs studied are shown in Table 1. These are an average of three experiments. Plots for a selection of the PCCs tested are shown in Figure 5.

No cup-burner values for the PCCs studied were available; however, it is interesting to compare the extinguishing concentrations with cup-burner values for compounds of similar molecular weight (e.g., perfluorohexane ( $C_6F_{14}$ , M.W. = 338) has a cup-burner value of 4.4% [9]). This compound gave an extinguishing concentration of 5.9% in our apparatus. The extinguishing concentration of  $1.3 \pm 0.2\%$  noted for Agent 5 (M.W. = 336) is therefore extremely encouraging.

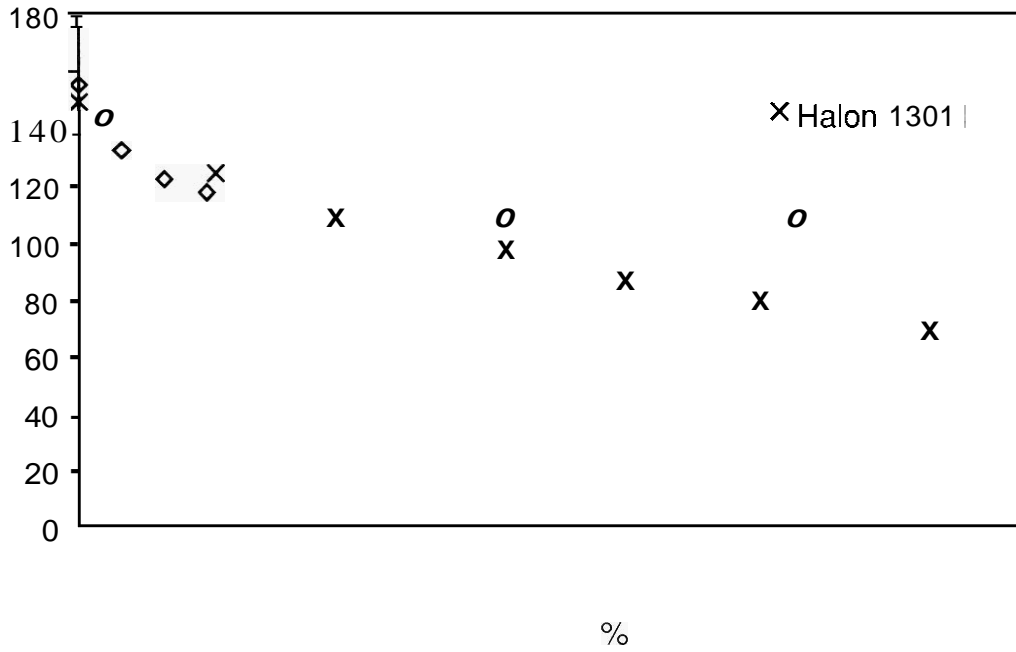


Figure 3. Plots of HRBB against agent concentration for Agent 1 and Halon 1301

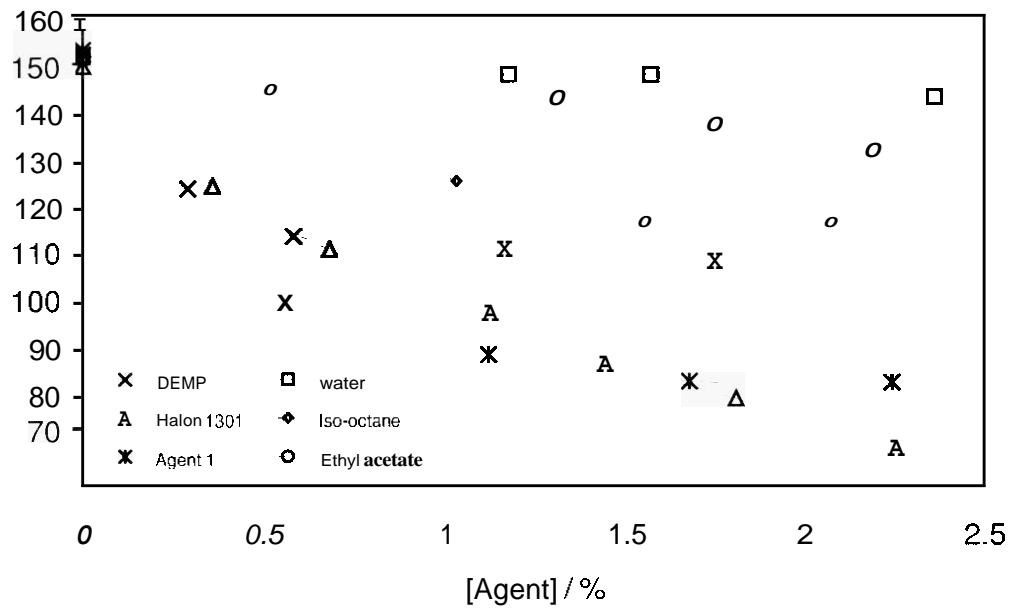


Figure 4. Plots of HRBB against agent concentration for Agent 1, DEMP, and fuels with structural similarities to DEMP.

TABLE 1. EXTINGUISHING CONCENTRATIONS FOR PCCs.

| Agent   | Molecular Weight | Extinguishing Concentration / % |
|---------|------------------|---------------------------------|
| DMMP    | 124              | $2.2 \pm 0.2$                   |
| TMP     | 140              | $2.1 \pm 0.2$                   |
| DEMP    | 152              | $1.7 \pm 0.2$                   |
| Agent 1 | 208              | $2.1 \pm 0.2$                   |
| Agent 2 | 236              | $1.7 \pm 0.2$                   |
| Agent 3 | 286              | $1.5 \pm 0.2$                   |
| Agent 4 | 304              | $1.4 \pm 0.2$                   |
| Agent 5 | 336              | $1.3 \pm 0.2$                   |

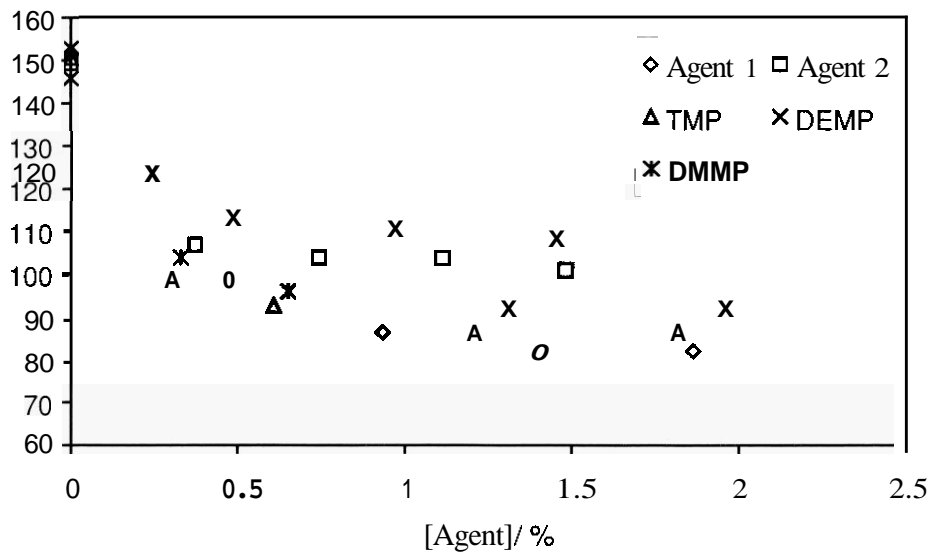


Figure 5. Plots of HRBB against agent concentration for a range of PCCs.

Other agents tested, which are liquids at room temperature and for which reference cup-burner values are available, were 3-bromo-1,1,1-trifluoropropene and 2-bromo-3,3,3-trifluoro-2-propanol. These compounds gave extinguishing concentrations of 3.1 and 5.9%, respectively, compared with cup-burner values of 2.6 and 5.3% [9]. It can be seen therefore that extinguishing concentrations as calculated for liquid agents in our apparatus are higher than the corresponding cup-burner values. Extinguishing concentrations for gaseous agents were generally slightly lower than the cup-burner values. For example, Halon 1301 gave an extinguishing concentration of 2.3% compared to the cup-burner value of 2.9%.

A reduction in extinguishing concentration with molecular weight was observed for the fluorine-containing PCCs as shown in Figure 6. The non-fluorinated PCCs (also plotted on Figure 6) were more effective than the fluorinated PCCs on a weight basis. These data support previous

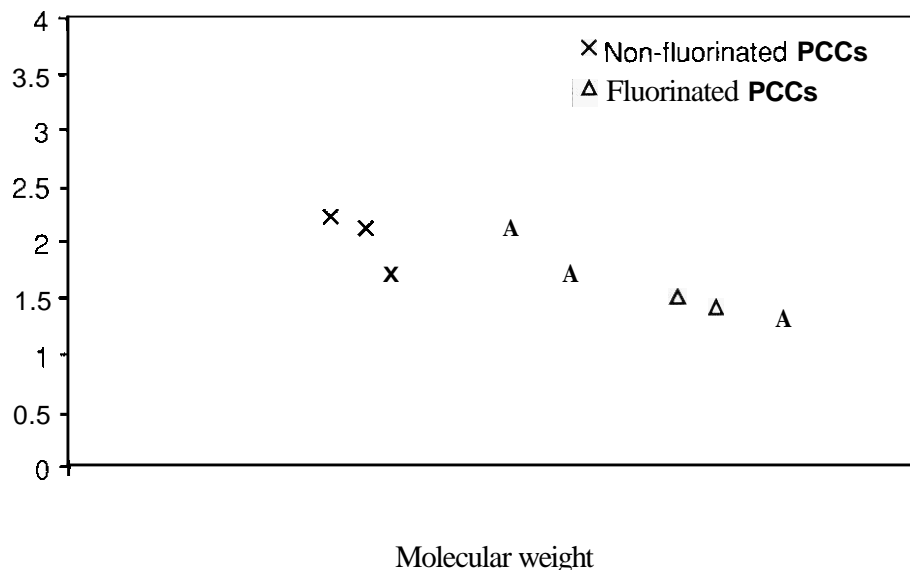


Figure 6. Plot of extinguishing concentration against molecular weight for PCCs.

suggestions [10] that it is the presence of phosphorus radicals in the flame rather than the nature of the parent compound that is important in flame suppression.

The effect of flame stoichiometry was studied for TMP and Agent 1. The plot of HRBB against flame stoichiometry (Figure 7) shows that both the PCCs are equally effective in suppressing the flame over the lean to stoichiometric range. This shows that the flame suppression behaviour of these agents is not influenced by their fuel content in these experiments.

### Infrared Spectra

Infrared spectra of the combustion products of the non-fluorinated PCCs showed broad absorbances in the  $1300$  to  $1000\text{ cm}^{-1}$  region. There was some indication of undegraded agents in the spectra near extinguishment. Infrared spectra recorded for TMP near extinguishment overlaid with the spectrum of the uncombusted agent recorded after the flame had been extinguished are shown in Figure 8.

Infrared spectra of combustion products from the fluorinated PCCs **also** revealed broad absorbances in the  $1300$  to  $1000\text{ cm}^{-1}$  region, which could not be assigned to specific phosphorus-containing species. Hydrogen fluoride and carbonyl fluoride were the main combustion products identified, in addition to carbon dioxide and water, and there was some evidence of uncombusted agents (P=O stretch). Phosphorus acids were not detected based on the absence of absorptions at  $2700$  to  $2550\text{ cm}^{-1}$ . The infrared spectrum recorded for Agent 1 near extinguishment overlaid with that for the uncombusted agent is shown in Figure 9.

This work on the flame suppression potential of PCCs is at an early stage but has revealed some interesting observations. A range of PCCs have been shown to inhibit pre-mixed methane/air

flames, and a catalytic extinguishing mechanism seems likely to be based on plots of the heat removed from these flames against agent concentration.

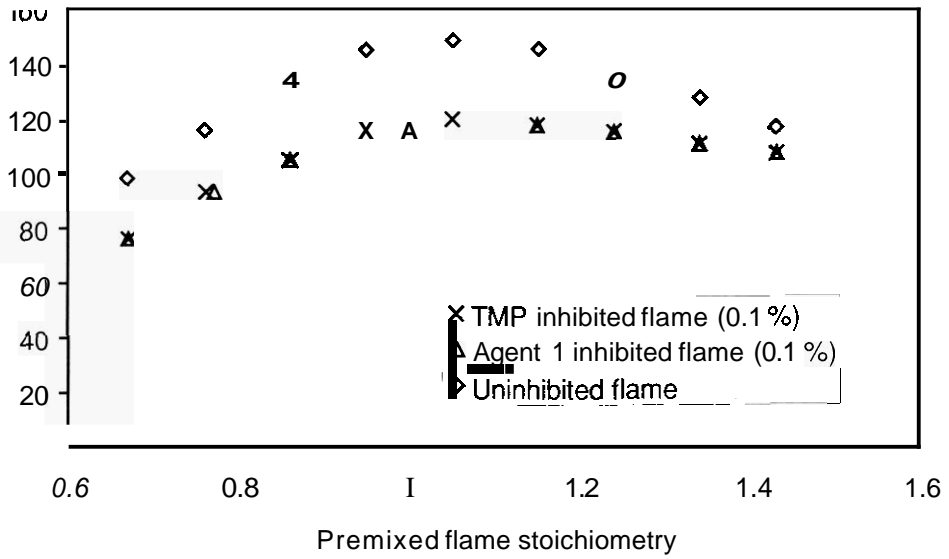


Figure 7. Effect of flame stoichiometry on flame suppression for TMP and Agent 1.

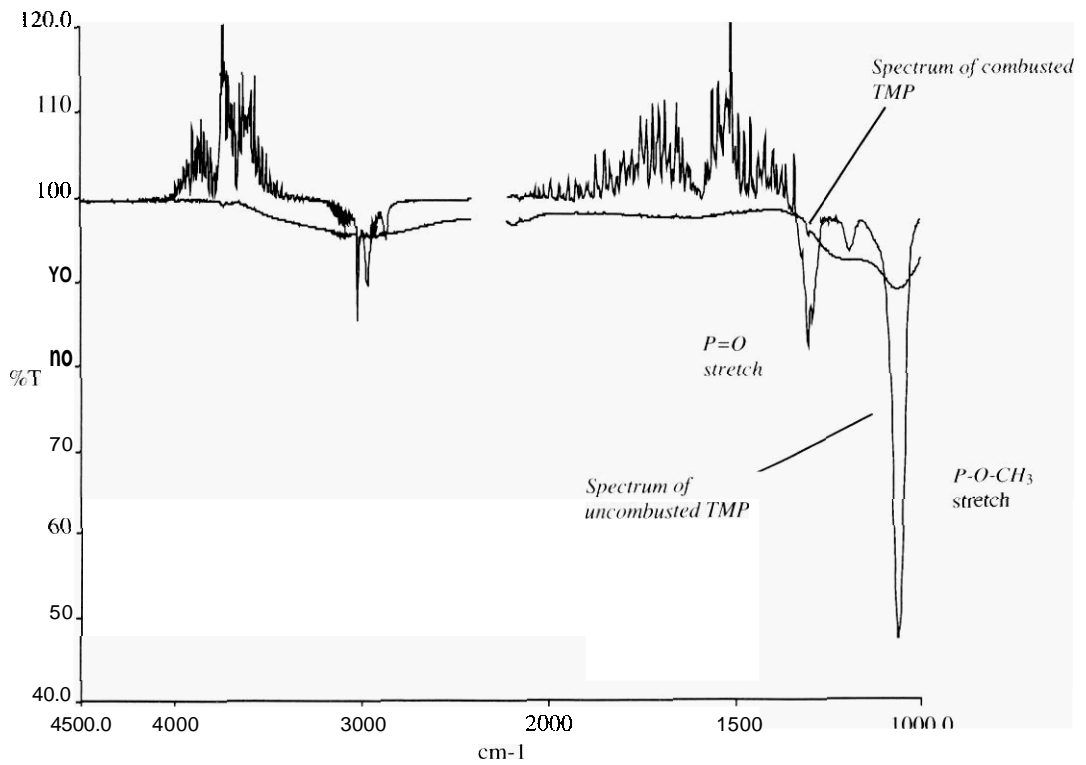


Figure 8. Infrared spectra of TMP.

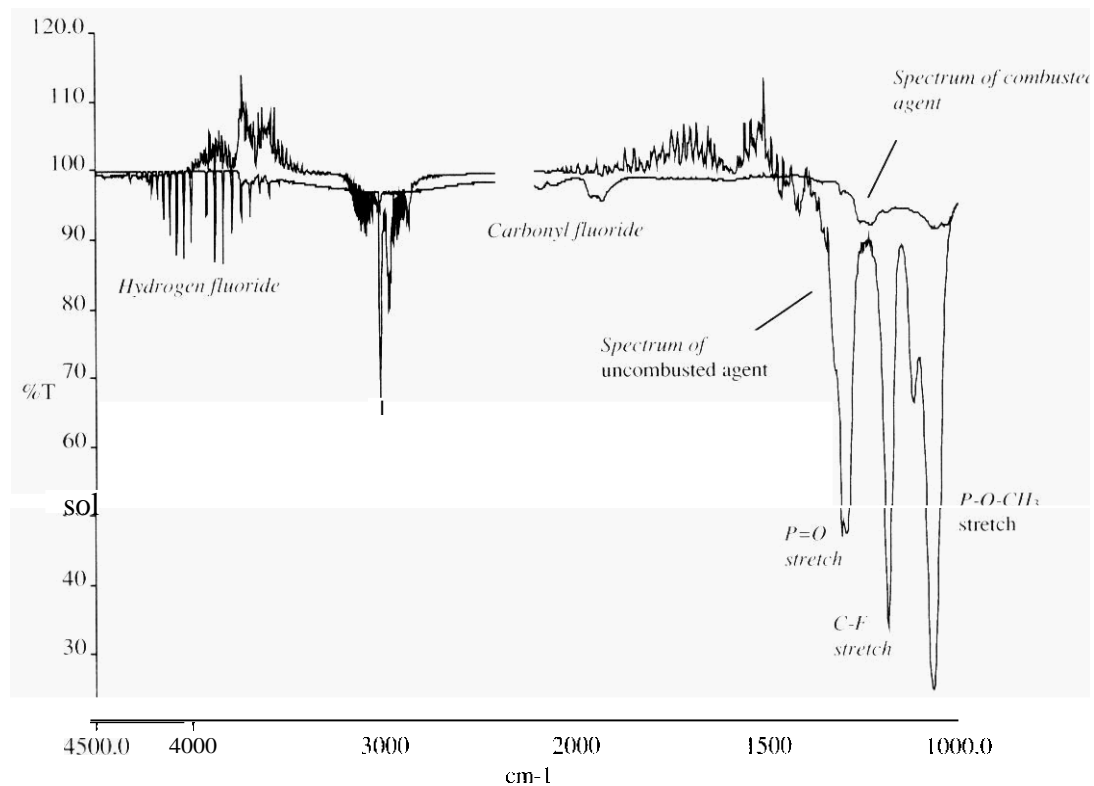


Figure 9. Infrared spectra of Agent 1.

## CONCLUSIONS AND FUTURE WORK

Extinguishing concentrations of between 1.2 and 2.2 % were determined for the PCCs tested. This is an encouraging result and justifies further work on PCCs. The relative effectiveness of more PCCs, including fluorinated and non-fluorinated phosphites, will be investigated in future work. If further tests reveal that the presence of phosphorus rather than the nature of the parent compound is the main factor in the effectiveness of PCCs, this should give good scope for designing a nontoxic agent.

Particulate formation is very likely to be important in the extinguishing mechanism based on visual observations of smoke for all PCCs tested. Particulate formation in flame extinguishment mechanisms has been discussed extensively in relation to the study of flame suppression with iron-containing compounds [11,12] and may also be of relevance to this work.

Infrared spectra of combustion products from the PCCs revealed broad absorbances in the 1300 to  $1000\text{cm}^{-1}$  region, which could not be assigned to specific structural features of PCCs. There was some evidence of uncombusted agent near extinguishment for all the PCCs. Hydrogen fluoride and carbonyl fluoride were the main combustion products identified, in addition to carbon dioxide and water, for the fluorinated PCCs. Phosphorus containing acids were not detected based on the absence of absorptions in the range  $2700$  to  $2550\text{cm}^{-1}$ .



## ACKNOWLEDGMENTS

The work reported in this paper was funded by the Ministry of Defence's Corporate Research Programme. The authors would like to thank Dr. Chris Timperley and colleagues at CBD Porton Down who synthesised the novel PCCs.

## REFERENCES

1. Fisher, E. M., MacDonald, M. A., Jayaweera, T. M., and Gouldin, F. C., "Inhibition of Non-Premixed Flames by Phosphorus-Containing Compounds," *Combustion and Flame*, 116 (1/2), 166-176, 1998.
2. Korobeinichev, O. P., Chernov, A. A., and Shvartsberg, V. M., "Destruction Chemistry of Trimethyl Phosphate in H<sub>2</sub>/O<sub>2</sub>/Ar Flames Studied by Molecular Beam Mass Spectrometry," presented at the 3<sup>rd</sup> Asia-Pacific International Symposium on Combustion and Energy Utilisation, 1995.
3. Korobeinichev, O. P., Il'in, S. B., and Mokrushin, V. V., "Destruction Chemistry of Dimethyl Methylphosphonate in H<sub>2</sub>/O<sub>2</sub>/Ar Flames Studied by Molecular Beam Mass Spectrometry," *Combustion Sci. and Tech.*, 116-117, S1-67, 1996.
4. Ibiricu, M. M. and Gaydon, A. G., "Spectroscopic Studies of the Effect of Inhibitors on Counterflow Diffusion Flames," *Combust. Flame*, 8, pp. 51-62, 1964.
5. Hastie, J. W. and Bonnell, D. W., *Molecular Chemistry of Inhibited Combustion Systems. National Bureau of Standards*, Final NBSIR 80-2169, PB81-170375, 1980.
6. Kaizerman, J. A. and Tapscott, R. E., *Advanced Streaming Agent Development, Volume II: Phosphorus Compounds*, NMERI 96/5/32540, 1996.
7. Timperley, C., Morton, I. J., Waters, M. J., and Yarwood, J. L., "The Synthesis and Reactions of Dialkyl Fluoroalkylphosphates," submitted for publication in the *Journal of Fluorine Chemistry*, 1998.
8. Brabson, G. D., Schiro, J., Patterson, R. A., Walters, E. A., and Tapscott, R. E., "Determination of Extinguishment Mechanisms," *International CFC and Halon Alternatives Conference*, Washington DC, Abstracts, 23-25 October 1995.
9. *NEW Mexico Engineering Research Institute Cup Burner Flame Extinguishment Concentrations*. Technical Update Series, June 1997.
10. Marowlewski, T. A. and Weil, E.D., "A Review of Phosphate Ester Fire Resistance Mechanisms and their Relevance to Fluid Testing," in *Fire Resistance of Industrial Fluids*, Vol. ASTM STP1284, Totten, G. E., Jurgen, R., (Eds.) American Society for Testing and Materials, Philadelphia, 1996. pp. 102-109.
11. Rumminger, M. D., Reinelt, D., Babushok, V., and Linteris, G. T., "Inhibition of Flames by Iron Pentacarbonyl," *Proceedings*, Halon Options Technical Working Conference, pp. 145-156, 1998.
12. Patterson, R. A., Gobeli, G. W., Brabson, D., and Tapscott, R. E., *Advanced Streaming Agent Development; Volume II: Metal Compounds*. NMERI 96/3/32540, 1996.