

Phosphorus Nitrides As Fire Extinguishing Agents

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As part of the U. S. Air Force Advanced Streaming Agent Program and the Advanced Agent Working Group (AAWG) program on total-flood agents, the Center for Global Environmental Technologies (CGET) is investigating phosphorus nitrogen compounds as fire extinguishing agents. Phosphorus nitride compounds, also known as phosphazenes, contain a backbone of alternating phosphorus and nitrogen atoms either as cyclic ring structures or linear chains (but which also may contain cyclic substituents along the chain). The latter are often polymers whose exact structures have not been fully characterized. The phosphorus atoms of the cyclic or linear backbones may contain substituents which include halogens, alkyl groups, and/or aryl groups. CGET has synthesized a mixture of fluorinated phosphazenes and has tested the compounds in the cup burner and laboratory streaming apparatus. Initial cup burner results showed that these agents extinguish flames at concentrations as low as 1/10th that of halon.

INTRODUCTION

In the 1990 National Institute of Standards and Technology (NIST) chemical search, phosphorus halides were examined and discarded as too toxic and too hydrolytically unstable for use as fire extinguishing agents.¹ Phosphorus and nitrogen containing salts, such as ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), have long been known to be effective fire suppressants.² However, these salts are not regarded as clean fire extinguishants, and thus, are not suitable for many halon replacement applications. Recently, we reviewed the literature in search of novel phosphorus-containing compounds that hold potential as halon replacement agents. The presence of two elements active in flame retardancy (phosphorus and nitrogen), which may behave synergistically, makes phosphorus nitrides or phosphazenes particularly attractive in

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preventing or extinguishing flames.³ Addition of halogen atoms to the phosphazene backbones increases the flame retardancy⁴, and presumably the flame extinguishing capability.

Historically, phosphorus nitride chemicals have been investigated and used extensively as flame retardants or fire-proofing additives for plastics, textiles, synthetic fabrics, foam, and rubbers.³ However, in most of these uses, phosphazenes are added either as a solid to materials being manufactured or are applied as coatings to materials that are being fire-proofed. No references have been found where a phosphorus nitride, in any state or form, is used to extinguish flames.

WHAT ARE PHOSPHAZENES?

Phosphorus nitride compounds or phosphazenes include two groups of chemicals: cyclic compounds containing alternating phosphorus and nitrogen atoms forming a ring structure and linear compounds having chain-like backbones of alternating phosphorus and nitrogen atoms. Linear phosphazenes may also contain cyclic substituents bound to either the phosphorus or nitrogen atoms along the chain backbone. The latter are often, but not always, polymers whose exact structures have not been fully characterized. Examples are shown below for a six-member cyclic ring containing three alternating P-N subunits referred to as a cyclic trimer (I), for an eight-member cyclic ring comprised of four alternating P-N subunits representing a tetramer (II), and for a linear polymer containing multiple P-N subunits (III).⁵

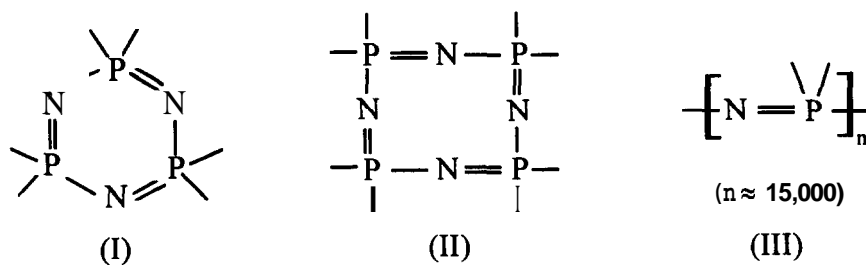


Figure 1. Phosphazene Schematic Examples

The P-N backbones may contain substituents, usually bound to the phosphorus atom, such as the halogens fluorine (F), chlorine (Cl), bromine (Br), and iodine (I); imino groups (=NH); alkyl and substituted alkyl groups; *aryl* and substituted aryl groups; **and** alkoxides. Alkyl

groups are groups containing only carbon and hydrogen atoms such as methyl (-CH₃), ethyl (-CH₂CH₃), n-propyl (-CH₂CH₂CH₃), and iso-propyl (-CH(CH₃)₂). Substituted alkyl groups are alkyl groups in which one or more of the hydrogen (H) atoms have been replaced by other atoms or groups. Examples are -CH₂F, -CHF₂, and -CF₃. Aryl groups are groups containing only carbon and hydrogen atoms in “aromatic” rings. The most common of these is the phenyl group, -C₆H₅. Substituted aryl groups have one or more of the hydrogen atoms replaced by some other substituent. An example is perfluorophenyl, -C₆F₅. Alkoxide groups have the structure -OR, where R is an alkyl or a substituted alkyl group. By changing the substituents bound to the P-N backbone and varying molecular weight, the physical/chemical properties of phosphazene materials can be changed considerably. Many cyclic phosphazenes are either liquids or low-melting crystalline solids.⁴ As molecular weight increases by either increasing the size of the substituent or the number of P-N subunit, oils and greases are formed. High molecular weight elastomers and thermoplastics are ultimately formed. Table 1 demonstrate how the substituents can influence the melting and boiling points of phosphazenes.

Table 1. Melting and Boiling Points of Selected Phosphazenes*

Chemical Name	Chemical Formula	Boiling Point, °C	Melting Point, °C
Hexachlorotriazaphosphazene	N ₃ P ₃ Cl ₆	256	114
Hexafluorotriazaphosphazene	N ₃ P ₃ F ₆	50	28
Chloropentafluorotriazaphosphazene	N ₃ P ₃ ClF ₅	81	-30
Dichlorotetrafluorotriazaphosphazene	N ₃ P ₃ Cl ₂ F ₄	114.7	-46
Trichlorotrifluorotriazaphosphazene	N ₃ P ₃ Cl ₃ F ₃	150	-35
Decafluoropentaazaphosphazene	N ₅ P ₅ F ₁₀	120	-50
Hexamethoxytriazaphosphazene	N ₃ P ₃ (OCH ₃) ₆	114-128**	48
Hexaethoxytriazaphosphazene	N ₃ P ₃ (OCH ₂ CH ₃) ₆	114-116**	---
Dimethylaminopentaphenoxy-triazaphosphazene	N ₃ P ₃ (OC ₆ H ₅) ₅ (N(CH ₃) ₂)	---	-11

* Reference 5

** @ 0.1mm

HEALTH EFFECTS OF PHOSPHAZENES

The literature pertaining to health effects of phosphazenes is quite limited. However, promising indication of low toxicities exist in what literature is available and from personal communications with experts in the field of phosphazene chemistry field (H. R. Allcock, C. W. Allen, R. E. Singler). For example, a number of phosphazene polymers and cyclics are being investigated for use in biomedical applications where these materials are used to form biodegradable controlled drug delivery systems⁶ or coatings for artificial implants.’ In the biodegradable controlled drug delivery systems, capsules of phosphazene polymers [poly(imidazole methylphenoxy)phosphazene] are filled with drugs (progesterone, in this case) and implanted under the skin of test animals.⁶ No inflammation was observed around the implant site, the capsules disintegrated making surgical removal of the drug delivery device unnecessary, and the drug was released from the capsule over an extended time period. In the study on coatings for artificial implants, the researchers found that none of the phosphazenes tested were mutagenic in an AMES-like test, but several phosphazenes possessed antibacterial activity.’ In this case it was important to differentiate the difference between mutagenic potential and antibacterial potential because for use on implants the antibacterial aspect is desirable whereas the mutagenic potential could have repercussions for the host. This concept may have significant when interpreting results from other studies.

Ethyl Corporation performed a number of genotoxicity tests with $P_3N_3Cl_6$ similar to the battery of tests performed with other halon replacement candidates.’ Results in these studies were both positive and negative for genetic alterations, similar to results with most halocarbon chemicals. It was noted throughout the reports documenting these studies that the experimental results were speculative because the researchers had difficulty finding a solvent to dissolve the phosphazene that in itself was not genotoxic. The agent usually ended up precipitating out of solution making the results not meaningful.

Because a number of organophosphates **are** used **as** pesticides, the pesticidal properties of phosphonitrilic chloride, $P_3N_3Cl_6$, was tested at the Department of Entomology at the University of Illinois in the 1940s.⁹ The compound was found to be considerably more potent at

exterminating “greenhouse leaf tyer” than acid lead arsenate, which was used in control tests. The phosphonitrilic chloride had a median lethal dose of 0.08 mg/g body weight, whereas the control agent required 0.205 g/g body weight. It was noted that the phosphorus nitrilic chloride also produced injury to foliage in the test chambers, making commercial potential as a pesticide impractical.

Renaud anecdotally described the physiological effects of phosphonitrilic chlorides, although it is difficult to discern whether the author described effects due phosphazenes themselves or to their combustion products.” In his work on the cracking of highly polymerized forms, Renaud mentions “severe eye pains, a very general pronounced apathy, and finally difficulty breathing, as resulting from excessive exposure to the gaseous decomposition products.” The physiological effects were not immediate and did not become apparent until several hours after the exposure. The symptoms of respiratory discomfort were alleviated by breathing air containing small amounts of ammonia gas. This description alludes to the possibility of hydrogen chloride exposure, which is not an unlikely degradation product formed by the decomposition of chlorophosphazenes.

Extensive toxicity evaluations, including acute toxicity tests, inhalation, and skin absorption kinetic studies, and 21-day repeated inhalation and dermal exposure testing, were performed by the Toxicology Detachment of the Naval Medical Research Institute on $N_3P_3(OCH_2CF_3)_{3.5}(OC_6H_5)_{1.25}(OC_6H_4-m-CH_3)_{0.87}(OC_6H_4-p-CH_3)_{0.38}$, a fire resistant hydraulic fluid.” The toxicity tests were chosen to determine the potential health effects from exposure to shipboard hydraulic fluids through dermal contact due to spills or leaks or from aerosol inhalation from pressurized system leaks. Test data showed “no evidence of toxicity” by inhalation or dermal absorption. This phosphazene compound was poorly absorbed into the body by any exposure route tested and appeared to produce little or no effect when artificially introduced into the body. It was concluded that this material was therefore “unlikely to have more than minimal health consequences if used in shipboard hydraulic system applications.”⁴

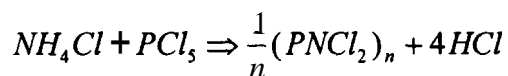
COMMERCIALY AVAILABLE PHOSPHAZENE

Despite the interest in phosphazenes in the 1970s as flame retardant materials, commercial sources for these chemicals are limited. The most widely available chemical is $P_3N_3Cl_6$. From discussions with experts in the field (H. R. Allcock, C. W. Allen, R. E. Singler), the purest samples of this chemical are acquired from Japan, either Otsuka Chemical Company or TCI America Inc. at a cost of just under \$1/g. Strem Chemicals also produces the chloride trimer at about the same price. Albemarle Corp. (originally Ethyl Corp.) also has manufactured the chemical in the past. Otsuka Chemical Company makes several other phosphazenes commercially [$P_4N_4Cl_8$, $P_3N_3(NH_2)_6$, and $P_xN_x(OCH_2CH_2CH_3)_{2x}$ where $x = 3, 6, \text{ or } 9$].¹² A number of other pilot- or laboratory-scale materials [$N_3P_3(OC_3H_7)_6$, $N_3P_3(OC_6H_5)_6$, $N_3P_3(OC_6H_5)_3(OC_6H_4OH)_3$, $2,2-N_3P_3(OC_6H_5)_4(NH_2)_2$, $N_3P_3(OCH_2CF_2CF_3)_3(OCH_2C_4F_8H)_3$, $N_3P_3(OCH_2C_4F_8H)_6$, and $[N_3P_3(NHC_6H_5)_6]$] are also available from Otsuka Chemical, Nippon Soda and others.³

The Army Materials Technology Laboratory, in cooperation with the Naval Surface Warfare Center, has developed “nontoxic, fire-resistant phosphazene hydraulic fluids.” Ethyl Corporation produce hundreds of gallons of phosphazene ester hydraulic fluid, $N_3P_3(OCH_2CF_3)_{3.5}(OC_6H_5)_{1.25}(OC_6H_4\text{-}m\text{-}CH_3)_{0.87}(OC_6H_4\text{-}p\text{-}CH_3)_{0.38}$, that met the Navy’s physical and chemical property specifications. However, after much work, including a number of toxicology tests (see section on health effects), the Navy curtailed its development program of phosphazene hydraulic fluids because the projected cost was \$12/lb.

SYNTHESIS OF CYCLIC PHOSPHAZENES

The simplest preparation of cyclophosphazenes is a modification of the process developed by H. N. Stokes in the late 19th century.¹³ Ammonium chloride and phosphorus pentachloride are made to react, either in the dry state or in a suitable refluxing solvent:



The products consist of the cyclic phosphazenes $(\text{PNCl}_2)_x$ ($x = 3-17$) and a linear polymer $(\text{PNCl}_2)_n$ with average molecular weight in the range 5000-18,000 daltons. A considerable amount of information has been generated in the last 50 years concerning influences on the yields of certain products by reaction conditions, catalysts, materials, etc. A detailed analysis of the conditions affecting the yields of cyclic products and description of separation methods was reported by Emsley and Udy, 1971.¹⁴

In our laboratory, $\text{N}_3\text{P}_3\text{Cl}_6$ was prepared using equimolar quantities of phosphorus pentachloride and ammonium chloride. This chemical was then used as a starting material for the synthesis of other trimeric phosphazenes. Originally, chlorofluorophosphazenes were selected for study as streaming agent candidates because of their ease of synthesis and attractive physical properties (high boiling points and low melting points as seen in Table 1).

The synthesis of fluorinated cyclotriphosphazenes was achieved by anionic fluorination, which effects the metathetical replacement of chlorine with fluorine on the phosphorus atoms in the ring.⁵ The literature indicates that several fluorinating agents have been used successfully in this reaction, including silver and lead(II) fluorides, potassium fluorosulfite, and sodium fluoride. The reaction proceeds by the nucleophilic attack of fluoride ion at a phosphorus atom, followed by the elimination of chlorine. The electron withdrawing effect of the newly attached fluorine atom renders the phosphorus even more susceptible to attack by fluoride and the attachment of the second fluorine atom occurs rapidly. By this mechanism, geminally substituted products are formed preferentially and compounds with an even number of substitutions predominate.

On three separate occasions, we performed fluorination using sodium fluoride as the fluorinating source. A mixture of partially and fully fluorinated phosphazenes was obtained. Initially, no attempt was made to separate the various fluorinated species since very small quantities were synthesized and testing of the fire suppression effectiveness could first be performed on the mixtures. Products were confirmed using gas chromatography/mass spectrometry and quantification was performed using ^{31}P and ^{19}F NMR. Several lots of mixed $\text{P}_3\text{N}_3\text{F}_6$, $\text{P}_3\text{N}_3\text{ClF}_5$, $\text{P}_3\text{N}_3\text{Cl}_2\text{F}_4$, and $\text{P}_4\text{N}_4\text{F}_8$ (a product formed from contamination of chlorinated tetramer with the chlorinated trimer starting material) compositions were synthesized in the

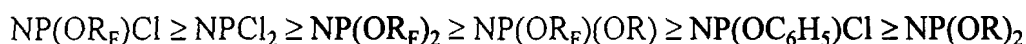
NMERI Chemistry Laboratory. While the exact composition of these lots has not been determined, component identifications are indicated in Table 2.

Table 2. Phosphazene Composition Synthesized at NMERI

Composition	Major Chemical Species
Composition A	$P_3N_3F_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, and $P_4N_4F_8$
Composition B	$P_3N_3F_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, and $P_4N_4F_8$
Composition C	$P_3N_3F_6$, $P_3N_3ClF_5$, $P_3N_3Cl_2F_4$, $P_4N_4F_8$, $P_5N_5F_{10}$, and $P_6N_6F_{12}$

FIRE SUPPRESSION AND EXPLOSION PREVENTION TESTING

Compositions A and B were tested in the NMERI cup burner using n-heptane as fuel. Composition A had an extinguishment concentration of 0.3 % v/v, whereas Composition B had an extinguishment concentration of 1.2 % v/v. The difference in the results obtained between the two mixtures indicates that a more active fire suppressant species exists in Composition A, possibly a chlorinated species since there appears to be a higher proportion of chlorinated product in Composition A. These findings are not unexpected since it has been stated that the flame retardancy efficiency of phosphazene derivatives, although not the same as flame suppression capability, exhibits the following order:



where $R_F = CH_2(CF_2)_nH$, $n = 2, 4, 6$ and $R = \text{alkyl}$.³ Future cup burner testing will be performed in order to identify the active chemical species. Nonetheless, even the less effective Composition B only required half as much chemical to extinguish the flame compared to Halons 1211 or 1301.

The explosion prevention or inertion capability of Composition C was measured in the NMERI 7.9-liter explosion sphere. An explosive overpressure was generated by sparking a mixture of propane and air with a DC discharge. When 2.0 % v/v Composition C was added to the propane/air mixture, the explosive overpressure was reduced by 58%. When 2.83 % v/v

Composition C was added to the propane/air mixture, the explosive overpressure was reduced by **84 %**. The results are presented in Table 3. In another series of tests, a higher explosive overpressure was generated by sparking a different mixture propane and air with a DC discharge. The control overpressure was higher than that described above because the propane concentration was further away from the upper flammability limit, making the mixture more flammable. When 3.11 % v/v Composition C was added to the propane/air mixture, the explosive overpressure was reduced by 92%. When 3.11 % HFC-227ea was added to the propane/air mixture, the explosive overpressure was reduced by 72 %. These results are also shown in Table 3.

Table 3. Explosion Prevention Effectiveness

Propane:Air Ratio = 9:91	Test 1: Composition C	Test 2: Composition C
Concentration of Agent	2.0 %	2.83 %
Control Overpressure	7.26 psi	7.26 psi
Suppressed Overpressure	3.06 psi	1.13 psi
Percent Reduction	58 %	84 %
Propane:Air Ratio = 8:92	Test 3: Composition C	Test 4: HFC-227ea
Concentration of Agent	3.11 %	3.11 %
Control Overpressure	21.46 psi	21.46 psi
Suppressed Overpressure	1.72 psi	6.21 psi
Percent Reduction	92 %	72 %

CONCLUSIONS

The investigation into the use of phosphazenes as halon replacement agents has revealed a class of compounds that are highly effective in flame suppression and show promise in explosion prevention. Physical properties of phosphazenes can vary depending on the number of P-N subunits and the substituents bound to the P-N backbone. Many, but not all, phosphazenes are very high boiling compounds, making them unsuitable as Halon 1301 “drop-in” replacement agents. However, such phosphazenes are potentially appropriate for streaming agents or for misted total-flooding agents. Dissolving high boiling phosphazenes in appropriate solvents may

make suitable Halon 1301 replacement agents. Several materials are commercially available, mainly from Japanese sources, and synthesis of other compounds are taking place in small laboratories around the country. Although the toxicity of many of the chemicals has not been studied in detail, except for one a high molecular weight phosphazene being investigated as a hydraulic fluid for the Navy, what is **known** suggests that selected compounds may have sufficiently low toxicities to warrant further research.

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