

Influence of Phosphorus-Containing Fire Suppressants on Flame Propagation

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Prohibition, under the Montreal Protocol, of the production of Halon 1211 and Halon 1301 has created a need for new, environmentally acceptable fire suppressants [1]. Literature data suggest that some phosphorus-containing compounds may be very efficient fire suppressants. Phosphorus-containing agents (powders) are mentioned as effective agents for smoldering combustion due to the formation of polymer films on the surface of burning materials, preventing penetration of oxidizer inside the burning material. They are considered to be effective compounds for the suppression of Mg combustion and combustion of some metals and are used as retardants in fire-resistant polymers. In spite of the large literature on the use of such compounds as flame-retardants in solids, there are only a few references to phosphorus-containing liquids or gases as flame suppressants. Thus, studies on the fire suppression efficiency of phosphorus compounds and its mechanism of influence are of interest.

In this work we report the results of numerical studies on the inhibition mechanism of methane flames by phosphorus-containing additives; dimethyl methylphosphonate, trimethyl phosphate and phosphorus tribromide (DMMP, TEP, PBr_3). Short survey of experimental data on fire suppression properties of phosphorus agents is presented. The dependencies of burning velocity on an inhibitor concentration and additive decomposition rate were analyzed. The influence of flame temperature on inhibition efficiency was also considered.

Experimental Data on the Fire Suppression Properties of Phosphorus Containing Compounds.

The literature data cover the results of experimental studies of the effect of phosphorus containing agents on burning velocity, agent concentrations, necessary for suppression, influence of additives on extinction strain rate for opposed diffusion flames and the results of streaming laboratory tests. The list of phosphorus compounds studied includes POCl_3 , PSCl_3 , PSBr_3 , PCl_3 , PBr_3 , TMP, DMMP, triphenylphosphine, monoammonium phosphate, diammonium phosphate, $\text{P}_3\text{N}_3\text{F}_6$, $\text{P}_3\text{N}_3\text{ClF}_5$, $\text{P}_3\text{N}_3\text{Cl}_2\text{F}_4$, $\text{P}_3\text{N}_3(\text{OCH}_3)_6$ and fluoroalkoxyphosphazenes.

Experimental data can be divided according to the concentration range of the inhibitor influence. In small concentration range, chemical effects are maximized. With increasing additive concentration, the contributions of heat capacity and dilution become more important. At the same time the chemical influence of additive decreases (saturation effect, [2]) due to the lowering of chain carrier concentration down to the equilibrium level.

Table 1 contains data on experimental studies of the inhibition properties of phosphorus containing compounds in small concentration ranges. Results are based on burning velocity measurements [3-6]. Lask and Wagner [3] included in their studies tests on $(\text{CH}_3)_4\text{PO}_4$.

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(C₂H₅)₃PO₄, PCl₃, PBr₃, PSCl₃ and PSBr₃. They obtained data on concentrations of agents required for burning velocity reduction, in a n-hexane/air flame, by 30%. These compounds were considerably more effective inhibitors than Cl₂, Br₂ and CCl₄. Note that according Lask and Wagner [3] there is almost no difference if a chlorine atom is exchanged by bromine atom, and, in addition, (CH₃)₃PO₄, containing no halogen, showed a much more pronounced effect than the halogens. These results are consistent with the great efficiency of phosphorus containing compounds in flame suppression.

Table 1. Experimental data on influence of P-compounds on burning velocity and counterflow diffusion flame in small concentration range.

Additives	Flame system	Parameter	Efficiency relative CF ₃ Br	Reference
TMP, POCl ₃ , triphenylphosphine	premixed/diffusion hydrogen, methane propane, benzene	S _u , flame surface area, concentrations, PO, HPO, HOPO	Registration of promotion effect	4
PSBr ₃	Hexane	S _u	6.7	3
	Hexane	S _u	6.9	7
PCl ₃	Hexane	S _u	6.9	8
	Hexane	S _u	6.9	9
	Hexane	S _u	6.7	7
	Methane	S _u	~7.5	5
	Hydrogen	S _u	~1.7	6
PBr ₃	Hexane	S _u	6.9	3
	Hexane	S _u	4.6	10
PSCl ₃	Hexane	S _u	8	3
(C ₂ H ₅) ₃ PO ₄	Hexane	S _u	3.75	7
(CH ₃) ₃ PO ₄	Hexane	S _u	3.9	3
	CH ₄ /air, counter diffusion flame	Extinction strain rate	2-4, 35% reduction of global strain rate for 0.15%	11 12
CH ₃ P(OCH ₃) ₂ O (DMMP)	CH ₄ /air, counter diffusion flame	Extinction strain rate	2-4, 35% reduction of global strain rate for 0.15%	11 12
	Hexane	S _u	5.2	7
POCl ₃	Methane	S _u	~7.5	5
	H ₂	S _u	~2.7	6

* S_u – burning velocity

Rosser et al. [5] in studies of the influence of various inhibitors on burning velocity and quenching diameter found that phosphorus oxychloride and phosphorus trichloride to be very effective inhibitors. The experimental data show that the two compounds are comparable in effectiveness and three to four times more effective than hydrogen bromide. The authors have shown that depending on experimental data treatment (e.g., using linear dependence of an inverse square of burning velocity on inhibitor concentration) previously acquired data for hydrogen bromide when expressed in the same terms reveal that PCl₃ and POCl₃ are 10-15 times as effective as HBr. Hastie et al. [4] have found TMP to be more effective than POCl₃.

Miller et al. [6] made burning velocity measurements for hydrogen flames inhibited by PCl₃ and POCl₃. The measurements show decreased effectiveness of the phosphorus-containing compounds in comparison with methane and hexane flames (Table 1). Note that these measurements have carried out for relatively high levels of inhibitor loading (more than 1%).

Fisher and co-workers [11,12] investigated the effect of DMMP and TMP on the extinction strain rate of opposed diffusion methane/air flames. DMMP and TMP were 2-4 times more effective than CF_3Br . Addition of 1500 ppm of phosphorus containing additive decreases global strain rate 35%. When introduced on the air side of methane/air flames, the phosphorus-containing agents showed effectiveness that was 2-4 times higher than literature data for CF_3Br (on the molar base) and 40 times higher than that of N_2 . Experiments with the variable-dilution methane/nitrogen/oxygen/nitrogen flames showed that, when results were normalized by the quantity of additive calculated to be at the flame location (reaction zone), air side delivery of DMMP produces significantly higher effect than fuel-side delivery. The effectiveness of DMMP has strong temperature dependence, with lower effectiveness at higher adiabatic flame temperatures. The DMMP effectiveness per unit mole fraction is roughly 100 times that of argon. Oxidizer side inhibitor addition shows effectiveness roughly twice that of the fuel side.

Table 2 contains literature data for the fire suppression characteristics of phosphorus containing compounds. The scattered data on suppression concentrations of phosphorus compounds show some inconsistencies. Phosphorus trichloride was studied in Purdue University tests [13], and it was found that it required for suppression one of the highest volume fractions, 22.5% (except CO_2 , CF_4 , HCl) of the 56 considered compounds. This result is contrary with data on the high effectiveness of PCl_3 for decreases in burning velocity.

Data on extinction by POCl_3 compound are more consistent. Extinction concentrations of POCl_3 range from 0.45 to 1.9 % depending on initial conditions. Jorissen et al. [17] indicated that POCl_3 is a very powerful inhibitor. Less than 1% of this compound is sufficient to prevent flame propagation in CH_4/air mixtures. Ibricu and Gaydon [16] have observed extinction concentrations of POCl_3 in the 0.45-1.5% concentration range depending on flow rate and place of agent addition (fuel or oxidizer side).

Monoammonium phosphate is widely used in practice as a fire suppressant and is included in different agent compositions. It should be noted that $\text{NH}_4\text{H}_2\text{PO}_4$ is a solid compound. Its efficiency depends on particle size distribution and the delivery procedure into the flame zone. The data in Table 2 showing mass extinction concentrations for coal/air combustion correspond roughly to 2-6 % by volume. They are in reasonable agreement with data for methane combustion. The minimum value of suppression concentration (1.1%) has been obtained by Ewing et al. [18] for finely divided powder.

Kaizerman et al. [28] and Liflke et al. [29] have tested several P-containing compounds using cup burner and laboratory scale streaming procedures. The extinguishing concentrations for hexafluorocyclotriphosphazene ($\text{P}_3\text{N}_3\text{F}_6$), $\text{P}_3\text{N}_3\text{ClF}_5$ and $\text{P}_3\text{N}_3\text{Cl}_2\text{F}_4$ have been determined using the cup burner test (Table 2). They indicated that in the initial work, some impure mixtures of cyclic phosphorus nitrides exhibited cup-burner extinguishment concentrations as low as 0.3%. The purified compounds were found to have higher cup-burner values. The concentrations found were still well below those determined for Halon 1301. Laboratory-scale streaming tests show extinguishment times for the halocyclotriphosphazenes that are considerably shorter than those determined for Halon 1211. The peak values of these compounds in cup burner tests are around 1% and this is in approximate agreement with 2.3% suppression concentration calculated for DMMP (premixed methane/air stoichiometric flame, this work).

Table 2. Data on flame suppression characteristics of phosphorus-containing agents.

Additives	Flame system	Parameter	Extinction concentration	Reference
PCl ₃		Extinction concentr.	22.5 % by volume	13
CH ₃ P(OCH ₃) ₂ O DMMP	C ₃ H ₈ /air, counter diff.flame CH ₄ , premixed	Extinction Suppression concentr.	0.4% by volume 2.3%, stoichiom.mixture	14 This work
POCl ₃	Methane Methane, ethylene, Diffusion flame CH ₄ /air	peak concentr. Emission spectra Flame propagation	1.9(prem.,0.01atm) (extin.conc. ~ 0.45-1.45 % depending on flow rate) <1% for prevention of flame	15 16 17
NH ₄ H ₂ PO ₄	n-heptane methane methane coal/air coal/air coal/air dust(from a wheat elevator)/air dust(melamine; wood dust; wheat flour, coal)/air coal/air	Suppr.conc.,diff.flame Premixed,peak conc. Inerting conc. Inerting conc. Peak conc. Peak conc. Suppression, pressure Explosion dynamics Suppression, pressure Explosion dynamics Peak concentr.	1.1 % by volume 5.2 5 2 31(mass.%,addit/coal+addit,Foray-ABC) 15-30 (mass.%, addit/coal+ addit) suppr.conc. ~20%, by volume (estimation of this work) Relative efficiencies of NH ₄ H ₂ PO ₄ and NaHCO ₃ depend on the procedure 8-9 weight %	18 19 20 20 21 22-24 25 26 27
Trademark: P-11-24A (ammonium- phosphorus- containing salts, France) AK (diamonium phosphate, Russia) A-1a (ammophos, Russia)		Suppression concentration	1.5-2 kg/m ² 1.5 - 2 kg/m ² (volumetric suppression - 0.5-3 kg/m ³ , at the rate 0.08 kg/m ² s) 2.5-3.5 kg/m ² (volumetric suppression - 0.5-3 kg/m ³ , at the rate 0.08 kg/m ² s)	19
P ₃ N ₃ (OCH ₃) ₆ , Fluoroalkoxyphos- phazenes - P ₃ N ₃ (OR) ₃ (OR) ₃	n-heptane fire, suppression by inhibitor spray, streaming test	Flow rate of suppressant; time for extinction	Blends of HFE-449s1 with phosphazenes show enhanced extinguishment (25% in blend decreases extinction time twice)	28
Phosphazenes P3N3F6 P3N3ClF5 P3N3Cl2F4 P3N3F6	C ₃ H ₈ /air, counter diffusion flame	Cup burner • Extinction	1.08 % by volume 0.91 0.96 6 % by volume	29 14

For laboratory scale streaming tests (n-hexane pan flame), the rate of agent consumption and extinction time have been determined using blends of halogenated fluorocarbons (HFE) and fluoroalkoxyphosphazenes [28]. Each of the fluoroalkoxyphosphazenes (four tested compounds), when blended with HFE, shows a significant improvement over neat HFE. These phosphazenes were blended with HFE as a carrier since the neat fluoroalkoxyphosphazenes was too viscous. At the same time a 10% by weight aqueous solution of P₃N₃(OCH₃)₆ did not affect extinguishment. The literature data demonstrate that the extinction concentrations of phosphorus containing compounds are in the range 0.5-5% by volume.

Calculational procedure and kinetic model.

The modeling results described were derived from the CHEMKIN suite of programs. The kinetic model is based on the kinetic data used for the analysis of the influence of PH_3 combustion products on the recombination of hydrogen atoms in a hydrogen flame [6], and those [31,32] used for describing destruction of DMMP and TMP in low pressure hydrogen flame. Reactions of simple phosphorus containing species with radicals and some intermediate species of methane system to reflect methane combustion have been included. It has been assumed that phosphorus-species are non-reactive to the stable hydrocarbons. Reactions have been added to the scheme to complete the reaction pathways for the consumption of some of the species. The model has been adjusted to take into account recent data for P-species. Thermochemical data are from a variety of sources [33,34,35,30]. For the modeling of TEP influence on flame propagation, the overall decomposition kinetics has been used [36].

Modeling of Inhibited Flames by Phosphorus Compounds

Inhibition Mechanism of Phosphorus Compound Influence on Flame Propagation.

The effect of three phosphorus-containing compounds, DMMP, TEP and PBr_3 was studied. DMMP is the most stable compound. The activation energy of decomposition is about 87 kcal/mol according data of Melius [31]. Thus destruction of DMMP will proceed through the reactions of chain carriers (H, O, OH) with DMMP. Numerical modeling of stoichiometric methane flame show that reactions of H and OH with DMMP lead to the formation of $\text{PCH}_3\text{OCH}_3(\text{OCH}_2)\text{O}$ followed by the formation $\text{CH}_3\text{P}(\text{OCH}_3)\text{O}$ (Fig.1). $\text{CH}_3\text{P}(\text{OCH}_3)\text{O}$ decomposes rapidly to CH_3PO_2 . CH_3PO_2 reacts with H and OH leading to formation of HOPO and HOPO₂ species. At this stage, reactions of HOPO, HOPO₂ and PO₂ with chain carriers form two inhibition cycles. These can be found in Fig.1. In this work we follow the suggestion of Cool and Werner on the DMMP decomposition mechanism [31]. As will be discussed later, the details of decomposition mechanism have relatively small influence on the inhibition properties of the agent, since the main scavenging reactions of an inhibition cycle are the reactions of simple phosphorus-containing species. Reactions of HOPO₂ and HOPO species with H, O and OH lead mostly to PO₂ radical. PO₂ recombine with H and OH with formation, again of HOPO₂ and HOPO, thus leading to inhibition cycles.

Table 3 contains equilibrium concentrations of main P-containing species for stoichiometric methane/air flame with 1% DMMP as the additive. Calculations for different additive concentrations show that the main species are $\text{HOPO} > \text{PO}_2 > \text{HOPO}_2 > \text{PO}$.

Table 3.

Species	P	PO	PO ₂	PO ₃	HOPO	HOPO ₂	HPO	OP(OH) ₃
Equilibrium concentration mole fraction	1.E-7	6.E-4	1.7E-3	3.2E-7	6.5E-3	7.7E-4	4.8E-6	1.E-5

Fig.2 contains dependencies of burning velocity on the concentration of DMMP and TEP. The calculated decreases in burning velocities show that the use of original rate constants of the model [30] leads to the efficiency of DMMP relative to CF_3Br by a factor of about 1.5-2 on the basis

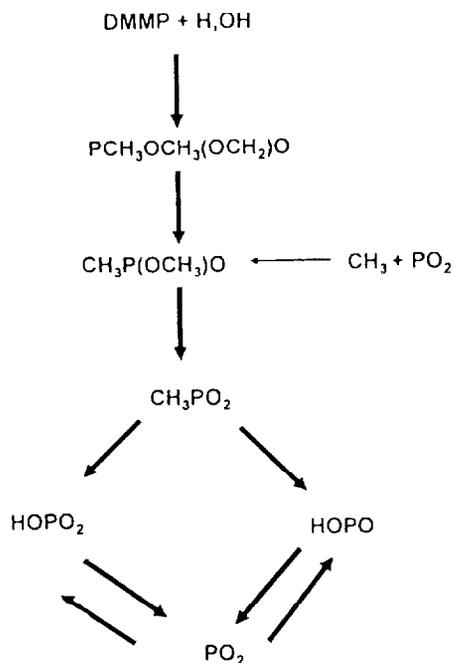


Fig.1 The abbreviated inhibition cycle of DMMP effect.

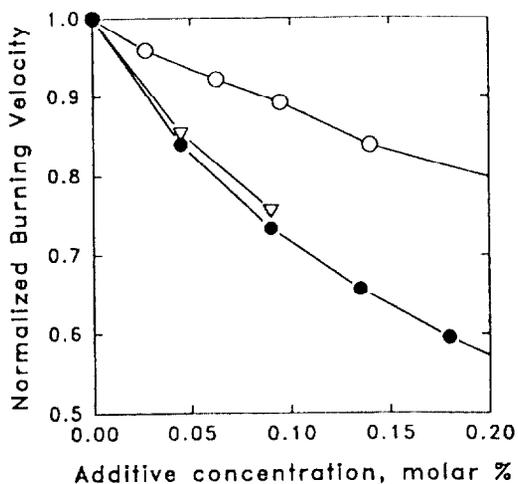
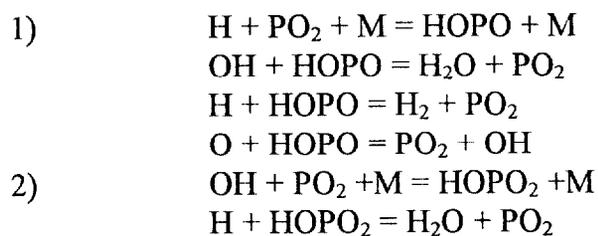


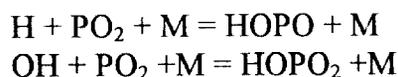
Fig.2 Burning velocity dependence on inhibitor concentration (stoich. air/methane flame). Open circles-DMMP, rate constant of [30]; closed circles - DMMP, modified model; triangles - TEP additive.

of burning velocity decreases. If DMMP effectiveness for burning velocity decrease is 3-4 times higher than for CF_3Br , then modification of the kinetic model is required.

Following the decomposition DMMP in flame zone the main phosphorus containing species are PO_2 , HOPO and HOPO_2 . The sensitivity and reaction pathway analysis show two main inhibition cycles with general species PO_2 (Fig. 1)

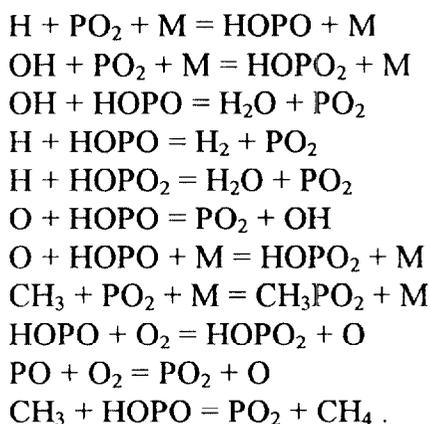


Numerical calculations and sensitivity analysis show that the burning velocity is most sensitive to the rate constants of the two recombination reactions of the PO_2 radical



Reasonable adjustment of rate constants of the addition reactions leads to approximate agreement with experimental data on the efficiency of DMMP and TEP relative to CF_3Br . Results are presented on Fig. 1.

The most important reactions for inhibition by phosphorus containing compounds, revealed for 1 atm and methane/air stoichiometric flame, are the following reactions



Influence of Decomposition Agent Rate on Inhibition Effectiveness.

The phosphorus content of the inhibitors studied should be the main factor affecting flame suppression. The influence of the type of parent molecule on inhibition properties of phosphorus containing compounds was studied through the modeling of the effect of the decomposition rate of the parent compounds. It is known that phosphorus compounds have a wide range of thermal stability. Overall activation energies of decomposition are in the 15 - 90 kcal/mol range. The influence of the decomposition rate has been studied using global kinetics of decomposition to PO_2 or to HOPO species and by variation of activation energy of the decomposition reaction. Fig.3 demonstrates that, for assumed kinetic model and with a stoichiometric methane/air mixture, decomposition reactions with activation energy less than 60 kcal/mol has no effect on the burning velocity decrease. With increasing activation energy a decrease of inhibitor efficiency is observed.

For activation energies in the 80 kcal/mol range the degree of decomposition corresponds to 60-70% at the position of maximum H atom concentration. Calculations for lean methane/air flames (equivalence ratio 0.7) show dependencies approximately similar to the dependence for stoichiometric flame in spite of flame temperature being approximately 300 K less. The decomposition processes of phosphorus compounds do not influence inhibition until the overall activation energy reaches 60 kcal/mol

Influence of Flame Temperature on Fire Suppression Properties of Phosphorus-Containing Agents.

Hastie and Bonell [4] suggested that phosphorus-containing compounds may demonstrate promotion effect depending on initial conditions and that the increase of flame temperature may lead to decrease of inhibitor efficiency. The estimated crossover flame temperature point for changing of additive influence mode is near 2350 K. The probable reaction responsible for promotion is the reaction $\text{HPO}_2 + \text{OH} \rightleftharpoons \text{PO}_2 + \text{H}_2\text{O}$ which may be reversed as the flame temperature increases. Korobeinichev et al. [37] have found that the addition of DMMP leads to faster temperature increases at low pressures for burner stabilized hydrogen flame. They concluded that this is the result of DMMP promotive effect.

Experimental data of MacDonald et al. [11] for counterflow diffusion methane flame with DMMP show that the normalized effectiveness increases with stoichiometric mixture fraction or, equivalently, with flame temperature decrease. Thus the inhibition effectiveness per mole of DMMP decreases with increasing flame temperature, in accord with suggestion of the work [4]. Note that the authors mentioned that their results do not conclusively eliminate the possibility of

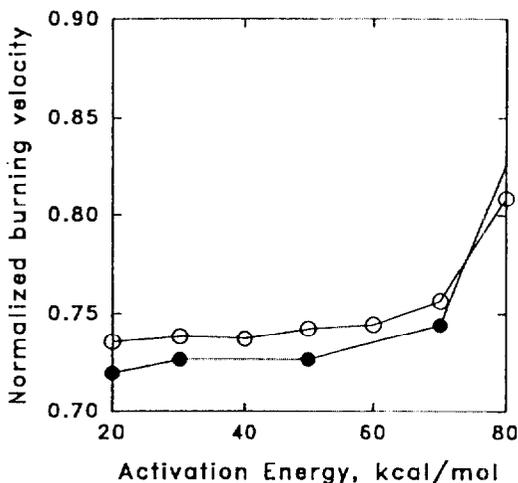


Fig. 3 Dependence of burning velocity on the activation energy of decomposition reaction. Closed circles – HOPO product; open circles – PO₂ product (stoichiometric flame, DMMP 0.09%)

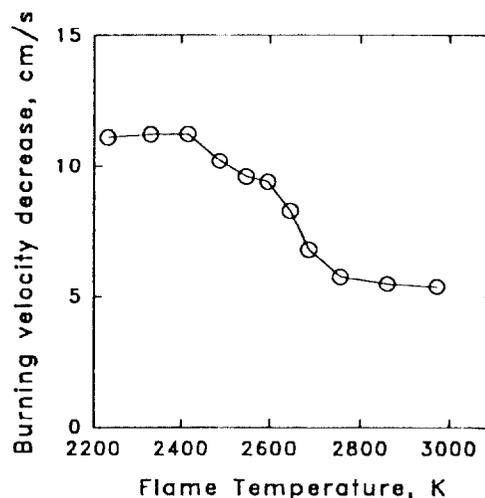


Fig. 4 Dependence of burning velocity decrease on flame temperature. Stoichiometric flame, 0.09% DMMP.

change of flame structure and detailed chemistry influencing dopant effectiveness. They also indicated that under no circumstances was flame promotion by phosphorus compounds observed.

Numerical calculations do not show that addition of DMMP leads to promotion effects in the temperature range 2100-3000K. Fig. 4 contains the dependence of burning velocity decrease due to inhibition on flame temperature. The decrease of nitrogen content in mixture $2yO_2 + xN_2 + yCH_4 + 0.09\%DMMP$ is used to provide the change of flame temperature. The same decrease of burning velocity per inhibitor quantity is observed in the flame temperature range 2200-2500K. Increase of flame temperature higher than 2500 K leads to decrease of inhibitor influence. Nevertheless, the crossover point was not observed until flame temperature corresponding to stoichiometric methane/oxygen flame. The decrease of inhibitor effect is mostly due to the relative increase of rates of formation of species of radical pool in comparison with recombination rates P-species with chain carriers.

Saturation of inhibition effect.

Calculations were performed for increasing additive loading until a burning velocity of 5 cm/s has been achieved. This is assumed as the extinction level since heat losses should be sufficiently large. All these calculations have been conducted in the framework of the gas phase model without taking into account condensation processes. The modeling results show strong saturation effect with the increase of the inhibitor concentration, e.g., decrease of burning velocity down to 10cm/s requires loading less than 0.9 %; an additional 1.4 % of DMMP is needed to decrease burning velocity from 10 cm/s down to the extinction level. Such strong saturation effect leads to a substantial increase in extinction concentration (2.3%) and to a decrease of inhibitor efficiency relative to CF₃Br.

Table 4 contains the extinction concentrations for iron pentacarbonyl (gas phase model) [38] showing the possible minimum level of inhibitor concentration required for flame extinction. The

analysis of saturation effect strongly supports the use of composite inhibitor [2]. Additionally, the effect of phosphorus tribromide PBr_3 on methane/air flame has been studied. For decreases of burning velocity of 30%, the inhibition effectiveness of PBr_3 relative CF_3Br is approximately 7. Calculated extinction concentration of PBr_3 is in the range 0.7-0.9 % by volume.

Table 4. Calculated extinction concentrations (molar %) for stoichiometric methane/air flame

DMMP	CF_3Br	PBr_3	$\text{Fe}(\text{CO})_5^*$
2.3	3.5	0.7-0.9	0.3-0.5

* Calculated values depend on assumed rate constants.

Summary

Phosphorus-containing compounds are more efficient fire suppressants than CF_3Br . Calculations for agent loading level of flame suppression concentrations demonstrate the existence of a strong saturation effect. This leads to substantial increases in extinction concentration or to decreases in inhibitor effectiveness. Extinction concentrations of phosphorus-containing compounds are in the range 0.5-5% by volume.

The main contribution to the inhibition effect is due to reactions with simple phosphorus containing species: PO_2 , HOPO , and HOPO_2 . The important reactions of the inhibition cycle include reactions of species $\text{HOPO} \rightleftharpoons \text{PO}_2 \rightleftharpoons \text{HOPO}_2$ with scavenging of chain carriers. Phosphorus containing radicals, such as HPO , PO , PO_2 , HOPO and HOPO_2 , catalytically recombine H and OH . Since the simple phosphorus-containing radicals participate in the main inhibition reactions, the form of the parent compound is probably unimportant. To obtain the agreement with experimental data on relative inhibition efficiency (DMMP, TEP) in comparison with CF_3Br , increases in the rates of PO_2 radical recombination reactions are required.

The important assumption used in this work is that the phosphorus content determines the inhibition properties of P-containing agents. For initial conditions considered (stoichiometric methane/air flame, 1 atm) the decomposition processes of phosphorus compounds do not influence results until the level of overall activation energy reaches 60 kcal/mol. The results demonstrate that details of agent destruction mechanism with overall activation energy of decomposition less than 50 kcal/mol will probably have a small effect on flame propagation. It should be noted that there exist some experimental data showing possible influence of parent molecule on fire suppression properties (data of Lask and Wagner for PBr_3 and PCl_3 [3]; large extinction concentration of $\text{P}_3\text{N}_3\text{F}_6$ obtained in the work [14]). The calculations do not demonstrate the possible promotion effect of DMMP, discussed in literature, on methane flame for the flame temperature range 2200-3000K.

REFERENCES

1. Halon Replacements: Technology and Science (Miziolek, A.W. and Tsang, W., Eds), ACS Symp. Ser. 611, Washington, DC, 1995.

2. Noto, T., Babushok V. I., Hamins, A., Tsang, W. Inhibition Effectiveness of Halogenated Compounds. *Combustion and Flame*, 1998, vol. 112, No 1/2, pp.147-160.
3. Lask, G., Wagner, H.G. Influence of additives on the velocity of laminar flames. 8-th Symp. (Int.) on Combustion, 1960, pp.432-438.
4. Hastie, J.W., Bonnell, D.W. *Molecular Chemistry of Inhibited Combustion Systems*. NBSIR 80-2169, 1980.
5. Rosser, W.A.Jr., Inami, S.H., Wise, H. The Quenching of Premixed Flames by Volatile Inhibitors. *Combust.Flame*, 1966, v.10, No 3, pp.287-294.
6. Miller, D.R., Evers, R.L., Skinner, G.B. Effects of Various Inhibitors on Hydrogen-Air Flame Speeds. *Comb.Flame*, 1963, 7, pp.137-142.
7. McHale E.T. Survey of Vapor Phase Chemical Agents for Combustion Suppresion. *Fire Res.Abstr.*, 1969, 11, No 2, pp.90-104.
8. Baratov, A.N. Chemical Inhibition of Flame. *J.All-Union Chem.Soc.Mendeleev*, 1967, 12, No 3, pp.276-284. (in Russian).
9. Friedman, R. Survey of Chemical Inhibition in Flames. *Fire Research Abstracts and Reviews*, 1961, vol.3, pp.128-132.
10. Wagner, H.G. Studies of Inhibitors as Anticatalytic Extinction Agents (Preliminary Report), Research contract No.3/55, 1955 (cited in: Morrison, M.E., Scheller, K., 1972, *Combust.Flame* 18, pp.3-12).
11. MacDonald, M.A., Jayaweera, T.M., Fisher, E.M., Gouldin, F.C. Inhibition of Non-Premixed Flames by Phosphorus-Containing Compounds. *Combust.Flame*, 116:166 (1999).
12. MacDonald, M.A., Jayaweera, T.M., Fisher, E.M., Gouldin, F.C. Variation of Chemically Active and Inert Flame-Suppression Effectiveness with Stoichiometric Mixture Fraction. 27-th Symp.Int.Combustion, 1998.
13. Purdue Research Foundation and Department of Chemistry, Purdue University. Final Report on Fire Extinguishing Agents for the Period 1 September 1947 to 30 June 1950 (Contract W-44-009 eng-507 with Army Eng.Res. And Dev.Labs), West Lafayette, IN, 1950.
14. Skagg, R.R., Daniel, R.G., Miziolek, A.W., McNesby, K.L. Spectroscopic Studies of Flame Inhibition in an Opposed Flow Propane/Air Flame. *Proceedings of Joint Meeting of US Sections of the Combustion Institute*, 1999, pp.575-578.
15. Miller, W.J. Inhibition of Low Pressure Flames. *Combust.Flame*, 1969, 13:210-212.
16. Ibricu, M.M., Gaydon, A.G. Spectroscopic Studies of the Effect of Inhibitors on Counterflow Diffusion Flames. *Combust.Flame*, 1964, 8, pp.51-62.
17. Jorissen, W.P., Booy, J., van Heiningen, J. *Recueil des Travaux Chimiques des Pay-Bas*, vol.51, pp.868-877, 1932.
18. Ewing, C.T., Faith, F.R., Romans, J.B., Hughes, J.T., Carhart, H.W. Flame Extinguishment Properties of Dry Chemicals: Extinction Weights for Small Diffusion Pan Fires and Additional Evidence for Flame Extinguishment by Thermal Mechanisms. *J.Fire Prot.Engr*, 1992, 4(2), pp.35-52.
19. Baratov, A.N., Vogman,L.P. *Fire Suppression Powder Compositions*. Moscow, "Stroiizdat", 1982
20. Hertzberg, M., Cashdollar, K.L., Zlochower, I., Ng, D.L. Inhibition and extinction of explosions in heterogeneous mixtures. 20-th Symp. (Int.) on Combustion, 1984, pp.1691-1700.
21. Choi, T., Rahimian, S., Essenhigh, R.H. Studies in Coal Dust Explosions: Influence of Additives on Extinction of High Intensity Coal Dust Flames. 21-st Symp.(Int.) on Combustion. 1986, pp.345-355.
22. Hertzberg, M., Cashdollar, K.L., Jazara, C.P. 18-th Symp. (Int.) on Combustion, 1981, pp.717-726.
23. Grumer, J. Recent Research Concerning Extinguishment of Coal Dust Explosions. 15-th Symp.(Int.) on Combustion, 1974, pp.103-114.
24. Richmond, J.K., Liebman, I., Brusak, A.E., Miller, L.F. 17-th Symp.(Int.) Combustion, 1979.
25. Kordylewski, W. Amrogowicz, J. Comparison of NaHCO_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ Effectiveness as Dust Explosion Suppressants. *Combust.Flame*, 1992, 90, pp.344-345.
26. Amrogowicz, J., Kordylewski, W. Effectiveness of Dust Explosion Suppression by Carbonates and Phosphates. *Combust.Flame*, 1991, 85, pp.520-522.
27. Hastie, J.W. *High Temperature Vapors*. Academic Press, 1975.
28. Kaizerman, J.A., Tapscott, R.E. *Advanced Streaming Agent Development*. Vol.3. Phosphorus

- Compounds, NMERI, UNM, Albuquerque, NM, 1996.
29. Liftke, J.L., Moore, T.A., Tapscott, R.E. *Advanced Streaming Agent Development. Vol.5. Laboratory-Scale Streaming Tests.* NMERI, UNM, Albuquerque, NM, 1996.
 30. Twarowski, A. Reduction of a Phosphorus Oxide and Acid Reaction Set. *Combust.Flame*, 94:91-107(1993).
 31. Werner, J.H., Cool, T.A. A Kinetic Model for the Decomposition of DMMP in a Hydrogen/Oxygen Flame. *Combust.Flame*, 1999, 117, pp.78-98.
 32. Mokrushin, V., Bol'shova, T., Korobeinichev, O.P. A Kinetic Model for the Destruction of TMP in a Hydrogen/Oxygen Flame, unpublished.
 33. Mallard, W.G., Linstrom, P.J., Eds., *NIST Chemistry WebBook, NIST Standard Ref. Database 69, 1998* (<http://webbook.nist.gov>).
 34. *Thermodynamic Properties of Individual Substances.* Eds Gurvich, L.V., Glushkov, V.P. NIST special data base 5, IVTANTHERMO-PC.
 35. Melius, C. http://herzberg.ca.sandia.gov/carl_melius.html/
 36. Zegers, E.J.P., Fisher, E.M. *Combust.Sci.Technology*, 1998, 138, pp.85-103.
 37. Korobeinichev, O.P., Il'in, S.B., Mokrushin, V.V., Shmakov, A.G. *Combust.Sci.Technol.* 116-117:51-67 (1996).
 38. Rumminger, M.D., Reinelt, D., Babushok, V., Linteris, G.T. Numerical Study of the Inhibition of Premixed and Diffusion Flames by Iron Pentacarbonyl. *Combustion and Flame*, 116:207-219, 1999.