

A Novel Class of Halogenated Phosphate Fire Retardants for Use in Polypropylene

JAMES A. ALBRIGHT and CHESTER J. KMIEC, *Velsicol Chemical Corporation, Ann Arbor, Michigan 48105*

Synopsis

A novel class of 3,9-haloneopentoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxides has been synthesized. The method of preparation and physical properties of the compounds are described. The chemicals have been found to be excellent fire retardants for polypropylene. A polypropylene composition meeting the UL-94 V-0 specification can be achieved on both $\frac{1}{8}$ and $\frac{1}{16}$ -in.-thick specimens with as little as 15% addition of one of these compounds. The use of a typical inorganic synergist such as antimony oxide is not required. The spirodiphosphates described exhibit good light, thermal, and hydrolytic stability.

INTRODUCTION

Over the past several decades, a much greater concern has developed for the fire safety of products formulated from plastics. Most plastics are extremely flammable and require the use of fire retardant additives or reactives to decrease potential fire hazards. A considerable effort has been underway within the plastics industry to meet an ever increasing number of regulations governing flammability.¹

Polypropylene is a plastic which over the years has been found to be extremely difficult to flame retard. In order to obtain a flame retardant polypropylene meeting the UL-94 V-0 specification, generally as much as 27% flame retardant and 13% antimony oxide synergist are required. The flame retardants most often used for this application are based upon Diels-Alder adducts of hexachlorocyclopentadiene.² These high loadings of fire retardant additives limit the applications of polypropylene requiring a high degree of flame retardance due to the adverse effect upon physical properties.

This paper will describe a new class of halogenated phosphates which has been found to be effective as flame retardants for polypropylene. Polypropylene meeting the UL-94 V-0 specification can be achieved with specimens of both $\frac{1}{8}$ -in. and $\frac{1}{16}$ -in. thickness with as little as 15% additive without the use of inorganic synergists.

RESULTS

Chemistry and Physical Properties

A novel class of 3,9-haloneopentoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxides was prepared. This class of spirodiphosphates based upon pentaerythritol is illustrated in Figure 1. The spirodiphosphates were prepared by the condensation of 2 moles of the

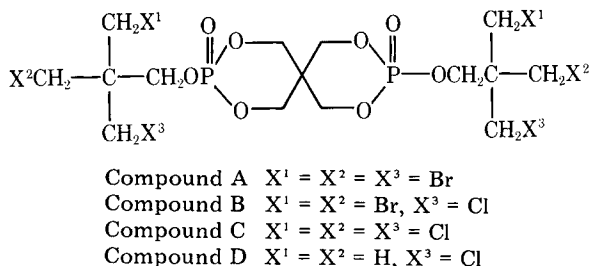


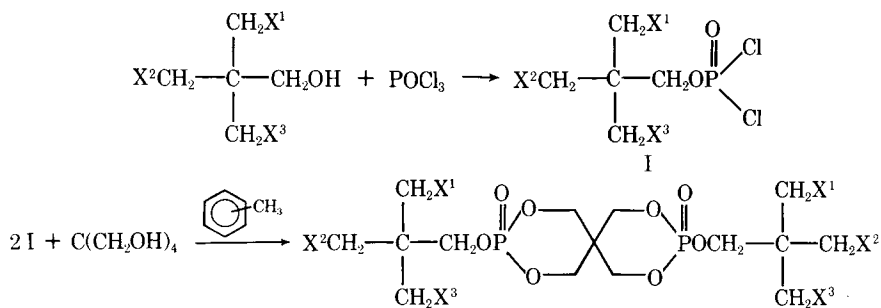
Fig. 1. Structure of 3,9-haloneopentoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxides.

desired halogenated neopentyl dichlorophosphate with 1 mole of pentaerythritol. These reactions were carried out in an inert solvent such as toluene using a magnesium salt catalyst. The halogenated neopentyl dichlorophosphates were usually prepared by the reaction of the halogenated neopentyl alcohol with an excess of phosphoryl chloride. Figure 2 illustrates the synthetic scheme used to prepare the spirodiphosphates.

The spirodiphosphates of this class are high melting crystalline white solids which are essentially insoluble in most common organic solvents.

An essential feature of a fire retardant for plastics is good thermal stability. It is important that a flame retardant be able to withstand high processing temperatures without decomposition or volatilization. A typical TGA/DSC of compound A is shown in Figure 3. A 5% weight loss by TGA is observed at 298°C, indicating the good thermal stability of these compounds. Furthermore, compound A has a melting point of 225°C making it melt blendable at normal processing temperatures for polypropylene and a number of other plastics. In addition to the good thermal stability of this class of halogenated phosphates, these compounds possess excellent hydrolytic stability. Leaching studies were carried out in a Soxhlet extractor for three weeks on UL-94 V-2 polypropylene specimens containing compound A, Figure 1. Little or no weight loss occurred with these samples, and retention of the initial flammability was maintained. These data are illustrated in Table I.

Compound A, a bromine-containing material, exhibits excellent light stability for a brominated flame retardant. Polypropylene samples containing 5, 12.5,



where X^1 , X^2 and X^3 are Br, Cl, or H (see Fig. 1)

Fig. 2. Method of preparation of 3,9-haloneopentoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxides.

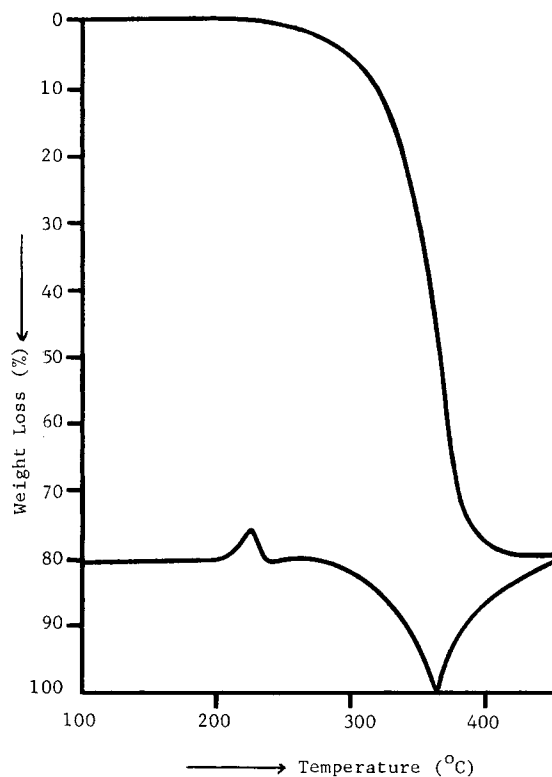


Fig. 3. Typical TGA/DSC of compound A.

and 15% of compound A were exposed to a xenon arc for 300 hr. Only a very slight discoloration of the samples was observed. The base resin also discolored slightly under these conditions. The data demonstrating this light stability can be found in Table II.

Flame Retardant Properties

A flame retardant plastic system may be defined as a plastic that passes a specific flammability test specification. This may be accomplished by modification of the polymer backbone or the use of flame retardant additives. One of the most commonly used methods for determining flame retardance for

TABLE I
Water Leaching Study Results with Flame-Retarded Polypropylene

Sample no. ^a	Time, weeks ^b	Weight loss, %	UL-94 ^c
1	0	0	V-2
2	1	0.3	V-2
3	3	0.3	V-2

^a Samples contained 5 wt-% compound A, Figure 1, in Hercules 6524 polypropylene.

^b Continuous Soxhlet extraction time with boiling water.

^c Thickness $\frac{1}{16}$ in.

TABLE II
Gardner Color Values for Polypropylene Exposed to 300 Hours of Xenon Arc

Concentration of flame retardant ^a	Unexposed ^b			Exposed			
	L	a	b	L	a	b	E
5	55.4	-1.3	-1.0	53.7	-1.9	1.1	1.8
5	54.4	-1.3	-0.6	52.1	-1.9	0.8	2.8
12	59.4	-1.1	0.7	56.4	-2.0	3.1	3.8
12	63.7	-1.1	1.0	61.7	-2.1	4.4	4.1
15	61.1	-0.7	2.4	59.4	-1.7	6.2	4.3
15	59.3	-0.5	3.2	58.8	-1.7	6.3	3.7
0	33.0	-1.0	-4.5	32.6	-1.2	-3.3	1.2
0	32.7	-0.9	-4.4	31.6	-1.2	-3.3	1.6

^a % Compound A, Fig. 1.

^b Gardner Tristimulus Colorimeter values.

polypropylene is the Underwriter Laboratory UL-94 test.³ The oxygen index determination is another test method for the evaluation of fire retardant efficiency in a specific polymer system.⁴ Although there are numerous examples in the literature of phosphorus/halogen compounds which show excellent oxygen index responses in polypropylene,⁵ a UL-94 V-0 rating in polypropylene cannot be achieved even at high concentrations of most of these flame retardants. There is little correlation between high oxygen index and the ability of a flame retardant to pass the more rigorous UL-94 test in polypropylene. Table III shows the UL-94 response of a series of compounds of this class. As can be seen from the table, a UL-94 V-0 can be achieved at a level as low as 12.5% for 1/8-in.-thick specimens using compound A.

At a 15% load level, a UL-94 V-0 rating is obtained for 1/16-in.-thick specimens using compound A. This can be achieved without the use of the usual inorganic synergists. In contrast, the commercial V-0 flame-retarded polypropylene system contains approximately 40% additives. It is also apparent from Table

TABLE III
UL-94 Vertical Burning Test Results for 3,9-Substituted 2,4,8,10-Tetraoxa-3,9-Diphosphaspiro[5.5]undecane-3,9-Dioxide in Hercules 6523 Polypropylene

Compound	% Br/Cl/P	% Additive	UL-94		Oxygen Index
			1/8 in.	1/16 in.	
A	54.9/0/7.1	5.0	V-2	V-2	—
A	54.9/0/7.1	6.25	V-2	V-2	25.5
A	54.9/0/7.1	9.0	V-2	V-2	26.5
A	54.9/0/7.1	12.5	V-0	V-2	27.5
A	54.9/0/7.1	15.0	V-0	V-0	—
A	54.9/0/7.1	18.0	V-0	V-0	24.0
B	40.9/9.8/7.8	6.25	V-2	—	24.0
B	40.9/9.8/7.8	10.0	V-2	—	25.0
B	40.9/9.8/7.8	12.5	V-0	V-2	25.5
B	40.9/9.8/7.8	15.0	V-0	V-2	23.5
C	0/38.3/11.1	18.0	HB	—	24.0
D	0/14.9/13.2	12.5	HB	—	19.5
D	0/14.9/13.2	18.0	HB	—	20.0
Control	—	—	HB	HB	18.0

III that better flame retardancy is achieved with the compounds that contain a higher percentage of bromine even though in these compounds the percent phosphorus is reduced. The chlorinated products (compounds C and D) are less effective.

Polypropylene with a UL-94 V-2 rating can be achieved with as little as 5% of compound A. Again, to obtain a V-2 classification, an antimony oxide synergist is not required.

Figure 4 is a plot of oxygen index versus concentration for compound A of this series. An interesting phenomenon is observed in which the oxygen index decreases at the higher concentrations. This is probably due to a lack of a plastification effect which occurs at the lower concentrations.

A comparison of the UL-94 response from Table III for sample A at an 18.0% level, sample B at a 6.25% level, and sample C at an 18.0% level indicates a complete range of V-0, V-2, and HB. All three of these samples exhibited the same oxygen index response of 24.0. These data exemplify the poor correlation of the oxygen index with the U-94 flame test in polypropylene for this class of compounds.

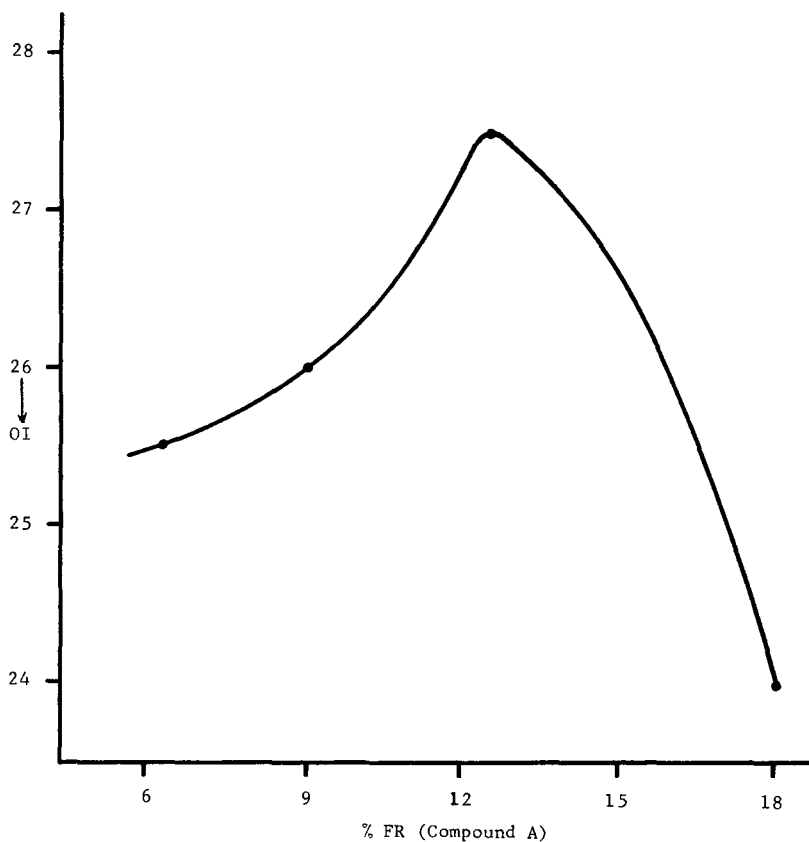


Fig. 4. Oxygen index response in polypropylene vs % compound A.

Physical Properties

Table IV is a list of important physical properties of compound A in polypropylene. For comparison, the physical properties of the unmodified base resin as well as those for a commercial system containing Dechlorane 515, a Diels-Alder adduct of hexachlorocyclopentadiene, are included. The physical properties of the polypropylene containing compound A are not as drastically affected as those containing Dechlorane 515.

CONCLUSIONS

A novel class of 3,9-disubstituted 2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]-undecane-3,9-dioxides has been discovered. When the 3,9-substituents are brominated neopentyl groups, these compounds were found to be excellent flame retardants for polypropylene. These new flame retardants, which can be used at low additive levels in polypropylene, possess excellent thermal, hydrolytic, and light stability. These compounds are also effective fire retardants in other polymer systems such as ABS, polystyrene, poly(butylene terephthalate), and poly(phenylene oxide).

EXPERIMENTAL

Preparation of 3,9-Bis[2,2-(dibromomethyl)-3-bromopropoxy]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-Dioxide (Compound A)⁶

A mixture of 500 g phosphoryl chloride and 0.4 g magnesium oxide was heated to 85°C and 300 g tribromoneopentyl alcohol was added in increments over a 1.25-hr period. The rapid evolution of hydrogen chloride was observed. The reaction mixture was heated at 85°C for 6 hr. The excess phosphoryl chloride was removed under vacuum, and 300 g toluene and 62.8 g pentaerythritol were added. The mixture was refluxed for 6.5 hr and additional toluene was added as needed. The mixture was cooled to room temperature, filtered, and dried.

The resultant white solid was washed successively with water, dilute aqueous ammonium hydroxide, and acetone. After drying at 100°C, 335 g (83%) of a white solid (mp 225°–228°C) resulted.

Preparation of 3,9-Bis[2,2-(dibromomethyl)-3-chloropropoxy]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-Dioxide (Compound B)⁶

To a solution of 279 g 2,2-dibromomethyl-3-chloropropyl dichlorophosphate in 300 ml toluene were added 0.5 g magnesium oxide and 47.7 g pentaerythritol. The mixture was refluxed for 12 hr and cooled, and the white precipitate was filtered. After washing the product with dilute aqueous ammonia, water, and methanol, the product was filtered and dried. A white solid, mp 212°–214°C, resulted.

In a similar manner, 3,9-bis[2,2-(dichloromethyl)-3-chloropropoxy]-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (compound C, mp 197°–200°C) and 3,9-bis(2,2-dimethyl-3-chloropropoxy)-2,4,8,10-tetraoxa-

TABLE IV
 Typical Physical Properties of Polypropylene Containing Compound A Compared with the Base Resin and a Commercial Standard in Hercules 6523 Polypropylene

Properties	Method	Polypropylene base resin			Compound A			Dechlorane 515/ Sb ₂ O ₃ , %	
		5%	12%	15%	27/13	24/12			
UL-94 Vertical burning test, 1/8 in.	—	V-2	V-0	V-0	V-0	V-0	V-0	V-1	
UL-94 Vertical burning test, 1/16 in.	—	V-2	V-2	V-0	V-0	V-0	V-0	V-2	
Izod Impact Strength, 1/2 in. × 1/8 in. ft.-lb/in. notch	ASTM-D256	1.3	1.2	1.2	1.2	1.2	1.2	1.2	
Tensile strength, psi	ASTM-D638	5332	5380	4973	3822	3631	3822	3631	
Flexural strength, psi	ASTM-D790	6641	7373	6693	6200	6000	6200	6000	
Flexural modulus, ×10 ⁵ psi	ASTM-D790	1.8	2.5	2.2	2.2	2.95	2.81	2.95	
Density, g/cc	ASTM-D792	0.903	0.931	0.951	—	—	—	—	
Melt flow index, g/10 min, cond. G	ASTM-D1238	6.2	10.4	19.1	4.9	4.6	4.9	4.6	

3,9-diphosphaspiro[5.5]undecane-3,9-dioxide (compound D, mp 282°–285°C) were also prepared.⁶

Flame Retardant Polypropylene Preparation

The flame retardant additive was first dry blended with the polypropylene base resin and then compounded using a Brabender Prep-Center fitted with a high-shear compounding mixer. Since the capacity of the mixing bowl was only 300 g, a dip technique for the compound was utilized which consisted of fluxing 300 g of the dry blend mixture and the removal of approximately 200 g of the fluxed mixture, followed by the addition of more of the dry blend mixture until the total dry blend had been compounded. Each charge was compounded under the same conditions: 400°F temperature, 120 rpm, with 2–3 min of compounding time.

Each flame-retarded system was then let down to the desired level by dry blending the ground concentrate and the base resin. The base resin and flame-retarded systems were injection molded using a Newbury 30 ton injection molding machine to obtain the necessary test specimens. The following is a set of standard injection molding conditions by which all of the systems were injection molded: rear zone, 410°F; front zone, 440°F; nozzle, 14°F; injection speed, 4–5 sec; cycle time, 60 sec; mold temperature, 86°F; flow mold time, 1–2 sec. The thus prepared specimens were subjected to various tests, and the data derived from said tests are reported in the tables.

References

1. C. J. Hilado, *Fire Technol.*, **11**, 282 (1975).
2. J. Green, *Plast. Technol.*, **44** (1975).
3. Underwriter's Laboratories, Inc., subjects 94/746, September 17, 1973.
4. ASTM Bulletin No. D-2863-74, *1976 Annual Book of ASTM Standards*, American Society for Testing and Materials, 1976, p. 701.
5. J. W. Lyons, *The Chemistry and Uses of Fire Retardants*, Wiley-Interscience, New York, 1970.
6. J. A. Albright, U.S. Pat. 3,978,167 and U.S. Pat. 3,997,505 (1976).

Received May 2, 1977