PATENT SPECIFICATION

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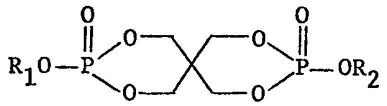
(54) FLAME-RETARDANT POLYOLEFIN POLYMERIC COMPOSITIONS CONTAINING 3,9-HALOPHENOXY-2,4,8,10-TETRAOXA-3,9-DIPHOSPHASPIRO(5.5)UNDECANE-3,9-DICHALCOGEN

(71) We, VELSICOL CHEMICAL CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 341 East Ohio Street, Chicago, Illinois 60611, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to 3,9-halophenoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dichalcogen compounds as flame retardants.

U.S. Patent Specification No. 3,090,799 (hereinafter referred to as Wahl et al.) discloses plasticisers comprising phosphoric acid esters of the generic formula:

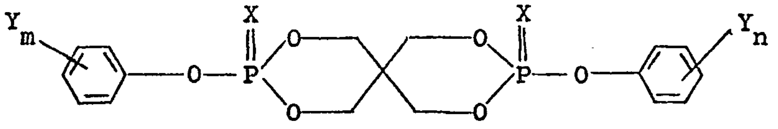


in which R_1 and R_2 represent aliphatic, cycloaliphatic, heterocyclic or aromatic radicals, the hydrogen atoms of which can be substituted, for example, by halogen, ester, keto, nitrile, or amino groups. R_1 and R_2 can be identical or different. Because of the relatively high phosphoric acid content of the above compounds of Wahl et al., the compounds are stated by Wahl et al. to impart a greater reduction in the combustibility for the same addition of plasticizer; in other words, smaller additions of Wahl et al.'s compounds are sufficient for producing the same effect.

The plasticizers of Wahl et al. are stated as being useful in the production of shaped plastic compositions, such as foils, fiber and lacquer materials, as well as molding materials, from organic compounds of high molecular weight, such as cellulose esters, cellulose ethers, polyvinyl compounds, for example polyvinyl chloride, polyvinyl acetate, polystyrene, chlorinated rubber, alkyd resins, polyesters, polymers of acrylic acid and derivatives thereof, polyethylene, polypropylene and other polymer and copolymers. Wahl et al. further state that their phosphoric acid ester compounds may be used in any suitable thermoplastic resin.

It has now been surprisingly discovered that a limited class of 3,9-halophenoxy-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dichalcogen compounds impart an unusually high level of flame retardant efficacy to polyolefin polymers.

According to the present invention there is provided a polymeric composition comprising a polyolefin and a flame retarding amount of a compound of the formula I



(I)

wherein

the X groups are the same and represent oxygen or sulfur atoms,

each of the Y groups, which may be the same or different, represents a chlorine or bromine atom,

m is an integer of 1 to 5, and

n is an integer of 1 to 5; the compound containing at least 45% by weight halogen.

In the compounds of formula I the X groups preferably represent oxygen atoms, m is preferably an integer of 3 to 5, and more preferably 3, and n is preferably an integer of 3 to 5, and more preferably 3. It is also preferred that n and m are the same. Further, it is preferred that both halophenoxy groups be the same. In addition, it is preferred that all Y groups be identical. Table I below describes flame retardants of Formula I according to this invention.

The numerical designations used in naming the compounds of formula I can be ascertained by reference to the following formula where the members of the heterocyclic and phenoxy rings are numbered.

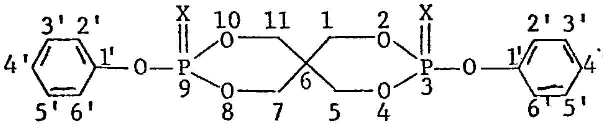


TABLE I

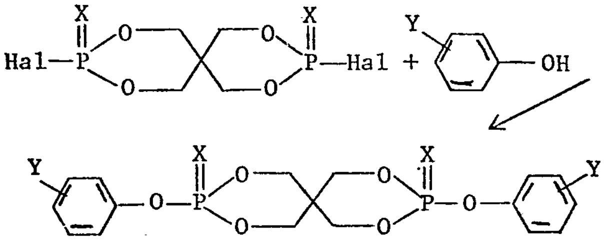
Compound	X	Y_m					Y_n					m	n
		2′	3′	4′	5′	6′	2′	3′	4′	5′	6′		
1	O	Br	–	Br	–	Br	Br	–	Br	–	Br	3	3
2	S	Br	–	Br	–	Br	Br	–	Br	–	Br	3	3
3	O	Br	–	Br	Br	Br	Br	–	Br	Br	Br	4	4
4	O	Cl	–	Br	–	Br	Cl	–	Br	–	Br	3	3
5	O	Cl	–	Br	Cl	Br	Cl	–	Br	Cl	Br	4	4
6	O	Br	–	Cl	Br	Cl	Br	–	Cl	Br	Cl	4	4
7	S	Br	–	Br	Br	Br	Br	–	Br	Br	Br	4	4
8	O	Br	–	Cl	–	Br	Br	–	Br	Br	Br	3	4
9	O	Br	–	Br	Br	Br	Br	Br	Br	Br	Br	4	5
10	S	Br	–	Cl	–	Br	Br	–	Cl	–	Br	3	3
11	O	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br	5	5
12	S	Br	Br	Br	Br	Br	Br	Br	Br	Br	Br	5	5
13	O	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	Cl	5	5
14	O	Br	Cl	Br	Cl	Br	Br	Cl	Br	Cl	Br	5	5
15	O	Cl	Br	Cl	Br	Cl	Cl	Br	Cl	Br	Cl	5	5

Preferred compounds of formula I include: 3,9-bis(2′,4′,6′-tribromophenoxy)-2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9-bis(2′,3′,4′,5′,6′ - pentabromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro-(5.5)undecane - 3,9 - dioxide; 3,9 - bis(2′,4′,5′,6′-tetrabromophenoxy)- 2,4,8,10-tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9 - bis(2′-chloro - 4′,6′ - dibromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)-undecane - 3,9 - dioxide; 3,9 - bis(2′,5′ - dichloro - 4′,6′ - dibromophenoxy)-2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5) - undecane - 3,9 - dioxide; 3,9 - bis(2′,5′ - dibromo - 4′,6′ - dichlorophenoxy)- 2,4,8,10 - tetraoxa - 3,9-diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9 - bis(2′,3′,4′,5′,6′ - pentachlorophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane-3,9-dioxide; and 3,9 - bis(2′,4′,6′ - tribromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro-(5.5)undecane - 3,9 - disulfide.

In addition to the 3,9-bis-substituted compounds, an even larger number of the

3,9-substituted compounds where the 3,9-substituents are different from each other may also be used according to the invention.

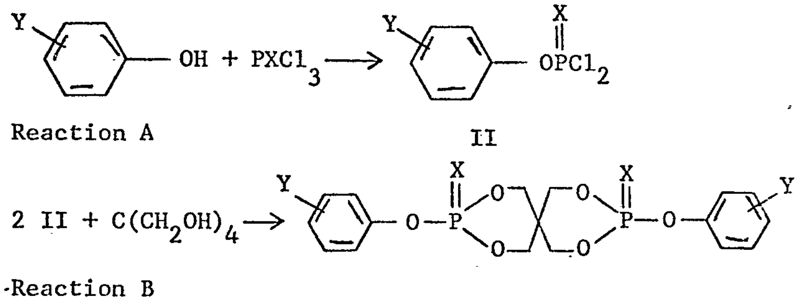
The compounds used in this invention can be prepared by reacting a 3,9-dihalo-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)-undecane-3,9-dioxide or disulfide with substituted halophenols to yield the appropriate diphosphate ester. The general reaction scheme is as follows:



wherein Y and X are as defined above and Hal represents a halogen atom. As an alternative reactant to the halophenol, metal salts of the halophenol can be used. If it is desired that the two halophenol groups be different from each other, two different halophenol reactants should be employed.

The reaction can be carried out by simply mixing the halophosphate and the halophenol or halophenol metal salt reactants together and heating the mixture gently at a temperature of 30° to 160°C. for a period of time of from 1 to 12 hours. The reaction can be conducted in the presence or absence of inert solvents.. Suitable inert solvents include aromatic solvents, e.g. benzene, and toluene, and dipolar aprotic solvents, e.g., dimethylformamide dimethylsulfoxide, and acetonitrile. Catalytic quantities of a metal salt or oxide such as magnesium oxide, magnesium chloride, calcium oxide, calcium chloride, titanium chloride, or vanadium acetate, or stoichiometric quantities of a weak organic base such as pyridine or triethylamine, can be used to accelerate the completion of the reaction. The halophosphate starting reactant can be prepared by reacting pentaerythritol with a phosphorus oxyhalide.

The compounds used in this invention can also be prepared according to the following reaction scheme:



wherein Y and X are as defined above. As an alternative reactant to the halophenol, metal salts of the halophenol can be used. If it is desired that the two halophenol groups be different from each other, two different halophenol reactants should be employed. Reaction A can be carried out by refluxing the halophenol or halophenol metal salt with an excess amount of either phosphorus oxychloride or phosphorus thiochloride for a period of 1 to 48 hours. Catalytic quantities of a metal salt such as potassium chloride, or sodium chloride, or stoichiometric quantities of a weak organic base such as pyridine or triethylamine, can be used to accelerate the completion of the reaction.

To conduct Reaction B, two moles of the crude halophenyl dichlorophosphate or dichlorothiophosphate of formula II may be suspended or dissolved in an inert solvent.

Suitable inert solvents include aromatic solvents, e.g., benzene, and toluene, and dipolar aprotic solvents, e.g., dimethylformamide, dimethylsulfoxide, and acetonitrile. One mole of pentaerythritol is added and the reactants are heated at

80° to 140°C.for a period of 1 to 10 hours. The final product is separated by filtration, purified by standard techniques known per se, e.g., washing, and recrystallisation, and dried.

The flame retardants within the scope of this invention as well as mixtures thereof have efficacy as flame retardants in polyolefin polymeric compositions. Exemplary polyolefins with which the flame retardants of this invention may be combined include homopolymers of ethylene, propylene, butene, and hexene and copolymers of two or more monomers, e.g., ethylene/propylene copolymers, ethylene/butene copolymers, and ethylene/hexene copolymers. A preferred class of polyolefins which can be used with the flame retardants of this invention are propylene homo- and co-polymers thereof. A further description of polyolefins capable of being used in this invention can be found in Modern Plastics Encyclopedia, Vol. 52, No. 10A, McGraw-Hill, Inc., New York, New York (1975), and the Encyclopedia of Polymer Science and Technology, Interscience Publishers, John Wiley & Sons, New York, N.Y. (Vol. 2, Butylene Polymers — 1965; Vol. 6, Ethylene Polymers — 1967 and Vol 11, Propylene Polymers — 1969).

The flame retardants of this invention can be incorporated into flammable polyolefin material by techniques which are standard or known to those skilled in the art. See, for example, J. M. Lyons, "The Chemistry and Uses of Fire Retardants", Wiley-Interscience, New York, 1970, and Z. E. Jolles, "Bromine and Its Compounds", Academic Press, New York, 1966. Depending on the substrate and the amount of flame retardancy desired, from 1 to 40 weight percent of the flame retardant compound of formula I can be incorporated therewith. However, in most applications it is preferred to use from 1 to 25 weight percent of the compounds of formula I. It should be noted that the optimum level of additive of the flame retardant of formula I depends upon the particular substrate being treated as well as the level of flame retardancy desired. For example, in polypropylene a flame retardant load level of from 5 to 25 percent by weight of the total polymeric composition is satisfactory.

In addition to the flame retardant compounds of formula I, the flame retadancy of a polymer can be further modified through the use of so-called "synergists" or enhancing agents, although preferably no synergist or enhancing agent is used with the flame retardant phosphates of this invention. These "enhancing agents" comprise the oxides and halides of groups IVA and VA of the Periodic Table, and are further described in Modern Plastics Encyclopedia, ibid., as well as U.S. Patent Specifications Nos. 2,993,924; 2,996,528; 3,205,196 and 3,878,165. Preferred enhancing agents include Sb_2O_3, $SbCl_3$, $SbBr_3$, SbI_3, SbOCl, As_2O_3, As_2O_5, $ZnBO_4$, $BaB_2O_4 \cdot H_2O$, $2 \cdot ZnO \cdot 3B_2O_3 \cdot 3{\cdot}5H_2O$ and stannous oxide hydrate. The more preferred enhancing agent is antimony trioxide.

The compositions according to the invention can also contain other materials where it is desired to achieve a particular end result. Such materials include adhesion promoters; antioxidants; antistatic agents; antimicrobials; colorants; heat stabilizers; light stabilizers and fillers. The above mentioned materials, including filler, are more fully described in Modern Plastics Encyclopedia, ibid.

The amount of the above described materials employed in the present compositions can be any quantity which will not substantially adversely affect the desired results derived from the compositions. Thus, the amount used can be zero (0) percent, based on the total weight of the composition, up to that percent at which the composition can still be classified as plastic. In general, such amount will be from 0% to 75% and more specifically from 1% to 50%.

The following Examples further illustrate the invention. Unless otherwise specified, all temperatures are expressed in degrees centigrade; all weights are expressed in grams; and all volumes are expressed in milliliters.

Example 1.

Synthesis of 3,9 - bis (2',4',6' - tribromophenoxy) - 2,4,8,10 - tetraoxa-3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide (compound 1 of Table I):

The sodium salt of tribromophenol (282 grams) was partially dissolved and suspended in one liter of acetonitrile. To this mixture 119 grams of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide were added over a one-half hour period. A slight exotherm was noted. Upon complete addition, the mixture was stirred and heated to 70°C for three hours. The resulting solid white mass was filtered and the product washed thoroughly with two liters of warm water. The solid was subsequently washed twice with boiling acetone to yield 322 grams

(81 percent) of a white solid, m.p. 282° to 286°C. Percent bromine calculated: 54.0; percent bromine found: 52.06.

Example 2.

Synthesis of 3,9 - bis(2′,3′,4′,5′,6′ - pentabromophenoxy) - 2,4,8,10 - tetraoxa-3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide (compound 11, Table I):

The sodium salt of pentabromophenol (460 grams) was suspended in about 3 liters of acetonitrile in a 5-liter flask. To this suspension were slowly added 133.7 grams (0.45 mole) of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide. The reactants were stirred for half an hour and then heated gently. An additional liter of acetonitrile was added to the reaction system and then said system was heated up to 70°C. and held at that temperature for 2.5 hours. The system was cooled, filtered, reslurried with water, refiltered with a centrifuge, and then air dried. The dried residue was given a boiling acetone wash, filtered through a centrifuge, and then dried at 95°C. A yield of 69.7 percent (377 grams) was obtained. Melting point: 324° to 326°C.

Example 3.

Synthesis of 3,9-bis(2′,3′,4′,5′,6′-pentachlorophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5) undecane-3,9-dioxide (compound 13, Table I):

Pentachlorophenol (97 grams; 0.364 mol), potassium chloride (3.6 grams), and phosphorus oxychloride (447 grams) were heated to the solutions refluxing temperature in a 1-liter flask equipped with a magnetic stirrer. The reaction was refluxed for 16 hours, cooled to room temperature, and then filtered. Excess phosphorus oxychloride was removed under vacuum. The pentachlorophenyl dichlorophosphate residue (125 grams; 0.326 moles) was dissolved in toluene. To this solution were added 22.2 grams (0.163 mole) of pentaerythritol. This reaction system was heated to reflux, held at the reflux temperature 2.75 hours, cooled to room temperature, and then filtered. The residue was air dried and then dried for 2 hours at 110°C. Yield: 117.5 grams (95.3%); Percent chlorine: theory: 46.9%; found: 46.44%; melting point: greater than 380°C.

In a manner similar to Examples 1 to 3, other compounds within the scope of this invention, e.g., 3,9-bis(2′,4′,5′,6′-tetrabromophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide; 3.9-bis(2′-chloro-4′,6′-dibromophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide; 3,9 - bis(2′,5′ - dibromo - 4′,6′ - dichlorophenoxy) - 2,4,8,10 - tetraoxa - 3,9-diphosphaspiro(5.5)undecane-3,9-dioxide; and 3,9-bis(2′,4′-6′-tribromophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-disulfide can be prepared.

Example 4.

A solution of 600 grams of polystyrene, 2670 grams of methylene chloride, and 60 grams of hexane, and 5 parts per hundred resin (phr) of the flame retardant of Example 1 was prepared. To the above solution was added 3 grams of dicumyl peroxide as a flame retardant synergist. This mixture was poured into an aluminum dish and the methylene chloride was allowed to evaporate. Following this, the casting was steamed to produce a crude foam. This foam was then cut into sufficient specimens of appropriate sizes in order to subject said foam to various tests and the data obtained therefrom are reported in Table II.

The same processing conditions as above were used to make additional polystyrene foam samples having different flame retardant load levels. These samples were tested in the same manner and the results obtained are also tabulated in Table II.

Example 5.

The flame retardant of Example I (40% of the total mixture by weight) was dry mixed with high impact polystyrene (HIPS) resin (52% by weight), and 8% by weight antimony oxide (Cosden 825 TV—K brand HIPS, Cosden Oil & Chemical Co., Big Springs, Texas). The mixture was melt blended in a compounding machine under the following conditions: temperature: 240°C.; rpm: 100 to 120; and mixing time: 2 to 3 minutes (Prep-Center brand compounding machine, C. W. Braebender Instruments, Inc., S. Hackensack, New Jersey). The discharge mass was cooled, ground, let down to a flame retardant load level of 18% by weight and 3.6% by weight antimony oxide by dry blending the ground concentrate discharge mass with the HIPS resin, and then injection molded using a 30-ton Newbury 1 ounce injection molding machine under the following parameters: screw speed: 250 rpm; injection pressure: initial: 2000 pounds per square inch (psi); internal barrel temperature: rear zone: 440°F., front zone: 470°F.; cycle time: 60 seconds (sec.); total injection time: 20 sec.; total stroke time: 5 sec. The final HIPS polymeric composition was subjected to various tests and the data obtained therefrom are reported in Table II.

The same processing conditions as above were used to make additional HIPS polymeric samples having different flame retardant and antimony oxide load levels. Using the same injection molding conditions as above save that the internal barrel temperature rear and front zones were 420° and 470°F. respectively, HIPS samples were also prepared with neither flame retardant additive nor antimony oxide present. The absence of the prior melt blending step and the difference in the rear and front zone internal barrel temperatures have no impact on the flame retarding efficacy of the HIPS base resin. These samples were tested in the same manner and the results obtained are also tabulated in Table II.

Example 6.

The flame retardant of Example 1 (36% of the total mixture by weight) was dry mixed with low density polyethylene (LDPE) resin (64% by weight) (Union Carbide 3900 brand LDPE, Union Carbide Corp., New York, New York). The mixture was melt blended in a Brabender Prep-Center compounding machine under the following conditions: temperature: 220°C.; rpm: 100; and mixing time: 2 to 3 minutes. The discharge mass was cooled, ground, let down to a flame retardant load level of 18% by weight flame retardant by dry blending the ground concentrate discharge mass with the LDPE resin, and then injection molded using a 30-ton Newbury 1 ounce injection molding machine under the following parameters: screw speed: 250 rpm; injection pressure: initial: 2000 psi; internal barrel temperature: rear zone: 410°F., front zone: 440°F.; cycle time: 60 sec.; total injection time: 20 sec.; total stroke time: 3 sec. The final LDPE polymeric composition was subjected to various tests and the data obtained therefrom are reported in Tables II and III.

Using the same injection molding conditions as above, additional LDPE samples were prepared without any flame retardant additive present. The absence of the prior melt blending step has no impact on the flame retarding efficacy of the LDPE base resin. These samples were tested in the same manner and the results obtained are also reported in Tables II and III.

Example 7.

The flame retardant of Example 1 (30% of the total mixture by weight) was dry mixed with polypropylene resin (70% by weight) (Hercules 6823 brand polypropylene, Hercules, Inc., Wilmington, Delaware). The mixture was melt blended in a Brabender Prep-Center compounding machine under the following conditions: temperature: 220°C.; rpm: 100; and mixing time: 1 to 2 minutes. The discharge mass was cooled, ground, let down to a flame retardant load level of 12.5% by weight flame retardant by dry blending the ground concentrate discharge mass with the polypropylene resin, and then injection molded using a 30-ton Newbury 1 ounce injection molding machine under the following parameters: screw speed: 250 rpm; injection pressure: initial: 2000 psi; internal barrel temperature: rear zone: 410°F., front zone: 440°F.; cycle time: 45 sec.; total injection time: 20 sec.; total stroke time: 4.5 sec. The final polypropylene polymeric composition was subjected to various tests and the data obtained therefrom are reported in Tables II and III.

The same processing conditions as above were used to make additional samples having different flame retardants, save that in the case of compound of Example 2, the compounding parameters were: temperature: 225°C., rpm: 120; and mixing time: 2 to 3 minutes and cycle time was 60 seconds and the stroke time was 4.5 seconds; and in the case of compound of Example 3 the mixing time was 2 to 3 minutes, the cycle time was 60 seconds, and the total stroke time was 4 seconds. The different parameters used in preparing these additional polypropylene polymeric samples have no impact on the flame retardant efficacy of the flame retardant additive. Also, using the same injection molding conditions as above, additional polypropylene polymeric samples were prepared without any flame retardant additive present. The absence of the prior melt blending step has no impact on the flame retardant efficacy of the flame retardant additive. These samples were tested in the same manner and the results obtained are also reported in Tables II and III.

Table II clearly demonstrates that the flame retardant compounds of formula I, as exemplified by that of Example 1, are not universal flame retardants capable of imparting effective flame retardancy to all polymeric materials treated therewith. However, Table II clearly depicts the flame retardant efficacy of the flame retardant compounds of formula I, as exemplified by compounds of Examples 1, 2 and 3, in polyolefins, as exemplified by low density polyethylene and polypropylene. As shown in Table II, of the various polymeric compositions containing an exemplary flame retardant compound of formula I, only flame retarded polyolefins exhibit an exceptionally high increment in Oxygen Index. These beneficial results are achieved without the use of an "enhancing" agent.

Other flame retardant compounds of formula I which also impart a high increment in Oxygen Index to flame retarded polyolefins include 3,9 - bis(2',4',5',6' - tetrabromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9 - bis(2' - chloro - 4',6' - dibromophenoxy) - 2,4,8,10-tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9 - bis - (2',5' - dichloro - 4',6' - dibromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9 - bis(2',5' - dibromo - 4',6'-dichlorophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9-dioxide; and 3,9 - bis(2',4',6' - tribromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9 - disulfide.

To distinguish the flame retardant efficacy of the compounds of formula I in polyolefin polymers over other

TABLE II

Polymer	Flame Retardant of Example No.	Flame Retardant/Antimony Oxide Load Level	O.I. (a), %	Δ O.I.
Base Resins:				
Polystyrene	–	0/0.5 phr (b)	19	–
HIPS	–	0/0	18	–
LDPE	–	0/0	19	–
Polypropylene	–	0/0	17	–
Comparative Polymeric Compositions:				
Polystyrene	1	5 phr/0.5 phr (b)	21	2
Polystyrene	1	10 phr/0.5 phr (b)	23	4
HIPS	1	12.5%/0	21	3
HIPS	1	18%/0	22	4
HIPS	1	12%/2.4%	20.5	2.5
HIPS	1	18%/3.6%	21.5	3.5
Polymeric Compositions of This Invention:				
LDPE	1	18%/0	29.5	10.5
Polypropylene	1	12.5%/0	24.5	7.5
Polypropylene	2	12.5%/0	25.5	8.5
Polypropylene	3	18%/0	24.0	7.0

(a) ASTM D–2863–74

(b) Synergist used was dicumyl peroxide rather than antimony oxide

3,9-halophenoxy-2,4,8,10-tetra-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide compounds outside the scope of this invention, 3,9-bis(4'-chlorophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)-undecane-3,9-dioxide (hereinafter referred to as A), and 3,9-bis-(2',4',6'-trichlorophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide (hereinafter referred to as B) were prepared and evaluated in polyolefin polymeric compositions as follows:

Example 8.

Synthesis of Compound B:

The sodium salt of trichlorophenol (253 grams) was partially dissolved and suspended in 1 liter of acetonitrile. To this mixture 171 grams of 3,9-dichloro-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide was added over a one-half hour period. A slight exotherm was noted. Upon complete addition, the mixture was stirred and heated to 70°C. for three hours. The resulting solid white mass was filtered and the product washed thoroughly with warm water. The solid was subsequently washed twice with cold acetone to yield 181 grams (51 percent) of a white solid, m.p. 283°C to 287°C. Percent chlorine calculated: 34.5 percent chlorine found: 30.9.

Example 9.

Synthesis of compound A:

Phosphorus oxychloride (3 kgm), potassium chloride (40 grams), and p-chlorophenol (309 grams; 2.4 moles) were magnetically stirred in a 3 liter flask and heated to reflux. The reactants were refluxed for 12.75 hours and then cooled to room temperature.

The reactants were filtered and excess phosphorus oxychloride was removed under vacuum. The crude product (538 grams; 2.19 moles) was transferred to a 2 liter flask into which was also added 502 ml of toluene and 152 grams (1.09 moles) of pentaerythritol. These reactants were heated to reflux and then held there for 5.25 hours. The reactants were then cooled to room temperature, filtered, and the residue dried under vacuum at 80°C. The product was washed with 3 liters of a 50% aqueous solution of acetone, filtered, and then air dried. Yield: 348 grams (66.5%); Acid number: 0.86; Percent chlorine: theory: 14.8%; found: 15.06%.

Example 10.

Compound A (36% of the total mixture by weight) was dry mixed with LDPE resin (64% by weight) Union Carbide 3900 brand LDPE, Union Carbide Corp., New York, New York). The mixture was melt blended in a Brabender Prep-Center compounding machine under the following conditions: temperature: 220°C.; rpm: 100; and mixing time: 2 to 3 minutes. The discharge mass was cooled, ground, let down to a flame retardant load level of 18% by weight flame retardant by dry blending the ground concentrate discharge mass with the LDPE resin, and then injection molded using a 30-ton Newbury 1 ounce injection molding machine under the following parameters: screw speed: 250 rpm; injection pressure: initial: 2000 psi; internal barrel temperature: rear zone: 410°F., front zone: 440°F.; cycle time: 60 sec.; total injection time: 20 sec.; total stroke time: 3.5 sec. The final LDPE polymeric composition was subjected to various tests and the data obtained therefrom are reported in Table III.

The difference in parameters used to prepare the various LDPE samples of Examples 6 and 10 has no impact on the flame retarding efficacy of the flame retardant additive.

Example 11.

Compound A (25% of the total mixture by weight) was dry mixed with polypropylene resin (75% by weight) (Hercules 6823 brand polypropylene, Hercules, Inc., Wilmington, Delaware). The mixture was melt blended in a Brabender Prep-Center compounding machine under the following conditions: temperature: 220°C.; rmp: 100; and mixing time: 2 to 3 minutes. The discharge mass was cooled, ground, let down to a flame retardant load level of 12.5% by weight flame retardant by dry blending the ground concentrate discharge mass with the polypropylene resin, and then injection molded using a 30-ton Newbury 1 ounce injection molding machine under the following parameters: screw speed: 250 rpm; injection pressure: initial 2000 psi; internal barrel temperature: rear zone: 410°F., front zone: 440°F.; cycle time: 60 sec.; total injection time: 20 sec.; total stroke time: 4.5 sec. The final polypropylene polymeric composition was subjected to various tests and the data obtained therefrom are reported in Table III.

The same processing conditions as above, save that the compounding temperature was 210°C., the rpm was 120, and the total stroke time was 4 seconds, were used to prepare additional polypropylene samples containing compound B. The difference in parameters used to prepare the various polypropylene samples of Examples 7 and 11 has no impact on the flame retarding efficacy of the polypropylene base resin.

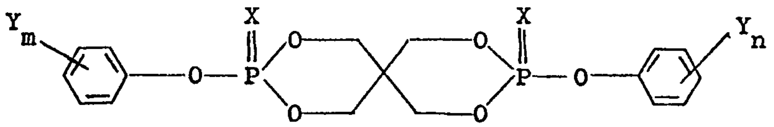
TABLE III

Polymer	Flame Retardant	Flame Retardant/Enhancing Agent Load Level	O.I. (a), %	ΔO.I.
Base Resins:				
LDPE	–	0/0	19	–
Polypropylene	–	0/0	17	–
Comparative Polymeric Compositions:				
LDPE	A	18%/0	24	5
Polypropylene	A	12.5%/0	20.5	3.5
Polypropylene	B	12.5%/0	21.0	4.0
Polypropylene	B	18%/0	21.0	4.0
Polymeric Compositions of This Invention:				
LDPE	Example 1	18%/0	29.5	10.5
Polypropylene	Example 1	12.5%/0	24.5	7.5
Polypropylene	Example 2	12.5%/0	25.5	8.5
Polypropylene	Example 3	18%/0	24.0	7.0

(a) ASTM D–2863–74

WHAT WE CLAIM IS:—

1. A polymeric composition comprising a polyolefin and a flame retarding amount of a compound of the formula I



(I)

wherein

The X groups are the same and represent oxygen or sulfur atoms,

each of the Y groups, which may be the same or different, represents a chlorine or bromine atom,

m is an integer of 1 to 5, and

n is an integer of 1 to 5; the compound containing at least 45% by weight halogen.

2. A polymeric composition according to claim 1 wherein, in the compound of formula I, the X groups represent oxygen atoms.

3. A polymeric composition according to claim 1 or 2 wherein, in the compound of formula I, m is an integer of 3 to 5 and n is an integer of 3 to 5.

4. The polymeric composition according to any of claims 1 to 3 wherein, in the compound of formula I, m and n are the same.

5. A polymeric composition according to any one of claims 1 to 4 wherein, in the compound of formula I, the halophenoxy groups are the same.

6. A polymeric composition according to claim 1 wherein the compound of formula I is 3,9 - bis(2',4',6' - tribromophenoxy) - 2,4,8,10 - tetraoxa-3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9 - bis - (2',3',4',5',6' - pentabromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9-dioxide, 3,9 - bis(2',4',5',6' - tetrabromophenoxy) - 2,4,8,10 - tetraoxa-3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide, 3,9 - bis(2' - chloro - 4',6' - dibromophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro - (5.5)undecane-3,9 - dioxide; 3,9 - bis(2',5' - dichloro - 4',6' - dibromophenoxy) - 2,4,8,10 - tetraoxa-3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide; 3,9 - bis(2',5' - dibromo - 4',6'-dichlorophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9-dioxide; 3,9 - bis(2',3',4',5',6' - pentachlorophenoxy) - 2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9 - dioxide; or 3,9 - bis(2',4',6' - tribromophenoxy)-2,4,8,10 - tetraoxa - 3,9 - diphosphaspiro(5.5)undecane - 3,9 - disulfide.

7. A polymeric composition according to any one of claims 1 to 6 wherein the polyolefin is polypropylene, polyethylene or a copolymer thereof.

8. A polymeric composition according to claim 7 wherein the compound of formula I is 3,9-bis(2',4',6'-tribromophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane-3,9-dioxide.

9. A polymeric composition according to claim 7 wherein the compound of formula I is 3,9-bis(2',3',4',5',6'-pentabromophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro-(5.5)undecane-3,9-dioxide.

10. A polymeric composition according to claim 7 wherein the compound of formula I is 3,9-bis(2',3',4',5',6'-pentachlorophenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro-(5.5)undecane-3,9-dioxide.

11. A polymeric composition according to any one of claims 1 to 10 wherein the compound of formula I is present in an amount from 1 to 40 weight percent based on the total weight of the total composition.

12. A polymeric composition according to claim 1 substantially as described in Example 6 or 7.

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