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(54) Title: NON-BLOOMING, STABILIZED FLAME RETARDANT COMPOSITIONS AND METHOD OF FLAME RETARDING POLYOLEFINS

(57) Abstract: A unique blend of brominated flame retardants that exhibits low surface migration (surface bleeding) and prevents the degradation of physical properties and/or color even under accelerated oven testing, while maintaining good flame retardancy despite the fact that one of the flame retardant components may show exudation when used by itself. The brominated flame retardant composition includes two or more flame retardant components, and must contain at least one oligomeric flame retardant. The oligomeric flame retardant component (component (a)) should contain aromatic bromine or a combination or aromatic bromine and aliphatic bromine while the monomeric of dimeric flame retardant component (component (b)) should contain aliphatic bromine, and may contain a mixture of aliphatic bromine and aromatic bromine.

NON-BLOOMING, STABILIZED FLAME RETARDANT COMPOSITIONS AND METHOD OF FLAME RETARDING POLYOLEFINS

BACKGROUND OF THE INVENTION

Field Of The Invention:

The present invention is directed to stabilized flame retardant compositions for polymers, preferably polyolefins, and methods of flame retarding polymers, particularly aliphatic polyolefins, by adding thereto a combination of flame retardant compounds (a) and (b) wherein (a) is an aromatic oligomeric compound, preferably having a weight average molecular weight of at least 2,000 and including aromatic bromine, (b) is a monomeric or dimeric aromatic compound, preferably having a molecular weight less than 2,000 and including aliphatic bromine, wherein the weight ratio of (a):(b) is in the range of about 1:10 to 10:1, preferably at least 1:1, more preferably at least 1.1:1, most preferably at least 1.3:1. Optionally, the composition also contains (c) an antioxidant process stabilizer; and (d) a UV degradation retardant selected from the group consisting of an ultraviolet (UV) stabilizer; a UV absorber; a UV screener; and a combination of any two or more of said UV degradation retarders. This combination of flame retardants, antioxidant process stabilizer and UV degradation retardant(s) shows low surface migration (bloom) characteristics in polymers, particularly aliphatic (non-aromatic) polyolefins; and good retention of physical properties and/or color in polyolefin fibers and films, particularly for polyethylene, polypropylene and copolymers thereof.

Background Of The Invention And Prior Art:

It is known that halogen-containing compounds, together with antimony oxide, are frequently utilized with polymers, to impart flame retardant properties to the polymers. Commercially available halogenated flame-retardants that have a high melting point tend to contain large amounts of aromatic halogens or are polymeric. These molecules tend to be inefficient flame retardants for polyolefins. Lower molecular weight halogen compounds that are efficient flame retardants and that contain aliphatic bromine tend to undergo surface migration in polyolefins. This leads to marring of the surface appearance of the polyolefin.

It is also known to add one or more antioxidant process stabilizers during the manufacture of polyolefins to prevent oxidation of olefins during the polymerization reaction, and to add one or more antioxidants to a polyolefin during processing, e.g., during fiber formation, to prevent oxidation of the polyolefin.

Commercially available halogenated flame retardants also are generally reactive with UV light in polyolefins, e.g., polypropylene, causing degradation of the polyolefin, as demonstrated by decreasing tensile strength of the polyolefin-containing polymer composition. The addition of one or more UV degradation retardants decreases the degradation rate.

GPP-39®, a trademark of Great Lakes Chemical Corporation, is a graft copolymer of polypropylene with brominated polystyrene. It was developed as a flame retardant for polypropylene fiber. Attempts to UV stabilize the GPP-39 in polypropylene gave results similar to unstabilized polypropylene - the polypropylene degradation rate was still too high for use of the GPP-39 flame retardant in polypropylene fiber applications.

This invention, accordingly, is directed to improvements in stabilized flame retarded polymer compositions, and in particular polyolefin compositions, more particularly, toward flame retarded and UV stabilized polyolefin fiber compositions, where there is a tendency for the flame retardant to bloom and a great tendency to degrade under exposure to UV light, and is directed towards inhibiting this bloom and degradation.

U.S. Patent No. 3,730,929 teaches that the use of a fatty acid or a metal salt of a fatty acid minimizes the tendency toward exudation. Dispersants have been disclosed to reduce blooming in U.S. Patent No. 4,006,118.

U.S. Patent No. 4,699,734 discloses that an epoxy resin, e.g., Epon 1031, an epoxy having an epoxy equivalent of about 220, an elastomeric resin, e.g., a styrene-butadiene-styrene block copolymer, and a nucleating agent, such as a fire-dried fumed silica gel, are needed to minimize surface migration of the flame retardant in polypropylene. When any one or more of the ingredients were omitted, then the surface appearance was poor to fair after aging.

WO 98/17718 discloses the use of aliphatic-containing bromine molecules as synergists for tris(tribromoneopentyl) phosphate in polyolefin resins. Tris(tribromoneopentyl) phosphate may act as a bloom suppressant for PE-68 and Nonen-52.

U.S. Patent No. 5,559,172 discloses the use of an oligomer based on tetrabromobisphenol A, ethylene dibromide, and end-capped with methyl bromide as a flame retardant for vinyl aromatic resins, such as ABS and HIPS, and blends with polycarbonate and polyphenylene oxide. The oligomer is disclosed to exhibit good thermal color stability and no bloom in these polymer compositions. U.S. Patent No. 5,530,044 discloses a composition of an oligomer material where the end group is an unreactive alkyl group. Neither patent discloses that the oligomeric flame retardant is an effective flame retardant for polyolefins, nor does either patent disclose reduced exudation in polyolefins.

Hei 5-320439 discloses that tetrabromobisphenol S bis(2,3-dibromopropyl) ether in combination with brominated bisphenol A carbonate oligomers, or with brominated bisphenol ethyl ether oligomers, gave less surface exudation than tetrabromobisphenol S bis(2,3-dibromopropyl) ether used alone in polypropylene. The tetrabromobisphenol S bis(2,3-dibromopropyl) ether monomer to oligomer weight ratio is 99:1 to 1:1, with the range of 19:1 to 3:2 being preferred.

Japanese Patent Application Kokai Sho 54-106557 discloses the use of a combination of tetrabromobisphenol A bis(2,3-dibromopropyl) ether and brominated bisphenol A carbonate oligomers as a low bloom, efficient flame retardant combination for polypropylene. The preferred weight ratio range of ether to carbonate flame retardants is 9:1 to 1:1. Ratios of less than 1:1 are not disclosed as being useful, and many of the oligomeric species tested had a weight average molecular weight below 2,000.

Japanese Patent Application Kokai Hei 8-59902 discloses the use of brominated epoxy resins as bloom inhibitors for tetrabromobisphenol A bis(2,3-dibromopropyl) ether. The weight ratio range of epoxy to tetrabromobisphenol A bis(2,3-dibromopropyl) ether is 1:1 to 1:2. An attempt to use bisphenol A carbonate oligomers or brominated bisphenol ethyl ether oligomers gave either poor flammability performance, high bleeding or both.

Japanese Patent Application Kokai Sho 57-192443 discloses a flame retardant composition obtained by combining polypropylene with a mixture comprising a brominated bisphenol A ethyl ether oligomer with a mixture of tetrabromobisphenol A bis(2,3-dibromopropyl) ether and tetrabromobisphenol S bis(2,3-dibromopropyl) ether and/or tris (2,3-dibromopropyl) isocyanurate. As stated in this published application, low bleeding and high flame retarding could not be achieved with only the oligomeric compound (a) and monomeric/dimeric compound (b); thus, at least a three component mixture is disclosed to be needed for acceptable flame retardancy and bloom characteristics since the higher molecular weight oligomer of the present invention and the correct weight ratios, were not utilized.

Japanese Patent Application Hei 4-309542 discloses a flame-retardant resin composition formed by compounding 100 parts by weight polyolefin resin with 5~50 parts by weight organic halogen flame retardant having a bromoalkyl group in its structure, antimony trioxide at 3/1~1/6 antimony/halogen in the organic halogen flame retardant (molar ratio), 0.05~2.0 parts by weight alicyclic aliphatic epoxy compound, and 0.1~10.0 parts by weight pentaerythritol and/or pentaerythritol oligomer.

There is still a need for a simple flame retardant/UV stabilizer composition that exhibits good flame retardant performance with low surface exudation, and reduced polymer degradation in polymer compositions, particularly polyolefins, when the polymer containing the flame retardant/stabilizer combination is exposed to UV light.

SUMMARY OF THE INVENTION

The present invention is directed to a unique blend of brominated flame retardants. Preferably, the composition also contains an antioxidant process stabilizer, and UV degradation retardant(s) combination including one or more UV degradation retardants selected from a UV stabilizer, a UV absorber, a UV blocker or screener, and any combination thereof that exhibits low surface migration (surface bleeding) even under accelerated oven testing while maintaining good flame retardancy despite the fact that one of the flame retardant components may show exudation when used by itself. The brominated flame retardant composition includes two or more flame retardant components, and must contain at least one oligomeric flame retardant. The oligomeric flame retardant component (component (a)) should contain aromatic bromine or a combination of aromatic bromine and aliphatic bromine while the monomeric or dimeric flame retardant component (component (b)) contains aliphatic bromine, and may contain a mixture of aliphatic bromine and aromatic bromine. Furthermore, the oligomeric flame retardant component should be compatible with the monomeric or dimeric flame retardant component, and should have a weight average molecular weight (M_w) of at least 2,000, as measured by GPC (Gel Permeation Chromatography). In addition, the weight ratio of the oligomeric flame retardant component (a) to the monomeric or dimeric flame retardant component (b) should be in the range of about 1:10 to

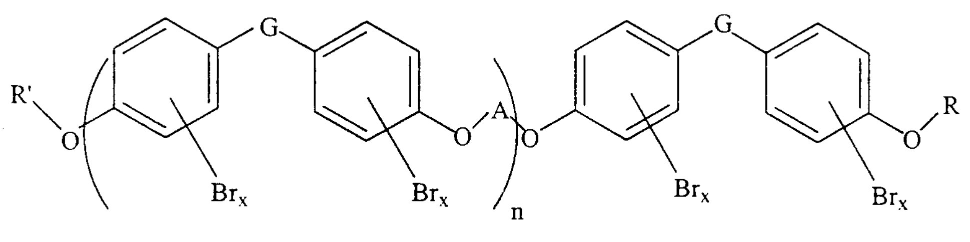
10:1, preferably at least 1:1, more preferably at least 1.1:1, most preferably at least 1.2:1 and to achieve the full advantage of the present invention, at least 1.3:1. If the ratio of component (a) to component (b) is too low, then good flame retardancy will be exhibited but the final composite will show bloom after 24 hours of accelerated aging. Conversely, if the ratio of component (a) to component (b) is too high, then the composite will show low surface migration but poor flammability performance.

In addition to the combination of brominated flame retardants, in accordance with the present invention, additional optional additives to the polymers, particularly polyolefins, include about 0.05% to about 2%, preferably about 0.1% to about 1%, based on the weight of the polymer, of an antioxidant acting as a process stabilizer, and about 0.1% to about 3%, preferably about 0.2% to about 2%, based on the weight of the polymer, of one or more UV degradation retardants selected from the group consisting of a UV stabilizer, a UV absorber, a UV blocker or screener, and any combination thereof. Typical antioxidant process stabilizers include aromatic phosphites, aliphatic phosphites, aromatic phosphonites, aliphatic phosphonites or combinations of these. Examples of UV degradation retarders include a hindered amine light stabilizer (HALS), UV absorber and/or a UV screener. Typical HALS include aliphatic hindered amines, dimeric hindered aliphatic amines, polymers containing the aliphatic amine in the backbone of the polymer or as a pendant group, or combinations of different HALS. The amine may be secondary or ternary and may be either a liquid or a solid. UV absorbers include alkoxy- or hydroxy-substituted benzophenones or hydroxyphenyl or substituted hydroxyphenyl benzotriazoles. UV screeners may consist of inorganic or organic pigments, metal oxides such as titanium dioxide and carbon black. Substituted phenols, especially hindered phenols and isocyanurate substituted cresols, may be used as antioxidants. The stabilizer package may also contain acid scavengers such as metal salts of carboxylic acids and other basic or alkaline materials.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purpose of promoting an understanding of the principles of the invention, reference will now be made to preferred embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications in the illustrated embodiments, and such further applications of the principles of the invention as illustrated herein being contemplated as would normally occur to one skilled in the art to which the invention pertains.

The present invention relates to a mixture of an oligomeric flame retardant component (a), preferably having a weight average molecular weight of at least 2,000, with a non-oligomeric (monomeric or dimeric) flame retardant component (b), preferably having a weight average molecular weight of less than 2,000. Preferably, a polymer stabilizer combination also is included in the composition comprising (c) an antioxidant process stabilizer and (d) a UV degradation retardant selected from the group consisting of (i) a UV stabilizer, (ii) a UV absorber, (iii) a UV blocker or UV screener; and (iv) any combination of two or more of the foregoing UV degradation retardants. In particular, the oligomeric flame retardant component (a) can be represented by the following formula I:



(I)

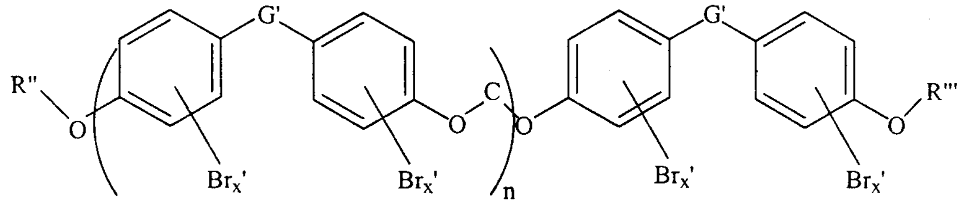
where G is a connecting group selected from the group consisting of a single bond, a branched or unbranched divalent aliphatic radical of from 1 to 10 carbons, oxygen, sulfur, sulfoxide, sulfone, or oxygen-silicon; x is an integer from 1-4; and R and R' are each (same or different) a phenyl or a halogen substituted aromatic group of from 6 to 12 carbon atoms; A is a carbonyl group or a dicarboxy-containing connecting group containing from 2-12 carbon atoms; and n is a positive integer greater than or equal to 2.

In certain embodiments, G is a connecting group of the formula -CYY' where Y and Y' (same or different) are each an aliphatic hydrocarbon radical and, in particular, methyl radicals. In other preferred embodiments, G is an SO_2 connecting group.

R and R', same or different, each may be a phenyl or tribromophenyl group.

In other embodiments, A may be CO or $OCCH_2CH_2CH_2CH_2CO$. In the preferred embodiment, G is a $C(CH_3)_2$ connecting group; A is a CO connecting group; and R and R' are phenyl groups.

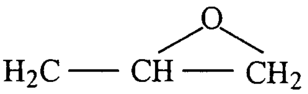
Alternatively, or in addition, the oligomeric flame retardant component (a) may consist of a bromine-containing epoxy oligomer with a weight average molecular weight of 1,000-50,000 of the following formula (II):



(II)

where G' is a connecting group selected from the group consisting of a single bond, a branched or unbranched divalent aliphatic radical of from 1 to 10 carbons, oxygen, sulfur, sulfoxide, sulfone, or oxygen-silicon, X is an integer from 1-4, and R'' and R''' are, independently, a branched or unbranched alkyl epoxy radical, branched or unbranched alkyl alcohol radical, branched or unbranched alkyl ether radical or branched or unbranched alkylhalide alcohol radical; C is a branched or unbranched alkyl diradical containing a hydroxy or ether group and n is a positive integer greater than or equal to 2.

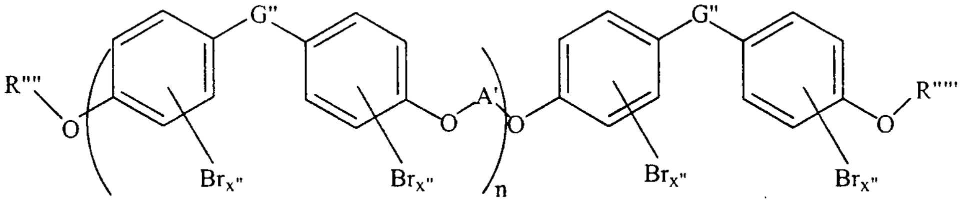
In the preferred embodiment for formula II, G' is a $(CH_3)_2C$ group, C is a $CH_2CHOHCH_2$ group, R''' is



$$H_2C - CH - CH_2 \text{ (O bridging CH and } CH_2)$$

x is 2 and n is greater than 2.

The second, monomeric or dimeric flame retardant component (b) comprises a material having the following formula III:



(III)

where G″ is a connecting group selected from the group consisting of a single bond, a branched or unbranched divalent aliphatic radical of from 1 to 10 carbon atoms, oxygen, sulfur, sulfoxide, sulfone, or oxygen-silicon; x″ is an integer from 0-4; and R″″ and R″‴ (same or different) each is selected from a branched or unbranched alkyl radical, branched or unbranched alkyl halide radical, and wherein at least of one R″″ and R″‴ contains bromine; A' is a branched or unbranched alkyl diradical or halogenated dialkyl radical; and n is a positive integer of 0 or 1.

In certain embodiments, G″ is a connecting group of the formula -CYY', where Y and Y' (same or different) each is an aliphatic hydrocarbon radical and, in particular, methyl radicals. In other embodiments, G″ is an SO_2 connecting group. In other embodiments, R″″ and R″‴ are 2,3-dibromopropyl groups.

In the preferred embodiment, G″ is a $C(CH_3)_2$ connecting group; n is 0; and both R″″ and R″‴ are $CH_2CH_2BrCH_2Br$ groups. In a separate embodiment, G″ is an SO_2 connecting group; n=0; and both R″″ and R″‴ are 2,3-dibromopropyl groups.

The second, monomeric or dimeric flame retardant component (b) may also be selected from the following flame retardants: ethylene bis(5,6-dibromonorborane-2,3-dicarboximide); hexabromocyclododecane; the Diels-Alder adduct of hexachlorocyclopentadiene with 1,5-cyclooctadiene; and tris(tribromoneopentyl)phosphate; bis(2,3-dibromopropyl) tetrabromophthalate, and the like.

The optional stabilizer package should contain an antioxidant, acting as a process stabilizer, and one or more UV degradation retardants. Typical process stabilizers contain aromatic phosphites, aliphatic phosphites, aromatic phosphonites, aliphatic phosphonites, benzufuran(2) ones, especially 3-arylbenzofuranones, hydroxyl amines, or any combinations of these. Examples are tris(2,4-di-tert-butyl-phenyl) phosphite, also known as Alkanox® 240 (Alknox® is a trademark of Great Lakes Chemical Corporation) or Irgafos® 168 (Irgafos® is a trademark of Ciba Specialty Chemicals); bis(2,4-di-tert-butyl-phenyl)pentaerythritol diphosphite, also called Alkanox® P-24 or Ultranox® 626 (Ultranox® is a trademark of General Electric Corporation); tetrakis (2,4-di-tert-butyl-phenyl)4,4'-biphenylene-diphosphonite, also known as Alkanox® 24-44 or Irgafos® P-EPQ; bis(2,4-dicumylphenyl)pentaerythritol diphosphite, also called Alkonox® 28 or Doverphos® S-9228 (Doverphos® is a registered trademark of Dover Corporation); and tris(p-nonyl-phenyl)phosphite, also called Alkanox® TNPP or Doverphos® 4-HR.

Substituted phenols, especially hindered phenols and isocyanurate substituted methylene phenols, may be used as antioxidant process stabilizers. Specific examples of such antioxidants are 2-(2'-hydroxy-3',5'-di-tert-butylbenzyl)isocyanurate, also known as Anox™ 1C-14 (Anox™ is a trademark of Great Lakes Chemical Corporation) or IRGANOX® 3114, a trademark of CIBA Specialty Chemicals; tetrakismethylene (3,5-di-t-butyl-4-hydroxyhydrocinnamate)methane, also called Anox™ 20 or IRGANOX® 1010; octadecyl 3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate, also called Anox™ PP18 or IRGANOX® 1076; and 1,3,5-tris(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl)isocyanurate, also called Cyanox® 1790. (Cyanox® is a registered trademark of Cytec Corporation).

The stabilizer package preferably also contains at least one of a UV degradation retarder or UV stabilizer such as a hindered amine light stabilizer (HALS), UV absorber or a UV screener. Typical HALS include aliphatic hindered amines; dimeric hindered aliphatic amines; polymers containing the aliphatic amine in the backbone of the polymer or as a pendant group; or combinations of different HALS, and hydroxyl amines. The amine may be secondary or ternary and may be either a liquid or a solid. Specific examples of HALS include bis-(1,2,2,6,6-pentamethyl-4-piperidinyl)-sebacate, also known as Lowlite® 76 (Lowlite® is a trademark of Great Lakes Chemical Corporation) or Tinuvin® 765 (Tinuvin® is a trademark of Ciba Specialty Chemicals) or Tinuvin® 292; bis-(2,2,6,6-tetramethyl-4-piperidinyl)-sebacate, also called Lowlite® 77 or Tinuvin 770®; butanedioic acid, dimethyl ester, polymer with 4-hydroxy-2,2,6,6-tetramethyl-1-piperidineethanol, also called Lowlite® 62 or Tinuvin® 622; poly-methylpropyl-3-oxy-[4(2,2,6,6-tetramethyl)piperdinyl] siloxane, also called Uvasil® 299 (Uvasil® is a trademark of Great Lakes Chemical Corporation); poly-methylpropyl-3-oxy-[4(1,2,2,6,6-pentamethyl)piperdinyl] siloxane, also called Uvasil® 816; decanedioic acid, bis[2,2,6,6-tetramethyl-1-(octyloxy)-4-piperidinyl] ester, also called Tinuvin® 123; (poly[[6-[1,1,3,3-tetramethylbuty)amino]-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[2,2,66-tetramethyl-4-piperidinyl)imino]], also called Chimassorb® 944 (Chimassorb® is a trademark of Ciba Specialty Chemicals), also known as Lowlite® 94; 1-piperidineethanol, 4-hydroxy-2,2,6,6-tetramethyl-, polymer with butanedioic acid, called Tinuvin® 622, Tinuvin® 111, 1,3,5-triazine-2,4,6-triamine; N,N'''-1,2-ethanediylbis[N-[3-[[4,6-bis[butyl(1,2,2,6,6-pentamethyl-4-piperidinyl)amino]-1,3,5-triazin-2-yl]methylamino]propyl]-N',N''-dibutyl-N',N''-bis(1,2,2,6,6-pentamethyl-4-piperidinyl), also known as Chimassorb® 119; 3-dodecyl-N-(2,2,6,6-tetramethyl-4-piperidinyl)succinimide, also called Cyasorb® UV 3604 (Cyasorb® is a trademark of Cytec Corporation); 3-dodecyl-N-(2,2,6,6-tetramethyl-4-piperidinyl)succinimide, also called Cyasorb® UV3581; poly[[6-(4-morpholinyl)-1,3,5-triazine-2,4-diyl][(2,2,6,6-tetramethyl-4-piperidinyl)imino]-1,6-hexanediyl[(2,2,6,6-tetramethyl-4-piperidinyl)imino]], also called Cyasorb UV 3346; and 7-oxa-3,20-diazadispiro[5,1,11,2]heneicosan-21-one, 2,2,4,4-tetramethyl-20-(oxiranylmethyl)-, homopolymer, also known as Hostavin® N 30 (Hostavin® is a registered trademark of Clariant Corporation). Specific examples of mixed HALS containing systems are Chimasorb® 111, a blend of Tinuvin® 622 and Chimasorb® 119, and FS 410® a blend of Chimasorb® 944 and di(octadecyl)hydroxyl amine.

UV absorbers include alkoxy or hydroxy substituted benzophenones or hydroxyphenyl or substituted hydroxyphenyl benzotriazoles. Specific examples of UV absorbers are 2,4-dihydroxybenzophenone, 2-hydroxy-4-n-octoxy-benzophenone, also called Lowlite® 22 or Chimassorb® 81; 2-(2'-hydroxy-3',5'-ditert-butyl-phenyl)-5-chlorobenzotriazole, also known as Lowlite® 27 or Tinuvin® 327; 2-(2'-hydroxy-3'-tert-butyl-5'-methyl-phenyl)-

5-chlorobenzotriazole, also called Lowlite® 26 or Tinuvin® 326; 2-(2'-hydroxy-3',5'-di-t-amylphenyl)benzotriazole, also called Lowlite ® 28 or Tinuvin® 328; and 2-(2'-hydroxy-5'-methyl-phenyl)benzotriazole, called Lowlite® 55 or Tinuvin® P. UV screeners may consist of inorganic or organic pigments, metal oxides such as titanium dioxide, and carbon black.

The stabilizer package may also contain acid scavengers such as metal salts of carboxylic acids. Typical examples include calcium stearate, zinc stearate, calcium lactate, aluminum-magnesium hydrotalcite and other basic or alkaline materials. Optionally, the stabilizer package, when added to the fibrous or non-fibrous polymer, may include a flame retardant synergist in an amount in a ratio of flame retardant:flame retardant synergist in the range of about 10:1 to 3:1, preferably in the range of about 2-6:1. Examples of flame retardant synergists include antimony trioxide, zinc borate, and sodium antimonate.

The combination of the flame retardant components, optional antioxidant process stabilizer and optionally one or more UV degradation retarders are useful as flame retardants, particularly when compounded with other plastic compounds or polymer compositions, particularly polyolefins, preferably aliphatic polyolefins, such as polyethylene and polypropylene and copolymers thereof. The combination of flame retardant compounds of the present invention is less prone to surface migration, while maintaining good flame retardancy. The preferred addition of the antioxidant process stabilizer and one or more UV degradation retarders prevents the degradation of physical properties and/or color in the polymer, particularly in polyolefin fibers and film, particularly polypropylene.

The combination of flame retardants of the present invention is useful as a stabilized flame retardant in polymeric materials such as polystyrene; high impact polystyrene; copolymers of styrene; polycarbonates; polyurethanes; polyimides; polyamides; polyethers; acrylics; polyesters; epoxies; phenolics; elastomers, such as butadiene/styrene copolymers and butadiene/acrylonitrile copolymers; terpolymers of acrylonitrile, butadiene and styrene; natural rubber; butyl rubber; polysiloxanes, and particularly polyolefins, including fibers made from any of the foregoing. Preferred polymers (particularly fiber or film) include those of olefinically-saturated monomers, such as ethylene, propylene, butene, butadiene and copolymers of two or more of such alkylene monomers. Blends of polymers may also be flame retarded and stabilized with the combination of flame retardants and stabilizers/UV degradation retardants disclosed herein.

The most preferred polymers are aliphatic polyolefins, particularly polyethylene, polypropylene, and copolymers of propylene and ethylene, preferably where the polyolefin and polyolefin copolymers are in fiber form.

The oligomeric flame retardant component (a) of the present invention may be prepared by reacting a diphenol with a divalent reactant, for example carbonyl dichloride, in the presence of a base, in a solvent such as methylene chloride. A second phenol can be added to end cap the oligomer.

The flame retarded polymer compositions of the present invention may be prepared by mixing the oligomeric flame retardant component (a), the monomeric or dimeric flame retardant component (b), preferably also the optional antioxidant process stabilizer (c), and the optional UV degradation retarder (d) with the polymer to be flame retarded, e.g., at the same time. However, a premixing of the flame retardant components (a) and (b) with the optional process stabilizer component (c) and the optional UV degradation retarder(s) (d) is preferred. The flame retardant components (a) and (b) , the optional stabilizer component (c), and the optional UV degradation retarder(s) (d) may be blended by mixing the powders; melting the components and then mixing; or one component may be melted or softened and the components then mixed. Typical mixing apparatus includes, but is not limited to, high shear mixers, such as a Banbury mixer; tumble type blenders; and extruders. It is further preferred to mix the components (a) and (b) with the optional stabilizer and UV degradation retarder(s) (c) and (d) and then blend the complete package with the polymer. The flame retardant stabilized mixtures of the present invention may be used as a fine powder, as a compacted material, or may be used with a small amount of a suitable binder as a master batch. Suitable binders include, but are not limited to, calcium stearate, antimony trioxide, polyethylene, polypropylene, propylene/ethylene copolymers, and poly(brominated styrene). Suitable forms of the compounds of this invention include powder, compacted, prilled, chilsinated, and the like.

The compositions of this invention, when including containing components (c) and (d), may also be added in a stepwise manner. For example, the antioxidant process stabilizer component (c) can be added to the polyolefin followed by addition of the flame retardant components (a) and (b) and then a UV degradation retardant (d), such as HALS; or followed by the flame retardant components (a) and (b) and then a UV degradation retarder, e.g., HALS, and then an acid scavenger. One skilled in the art can envision multiple methods of sequencing the addition of the ingredients of the composition of this invention.

Reference will now be made to specific examples using the description described above. It is to be understood that the examples are provided to more completely described preferred embodiments and that no limitation to the scope of the invention is intended thereby.

General Experimental Procedure:

The oligomeric component (a), monomeric or dimeric component (b), and antimony trioxide (5:1 weight ratio of total flame retardant to antimony trioxide), are weighed into the polyolefin and the mixture is thoroughly hand mixed in a poly bag. Alternatively, the oligomeric component (a) and monomeric or dimeric component (b) are mixed in a ribbon blender and then weighed, with antimony oxide, into the polyolefin and then thoroughly mixed. The material is compounded on a Berstorff ZE-25 twin screw extruder at the conditions shown below (see Table 1).

TABLE 1

Compounding Conditions On Berstorff ZE-25 Twin Screw Extruder

Barrel 2 Temperature (°C)	195	Screw Speed (rpm)	200
Barrel 3 Temperature (°C)	200		
Barrel 4 Temperature (°C)	200	Feeder	Belt
Barrel 5 Temperature (°C)	200	Feed Rate (g/min)	150-200
Barrel 6 Temperature (°C)	200		
Barrel 7 Temperature (°C)	200	Typical Melt Temperature (°C)	220
Die Temperature (°C)	205	Typical Melt Pressure (psi)	350-450

A belt feeder was used to feed the formulation mixture to the throat (i.e., barrel 1) of the twin screw. The throat was cooled to 80-90°F. The formulation strands were cooled in a 6 foot water bath (Ca. 75-80°F), then air dried and pelletized using a Conair/Jetro Model #304 pelletizer.

Experimental For Molding Bloom Plaques On A Boy 50 Ton:

Bloom plaques (Gardner impact plaques) and 1/16th inch UL-94 bars were molded on a Boy 50 Ton injection molder (Model #159-50 at the conditions shown below (See Table 2).

TABLE 2

Bloom Plaque And 1/16th Inch UL-94 Bar Molding On A Boy 50 Ton

Barrel 1 Temperature (°C)	200	Injection Time (sec)	10
Barrel 2 Temperature (°C)	200	Cooling Time (sec)	30
Barrel 3 Temperature (°C)	200		
Nozzle Temperature (°C)	225	Typical Melt Temperature (°F)	440-450
Mold Temperature (°F)	90	Typical Inject Pressure (psi)	450-475

Bloom plaques and UL-94 bars were conditioned at 70-75°F for 24 hours prior to start of testing.

Experimental For Accelerated Aging (Bloom) Test @ 80°C (24 and 168 hours):

Two sets of 3 Bloom plaques per formulation were placed in wire mesh racks and conditioned in a circulating/vented oven at 80°C for 24 and 168 hours. Each set was allowed to condition an additional 24 hours @ 70-75°F prior to performing the bloom test.

Visual haze was recorded. A 2.5" x 2.5" black cloth (broad cloth, 65% polyester/35% cotton blend) was used to swipe the surface of the plaques.

EXAMPLES OF BLOOM SUPPRESSION WHILE MAINTAINING V-0 OR V-2 FLAME RATING

Example	Flame Retardant Component (phr)		Bloom		Flame Rating
	(a)*	(b)**	24 hr	168 hr	
1		11	medium to heavy	medium to heavy	V-0
2		3	medium to heavy	medium to heavy	V-2
3	5.2		none	none	fail
4[B]	7.9	0	very light to light	medium to heavy	V-2
5[B]	5.7	5.7	light to medium	medium	V-0
6[B]	7	4.7	very light to light	very light	V-0
7[B]	7.9	4	no bloom to very light	no bloom to very light	V-0
8[B]	8.6	3.4	no bloom to very light	no bloom to very light	V-0
9[B]	9.1	3.0	no bloom	light to medium	V-2
10[C]	8[D]	4	light to medium	medium	V-0
11[B]	9.1	4.6	no bloom to very light	no bloom to very light	V-0
12[B]	10	5.1	very light	very light	V-0
13[E]	10	5	very light	very light	V-0

EXAMPLES OF BLOOM SUPPRESSION WHILE MAINTAINING V-0 OR V-2 FLAME RATING

Example	Flame Retardant Component (phr)		Bloom		Flame Rating
	(a)*	(b)**	24 hr	168 hr	
14^B	9.1	4.6	very light	no bloom to very light	V-0
15^B	10	5	very light	no bloom to very light	V-0

* a = oligomer (unless otherwise noted, the oligomer is phenoxy terminated carbonate oligomer of tetrabromobisphenol A, M_w=2500)

** b = monomer, dimer (unless otherwise noted, the monomer is tetrabromobisphenol A bis(2,3-dibromopropyl ether))

B = Amoco 1046 polypropylene homopolymer (ASR9930)

C = Montell 6501 polypropylene homopolymer

D = tribromophenoxy terminated carbonate oligomer of tetrabromobisphenol A, M_w=n=4

E = tribromophenoxy terminated carbonate oligomer of tetrabromobisphenol A, M_w=3500

The above examples show that the monomeric or dimeric flame retardant component (b), used alone, has good flame retardancy (examples 1 and 2) but unacceptable exudation. The oligomeric component has poor flammability when used alone (example 3). Good flame retardancy, as measured by the UL 94 V-0 rating, can be achieved at relatively low loading levels but at weight load ratios of 1:1 (example 8) of the oligomeric flame retardant component (a) to the monomeric or dimeric flame retardant component (b), bloom becomes unacceptable. At load ratios of 3:1 or above (oligomeric to monomeric or dimeric), the resistance to exudation is good but flammability properties decrease (e.g., example 11) at relatively low total flame retardant loadings (e.g., below about 15% by weight total flame retardants, based on the weight of the polymer). The preferred weight ratio of oligomeric flame retardant (a) to monomeric or dimeric flame retardant (b) is 1.1:1 to 5:1; more preferred in the range of 1.2:1 to 5:1, and most preferred in the range of 1.5:1 to 3:1 for V-0 flame rating applications.

EXAMPLES WITH ANTIOXIDANT AND UV DEGRADATION RETARDANT

Samples were first formulated with a stabilizer package and then compounded using a Killion KL-100 single screw extruder to minimize shear and eliminate cross contamination between formulations. The following temperature profile was used: 200 - 210 - 230 - 230°C with a screw speed of 115-116 RPM. The stabilized samples were compounded using a Bersdorff 25 mm twin screw extruder. The following temperature profile was used: *(Second extrusion)* 195 - 200 - 200 - 200 - 200 - 200 - 200 - 205°C with a melt pressure of 200-220 PSI and a screw speed of 270 RPM.

The formulations, after second extrusion, were spun into fiber on a commercial fiber unit.

TABLE 3

Parameters for fiber spin.

Extruder Pressure, PSI	500-750	Spin Finish (Type)	5656
Zone 1, °C	182/202	Spin Finish (%)	12
Zone 2, °C	210	Denier Roll RPM	195
Zone 3, °C	220/221	Tension Roll RPM	198
Zone 4, °C	229/230	Denier Roll Wraps	3
Melt, °C	232/233	Tension Roll Wraps	0
Filament	144	Draw Ratio	3:1
Shape	SC/Round	Spin Head Temp. °C	231
Feed Roll Speed (RPM)	209	Draw Roll Speed (RPM)	600
Feed Roll Temp. °C	100	Draw Roll Temp. °C	100

UV Exposure:

All systems were exposed in a Ci65 Xenon arc Weather-O-Meter accelerated testing apparatus at Great Lakes Chemical Corporation West Lafayette Laboratories. Table 4 shows the key parameters for the test. Fibers were wrapped around 6 cm x 15 cm cards and clamped into standard sample holders.

TABLE 4

Key parameters for Xenon arc Weather-O-Meter exposure.

Parameters	**ASTM G26 (dry)**
Irradiance at 340 nm	0.35 W/m^2
Black Panel Temp.	63°C
Relative Humidity	35%
Cycle	continuous light

Gas Fade Chamber Exposure:

Fiber from each formula was wrapped on the card using a winder. The samples and the test control fabric were mounted on a rotating carousel in gas fade chamber and were exposed simultaneously to oxides of nitrogen from burnt gas fumes @ 140°F.

Color Measurements:

Color measurements were preformed on a HunterLab ColorQuest II spectrophotometer utilizing Universal software. Both Hunter 10°/D65 and CIE lab color scales were available with "YID 1925" and "Delta E*" indices. The experimental error for color measurements was ± 0.5 YID or DE* units.

Tensile Measurement:

At specific intervals of exposure the fibers were removed from sample holders and subjected to tensile testing. Testing was done at Great Lakes Chemical Corporation West Lafayette Laboratories. The method used is outlined in Table 5. Peak force is measured for exposed samples and compared to unexposed samples to calculate the percentage of retained strength. A value of 50% retained strength is the failure point for comparison.

TABLE 5

Instron Tensile Testing of Fiber.

Load Cell	200 lb. Capacity (90.7 Kg)
Sample length	1.5 inc. (3.75 cm)
Pull Rate	6 in/minute (12.6 cm/minute)
Calibration Wt.	5 lb. (2.268 Kg)

RESULTS AND DISCUSSION:

TABLE 6

Represents components and abbreviations.

6301PP = Montell ProFax 6301

Al 28 = Alkanox® 28

U2000LMPE = Uvasil® 2000LMPE*

U816 = Uvasil® 816

LL62 = Lowlite® 62

LL22 - Lowlite® 22

GPP 39® = Great Lakes GPP 39

CaST = Calcium Stearate

C944 = Chimassorb® 944

C119 - Chimassorb® 119

T234 - Tinuvin® 234

CN2525
CN 2525 is a 2:1 mixture of an oligomeric brominated carbonate flame retardant having formula I and a monomeric brominated carbonate flame retardant of formula III

* Uvasil® 2000LMPE = 70% Uvasil® 299 in 30% polypropylene as a binder to bind the Uvasil® 299 powder.

TABLE 7

Evaluated formulations, weight percent.
Each formulation contains Alkanox® 28 @ 0.3% as processing stabilizer and calcium stearate as an acid scavenger.

Formulation	HALS	LL62	T234	LL22	GPP39	CN2525
Control-No. FR, no UV* (PP635)						
C944, LL 62, Tin 234, GPP 39	0.25	0.25	1.0		15.4	
C944, LL 62, Tin 234, CN2525	0.25	0.25	1.0			10.5
U816, LL22, LL62, GPP39	0.25	0.25		1.0	15.4	
U816, LL22, LL62, CN2525	0.25	0.25		1.0		10.5
U299, LL62, LL22, CN2525	0.42**	0.25		1.0		10.5
C119, LL62, LL22, CN2525	0.25	0.25		1.0		10.5

* Base 35 MFI Profax polypropylene PP635, no stabilizers or flame retardants added, was used as a control. (According to our analytical lab, it has 0.1% Alkanox 240 type molecule only).

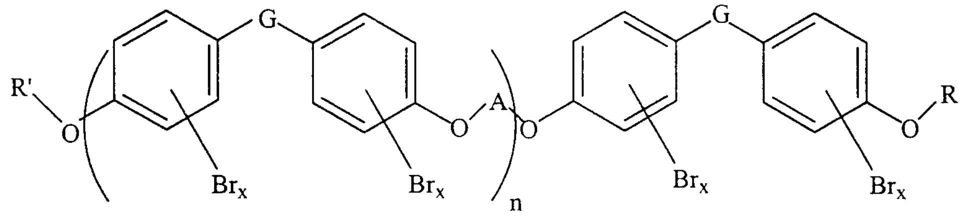
** Uvasil® 2000 was used for compounding. Uvasil® 2000 @ 0.42% load level is equal to Uvasil® 299 @ 0.25%.

Numerous modifications and alternative embodiments of the invention will be apparent to those skilled in the art in view of the foregoing description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the best mode of carrying out the invention. The details may be varied substantially without departing from the spirit of the invention, and the exclusive use of all modifications which come within the scope of the appended claims is reserved.

WHAT IS CLAIMED IS:

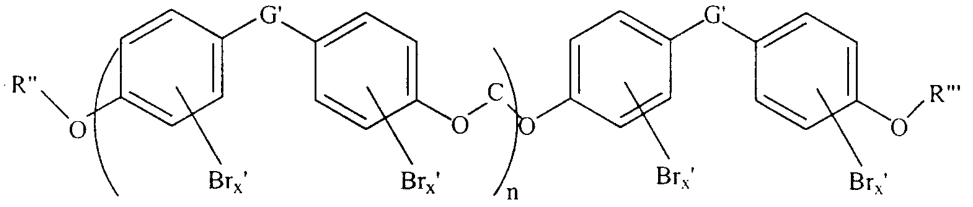
1. A reduced blooming flame retardant, stabilized polymer composition comprising a polymer. 0.1% to 20% by weight, based on the weight of the polymer, of

(a) an oligomeric flame retardant compound having a structure selected from the group consisting of formula I, an epoxy having a weight average molecular weight of about 1,000 to about 50,000 of formula II, and mixtures thereof:



(I)

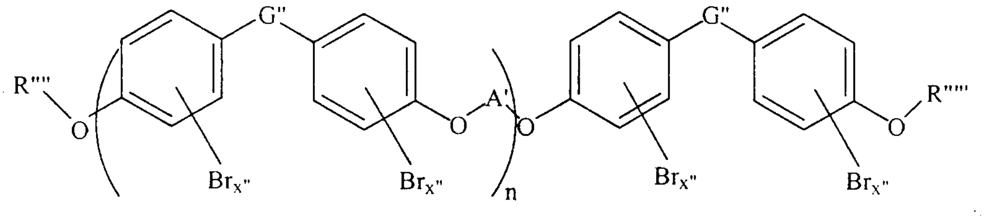
where G is a connecting group selected from the group consisting of a single bond, a branched or unbranched divalent aliphatic radical of from 1 to 10 carbons, oxygen, sulfur, sulfoxide, sulfone, or oxygen-silicon, x is an integer from 1-4, and R and R' are phenyl or halogen substituted aromatic group of from 6 to 12 carbon; A is a carbonyl group or a dicarboxy containing connecting group containing from 2-12 carbon atoms and n is a positive integer greater than or equal to 2;



(II)

where G' is a connecting group selected from the group consisting of a single bond, a branched or unbranched divalent aliphatic radical of from 1 to 10 carbons, oxygen, sulfur, sulfoxide, sulfone, or oxygen-silicon, X is an integer from 1-4, and R″ and R‴ are, independently, a branched or unbranched alkyl epoxy radical, branched or unbranched alkyl alcohol radical, branched or unbranched alkyl ether radical or branched or unbranched alkylhalide alcohol radical; C is a branched or unbranched alkyl diradical containing a hydroxy or ether group and n is a positive integer greater than or equal to 2; and

(b) 0.1% to 20% by weight of a monomeric or dimeric flame retardant compound having structural formula III:



(III)

where G″ is a connecting group selected from the group consisting of a single bond, a branched or unbranched divalent aliphatic radical of from 1 to 10 carbon atoms, oxygen, sulfur, sulfoxide, sulfone, or oxygen-silicon, x″ is an integer from 0-4, and R″″ and R″‴ are independently a branched or unbranched alkyl radical, branched or unbranched alkyl halide radical at least one of R″″ and R″‴ contains bromine; A' is a branched or unbranched alkyl diradical or halogenated dialkyl radical and n is a positive integer of 0 or 1.

2. The composition of claim 1, further including:

(c) an antioxidant process stabilizer in an amount of about 0.05% to about 2%, based on the weight of the polymer; and

(d) a UV degradation retarder in an amount of about 0.1% to about 3%, based on the weight of the polymer, selected from the group consisting of a UV stabilizer, a UV absorber, a UV screener and any combination thereof.

3. The composition of claim 1, wherein the weight ratio of oligomeric flame retardant compound of formula I to the monomeric or dimeric flame retardant compound of formula II is at least 1.1 : 1.

4. The composition of claim 1, wherein the weight average molecular weight of the oligomeric flame retardant compound is at least 2,000; the weight average molecular weight of the monomeric or dimeric flame retardant compound is less than 2,000; and the weight ratio of oligomeric flame retardant compound to monomeric or dimeric flame retardant compound is in the range of 1:10 to 10:1.

5. The composition of claim 4, wherein the weight average molecular weight of the oligomeric flame retardant compound is at least 2,000; the weight average molecular weight of the monomeric or dimeric flame retardant compound is less than 2,000; and the weight ratio of oligomeric flame retardant compound to monomeric or dimeric flame retardant compound is in the range of 1.1:1 to 5:1.

6. The composition of claim 1, wherein the weight average molecular weight of the oligomeric flame retardant compound is at least 2,000; the weight average molecular weight of the monomeric or dimeric flame retardant compound is less than 2,000; and the weight ratio of oligomeric flame retardant compound to monomeric or dimeric flame retardant compound is in the range of 1.2:1 to 3:1.

7. The composition of claim 1, wherein the weight average molecular weight of the oligomeric flame retardant compound is at least 2,000; the weight average molecular weight of the monomeric or dimeric flame retardant compound is less than 2,000; and the weight ratio of oligomeric flame retardant compound to monomeric or dimeric flame retardant compound is in the range of 1.5:1 to 3:1.

8. The composition of claim 1, wherein the weight ratio of oligomeric flame retardant compound of formula I to the monomeric or dimeric flame retardant compound of formula III is in the range of 1:10 to 10:1.

9. The composition of claim 6, wherein the weight average molecular weight of the oligomeric flame retardant compound is at least 2,000; the weight average molecular weight of the monomeric or dimeric flame retardant compound is less than 2,000; and the weight ratio of oligomeric flame retardant compound to monomeric or dimeric flame retardant compound is in the range of 1.3:1 to 3:1.

10. The composition of claim 1, where G is a connecting group of the formula -CYY', wherein Y and Y', same or different, are each an aliphatic hydrocarbon.

11. The composition of claim 10, wherein Y and Y' are methyl radicals.

12. The composition of claim 1, wherein R and R', same or different, are selected from phenyl and tribromophenyl.

13. The composition of claim 1, wherein A is a dicarboxy-containing connecting group having the formula $OCCH_2CH_2CH_2CH_2CO$.

14. The composition of claim 1, wherein $x=2$.

15. The composition of claim 1, wherein G'' is SO_2.

16. The composition of claim 1, wherein R'''' and R''''' are 2,3-dibromopropyl groups.

17. The composition of claim 1, wherein G'' is $C(CH_3)_3$; $n=0$; R'''' and R''''' are each $CH_2CH_2BrCH_2Br$.

18. The composition of claim 1, wherein G'' is SO_2, $n=0$, R'''' and R''''' are both 2,3-dibromopropyl groups.

19. The composition of claim 1, wherein component (c) is combined with the polymer in an amount of about 0.1% to about 1%, based on the weight of the polymer; and component (d) is combined with the polymer in an amount of about 0.2% to about 2%, based on the weight of the polymer.

20. The composition of claim 1, further including a flame retardant synergist in a weight ratio of flame retardant compound:flame retardant synergist in the range of about 10:1 to 3:1.

21. The composition of claim 20, wherein the flame retardant synergist is selected from the group consisting of antimony trioxide, zinc borate, sodium antimonate, and mixtures thereof.

22. The composition of claim 21, wherein the flame retardant synergist comprises antimony trioxide.

23. A method of flame retarding a polymer comprising adding to said polymer components (a), and (b), as recited in claim 1.

24. A method of flame retarding a polymer comprising adding to said polymer components (a), (b), (c), and (d), as recited in claim 2.

25. The method of claim 23, wherein the polymer is a polyolefin.

26. The method of claim 24, wherein the polymer is a polyolefin.

27. The method of claim 23, wherein the polyolefin is selected from the group consisting of polyolefin fiber and polyolefin film.

28. The method of claim 27, wherein the polyolefin is selected from the group consisting of polyethylene, polypropylene and copolymers of ethylene and propylene.