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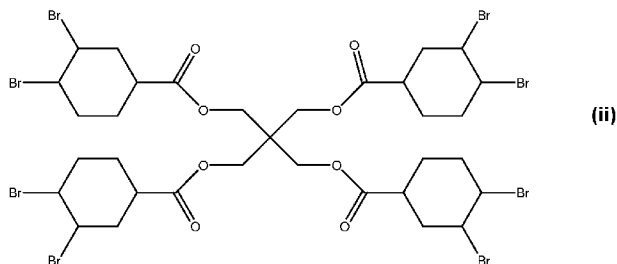
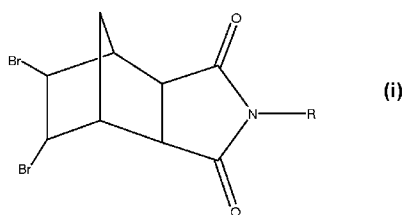
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- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

(54) Title: FLAME RETARDED STYRENIC POLYMER FOAMS AND FOAM PRECURSORS



(57) Abstract: This invention provides styrenic polymer foams, especially expanded and/or extruded styrenic polymer foams, which are flame retarded by use of one or more flame retardants. These flame retardants are (i) at least one compound having the formula: where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, (ii) a compound having the formula: or (iii) a combination of (i) and (ii).



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FLAME RETARDED STYRENIC POLYMER FOAMS AND FOAM PRECURSORS

TECHNICAL FIELD

5 [0001] This invention relates to polystyrenic foams flame retarded with a brominated flame retardant.

BACKGROUND

10 [0002] Styrenic polymer foams such as extruded polystyrene foams (XPS) and expandable polystyrene foams (EPS) are in widespread use. In many cases it is desired to decrease the flammability of such products by incorporating a flame retardant therewith. It is desirable therefore to provide flame retardants that can be used in the production of both types of products.

15 [0003] Flame retardant extruded styrenic polymers such as XPS are typically made by mixing the styrenic polymer, a flame retardant, and a blowing agent in an extruder, and extruding the resultant mixture through a die providing the desired dimensions of the product, such as boards with various thicknesses and one of several different widths. For use in this process it is important that the flame retardant have good thermal stability and low corrosivity toward metals with which the hot blend comes into contact in the process.
20 Also it is desirable that the flame retardant mix well with the other components in the extruder.

[0004] Flame retardant compounds for use in extruded polystyrene foams have many requirements, including thermal stability, substantial miscibility in polystyrene, and high flame retardancy. The flame retardant compound also must not interfere with the foaming
25 process. For example, if a brominated flame retardant exhibits off-gassing of HBr due to flame retardant degradation, it may be difficult to maintain a consistent closed cell structure. Thus, the flame retardant should exhibit low thermal HBr emission under extrusion and foaming conditions. Furthermore, significant off-gassing of HBr due to flame retardant degradation can cause the molecular weight of the polystyrene to be
30 diminished. While not wishing to be bound by theory, it is believed that the HBr forms bromine radicals that cause scission of the polystyrene chains.

[0005] Flame retardant expandable styrenic polymers such as EPS are typically made by suspension polymerization of a mixture of styrene monomer(s) and flame retardant in water to form beads of styrenic polymer. The small beads (*e.g.*, averaging about 1 mm in

diameter) so formed are then pre-expanded with steam and then molded again with steam to produce large foam blocks which can be several meters high, and 2-3 meters wide, that will be cut in the desired dimensions. For use in this process it is desirable for the flame retardant to have sufficient solubility in the styrenic monomer(s), especially in styrene, such that it does not adversely affect the suspension polymerization. The flame retardant desirably has a minimum solubility in styrene at about 25°C of at least about 0.5 wt% to about 10 wt%. In another aspect, the flame retardants preferably have a minimum solubility in styrene at about 40°C of about 0.5 wt % to about 10 wt %. There is no upper constraint on the solubility of the flame retardant in styrene.

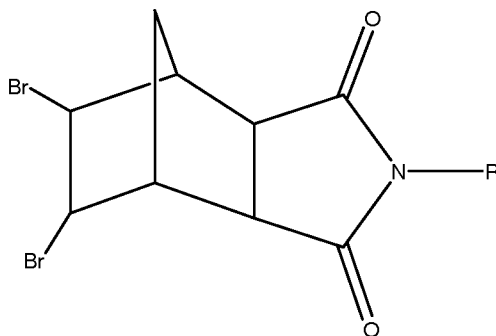
[0006] While some brominated flame retardants have been proposed or used in extruded styrenic polymers such as XPS and/or in expandable styrenic polymers such as EPS, typically high dosage levels of flame retardant have been required to achieve the desired effectiveness. The high cost of some of those flame retardants when coupled with the high dosage levels required for good effectiveness constitute a problem requiring an effective solution.

[0007] This invention provides new flame retardant expanded and extruded styrenic polymers and processes by which they can be prepared.

SUMMARY OF THE INVENTION

[0008] This invention provides styrenic polymer foams and styrenic polymer foam precursors that are flame retarded by use of one or more bromine-containing flame retardant additives which are

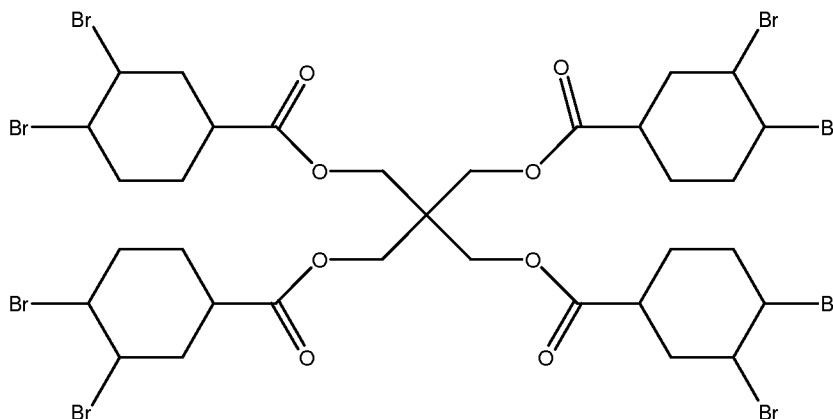
(i) N-substituted dibromonorbornane dicarboximides having the formula



where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a

halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or

- (ii) a brominated pentaerythritol tetracyclohexenate having the formula



or

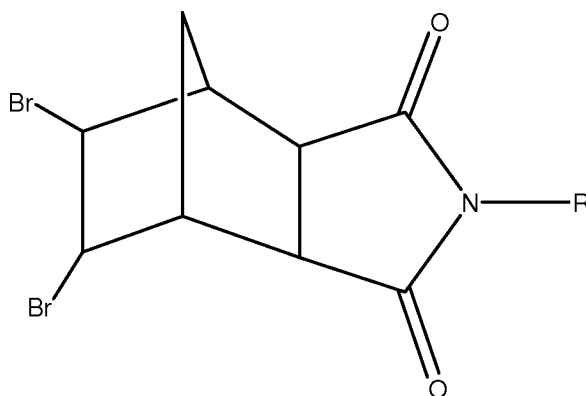
- 5 (iii) a combination of (i) and (ii).

Other embodiments of this invention are methods for producing such flame retarded styrenic polymer foam compositions and such flame retarded styrenic polymer foam precursor compositions.

[0009] These bromine-based flame retardants are characterized by suitably high bromine
 10 contents. In addition, they can be effectively used as flame retardants in both EPS and XPS type compositions, in that experience to date indicates that they should have good solubility in styrenic monomers such as styrene to facilitate use in forming EPS-type beads or granules, they should have adequate thermal stability for use in styrenic polymer foams, they should have desirable melting temperatures, and they should be effective at low
 15 dosage levels. Moreover, some if not all, of these flame retardants should be suitably cost-effective as flame retardants because of the low loading levels at which they can be effectively used.

[0010] An embodiment of this invention is a flame retardant styrenic polymer foam composition. The composition comprises a styrenic polymer and flame retardant amount
 20 of a flame retardant resulting from inclusion in the foam recipe before or during formation of the foam

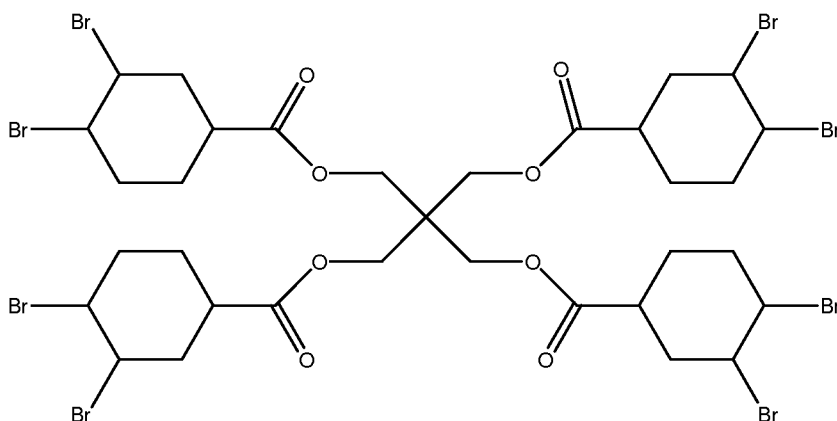
- (i) at least one compound having the formula:



where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having

5

(ii) a compound having the formula:



or

10 (iii) a combination of (i) and (ii).

In some embodiments of this invention, the styrenic polymer foam composition is either a) in the form of expandable styrenic polymer beads or granules or b) in the form of an extruded styrenic polymer foam, with the proviso that for compound (i), when said styrenic polymer foam composition is b), R is not hydrogen. In some embodiments, no other flame retardant is employed. In another embodiment of this invention, the sole flame retardant used in forming the expanded or extruded styrenic polymer is (i), (ii), or

15 (iii), and at least one synergist, such as dicumyl, or at least one thermal stabilizer, such as

dibutyl tin maleate or hydrocalcite is included in the expanded or extruded styrenic polymer. It will be noted that the expanded or extruded styrenic polymer compositions of this invention can be devoid of synergists usually employed in unfoamed or unexpanded styrenic polymers such as antimony oxide.

- 5 [0011] These and other embodiments and features of this invention will be still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

- 10 [0012] It will be understood and appreciated that when a given flame retardant is included in the foam recipe before or during formation of the foam, (a) the composition of the given flame retardant in the resultant foam may not be changed, or (b) the composition of the given flame retardant may in part be changed or altered such that the resultant foam contains some of the given flame retardant along with one or more different substances derived from the given flame retardant, at least one of which different substances
- 15 preferably is a flame retardant substance different from the given flame retardant, or (c) the composition of the given flame retardant may be entirely changed or altered such that the resultant foam contains in lieu of any of the given flame retardant one or more substances derived from the given flame retardant that are different from the given flame retardant, at least one of which different substances is a flame retardant substance. Thus,
- 20 when the phrase "flame retardant resulting from inclusion in the foam recipe" (or a phrase of similar import) is used herein, the words "flame retardant" (although used in the singular) does not in any way restrict the number of flame retardant substances that may result from the inclusion in the foam recipe of one or more given flame retardants. Also, as used herein and unless expressly indicated to the contrary, the term "flame retardant" or
- 25 "flame retardant amount" does not constitute a restriction on the number of flame retardant components that may be present or used in the foam recipe or resultant foam.

[0013] By the term "foam recipe" as used herein, is meant any combination of materials that can be expanded to form a foam. Thus, for example, a "foam recipe" can be:

- 1) a mixture formed from components comprised of at least styrenic polymer, at least
30 one flame retardant of this invention, and at least one blowing agent, such mixture being extrudable to form an XPS-type of foam; or
- 2) a mixture formed from components comprised of at least one styrenic monomer and at least one flame retardant of this invention, which mixture is in water or

other liquid medium in which suspension polymerization can be carried out to form beads or granules of styrenic polymer; or

- 3) beads or granules made by suspension polymerization of a mixture as in 2), which beads or granules can be pre-expanded, for example by steam to form larger beads; or

- 4) larger pre-expanded beads or granules formed by pre-expanding, for example, with steam, beads or granules made by suspension polymerization of a mixture as in 2), which larger pre-expanded beads can be molded, for example, with steam to produce large blocks of expanded styrenic polymer such as EPS-type foam. In other words, a "foam recipe" is any precursor mixture of a styrenic polymer foam of this invention.

It has been discovered that use of N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide to form a flame retardant composition results in a thermally stable and efficacious polystyrene foam. N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarbox-imide is readily melt blended into the molten polystyrene resin to form a flame retardant composition. Unlike other compounds that tend to degrade during processing and diminish foam quality, N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide remains stable during processing and does not adversely affect formation of the polystyrene foam.

In one embodiment of this invention, a flame retardant composition in which the flame retardant is an N-substituted dibromonorbornane dicarboximide has an initial shear viscosity that decreases less than about 15% after about 32 minutes at 190°C. In another embodiment, the styrenic polymer foam composition in which the flame retardant is an N-substituted dibromonorbornane dicarboximide may be formed from a mixture having an initial shear viscosity that decreases less than about 10% after about 32 minutes at 175°C. In another embodiment, the foam is formed from a composition in which the flame retardant is an N-substituted dibromonorbornane dicarboximide has an initial shear viscosity that decreases less than about 2% after about 32 minutes at 190°C.

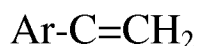
[0014] The styrenic polymer foam composition may be formed from a mixture in which the styrenic polymer has a molecular weight (M_w) of at least about 90% of the styrenic polymer in an identical composition without the flame retardant compound. In one aspect, the foam is formed from a composition in which the styrenic polymer has a molecular

weight (M_w) of at least about 97% of the styrenic polymer in an identical composition without the flame retardant compound.

[0015] Additionally, the color of the styrenic polymer foam composition is not altered significantly by the presence of N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide. Compared with the styrenic polymer without a flame retardant compound, the styrenic polymer foam composition may have an average Yellowness Index (YI) of about 1 to about 10. In another embodiment, the styrenic polymer foam composition has an average Yellowness Index of about 1 to about 5. In a further embodiment, the styrenic polymer foam composition has an average Yellowness Index of about 1 to about 3. In still another embodiment, the styrenic polymer foam composition has an average Yellowness Index of about 1 to about 2. In yet another embodiment, the styrenic polymer foam composition has an average Yellowness Index of about 1.

Styrenic Polymers

[0016] The styrenic polymer foams that are flame retarded pursuant to this invention are foamed (expanded) polymers of one or more polymerizable alkenyl aromatic compounds. At least a major amount (by weight) of at least one alkenyl aromatic compound of the formula



where Ar is an aromatic hydrocarbyl group and R is a hydrogen atom or a methyl group, is chemically combined to form a styrenic homopolymer or copolymer. Examples of such styrenic polymers are homopolymers of styrene, alpha-methylstyrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, ar-ethylstyrene, ar-vinylstyrene, ar-chlorostyrene, ar-bromostyrene, ar-propylstyrene, ar-isopropylstyrene, 4-tert-butylstyrene, o-methyl-alpha-methylstyrene, m-methyl-alpha-methylstyrene, p-methyl-alpha-methylstyrene, ar-ethyl-alpha-methylstyrene, and copolymers of two or more of such alkenyl aromatic compounds with minor amounts (by weight) of other readily polymerizable olefinic compounds such as, for example, methyl methacrylate, acrylonitrile, maleic anhydride, citraconic anhydride, itaconic anhydride, acrylic acid, vinyl carbazole, and rubber reinforced (either natural or synthetic) styrenic polymers. Preferably at least 80 weight % of styrene is incorporated in the styrenic copolymers. Thus in each and every embodiment of this

invention set forth anywhere in this disclosure, the styrenic polymer of the foam preferably comprises polystyrene or a styrenic copolymer in which at least 80 wt% of the polymer is formed from styrene.

[0017] The styrenic polymers can be a substantially thermoplastic linear polymer or a mildly cross-linked styrenic polymer. Among suitable procedures that can be used for producing mildly cross-linked styrenic polymers for use in foaming operations are those set forth, for example, in U.S. Pat. Nos. 4,448,933; 4,532,264; 4,604,426; 4,663,360 and 4,714,716.

[0018] Methods for producing styrenic foams including both XPS foams and EPS foams are well known and reported in the literature. Thus any suitable method can be employed as long as the resultant foam is flame retarded by use of a flame retardant amount of one or more flame retardants pursuant to this invention. As a guide for dosage levels for use in foamed styrenic polymers, it is desirable to blend small amounts of the flame retardant in unfoamed and/or foamed crystal styrenic polymer and determine the LOI (Limited Oxygen Index) of molded test specimens made from the unfoamed blend. If such test specimens give an LOI that is at least one unit higher than a molded specimen of the same neat styrenic polymer, the dosage level should be suitable when used in the same foamed or foamable styrenic polymer. Typically the amount of flame retardant used in the styrenic foams of this invention for XPS foams is in the range of about 1 to about 7 wt%, and preferably in the range of about 2 to about 5 wt% based on the total weight of the foam composition. More preferably, the amount of flame retardant used in the styrenic foams of this invention for XPS foams is in the range of about 3 to about 5 wt% based on the total weight of the foam composition. Typically the amount of flame retardant used in the styrenic foams of this invention for EPS foams is in the range of about 0.5 to about 7 wt% of the styrenic polymer foam composition. In still another embodiment, the flame retardant compound is present in an amount of about 1 to about 2 wt% of the EPS styrenic polymer foam composition.

Extruded Styrenic Foams

[0019] Flame retarded styrenic polymer foams can be prepared conveniently and expeditiously by use of known procedures. For example one useful general procedure involves heat plastifying a thermoplastic styrenic polymer composition of this invention in an extruder. From the extruder the heat plastified resin is passed into a mixer, such as a

rotary mixer having a studded rotor encased within a housing which preferably has a studded internal surface that intermeshes with the studs on the rotor. The heat-plastified resin and a volatile foaming or blowing agent are fed into the inlet end of the mixer and discharged from the outlet end, the flow being in a generally axial direction. From the mixer, the gel is passed through coolers and from the coolers to a die which extrudes a generally rectangular board. Such a procedure is described for example in U.S. Pat. No. 5,011,866. Other procedures include use of systems in which the foam is extruded and foamed under sub-atmospheric, atmospheric and super-atmospheric pressure conditions. As indicated in U.S. Pat. No. 5,011,866, one useful sub-atmospheric (vacuum) extrusion process is described in U.S. Pat. No. 3,704,083. This process is indicated to be of advantage in that the type of vacuum system therein described does not require a low-permeability/high permeability blowing agent mixture, due to the influence of the vacuum on the foaming process. Other disclosures of suitable foaming technology appear, for example, in U.S. Pat. Nos. 2,450,436; 2,669,751; 2,740,157; 2,769,804; 3,072,584; and 3,215,647.

[0020] The extruded polystyrene foam may be used to form an article of manufacture. For example, the extruded polystyrene foam may be used to form thermal insulation.

[0021] In some embodiments of this invention, a flame-retarded extruded styrenic polymer foam composition contains a flame retardant compound, which is an N-substituted dibromonorbornane dicarboximide, where the styrenic polymer foam composition has at least one of the following characteristics:

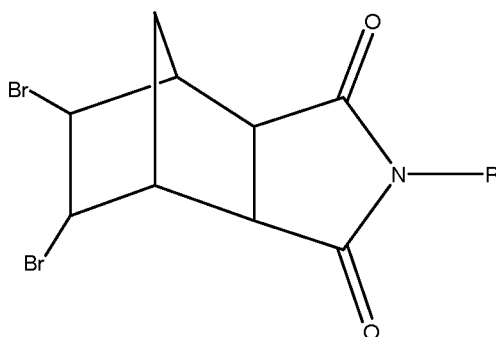
- (a) the styrenic polymer foam composition is formed from a mixture having an initial shear viscosity that decreases less than about 15% after about 32 minutes at 190°C;
- (b) the styrenic polymer foam composition is formed from a mixture having an initial shear viscosity that decreases less than about 10% after about 32 minutes at 175°C;
- (c) the styrenic polymer foam composition is formed from a composition in which the styrenic polymer has a molecular weight (M_w) of at least about 90% of the styrenic polymer in an identical composition without the flame retardant compound; or
- (d) the styrenic polymer foam composition has an average Yellowness Index of about 1 to about 5.

Expandable Styrenic Beads or Granules

[0022] The styrenic polymer compositions of this invention can be used in the production of expandable beads or granules having enhanced flame resistance. In general, these materials may be produced by use of equipment, process techniques and process conditions previously developed for this purpose, since the flame retardant compositions of this invention do not materially affect adversely the processing characteristics and overall properties of the styrenic polymer employed. Also, known and established techniques for expanding the expandable beads or granules, and for molding or forming the further expanded beads or granules into desired products are deemed generally applicable to the expandable beads or granules formed from the styrenic polymer compositions of this invention. Suitable technology for producing expandable beads or granules is disclosed, for example, in U.S. Pat. Nos. 2,681,321; 2,744,291; 2,779,062; 2,787,809; 2,950,261; 3,013,894; 3,086,885; 3,501,426; 3,663,466; 3,673,126; 3,793,242; 3,973,884; 4,459,373; 4,563,481; 4,990,539; 5,100,923; and 5,124,365. Procedures for converting expandable beads of styrenic polymers to foamed shapes is described, for example, in U.S. Pat. Nos. 3,674,387; 3,736,082; and 3,767,744.

Flame Retardants

[0023] Flame retardants of category (i) utilized in the practice of this invention are at least one compound having the formula:



where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms. Preferably, R is a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about three carbon atoms, or a halogenated linear or

branched substituted or unsubstituted aliphatic group having from two to about three carbon atoms. More preferably, R is a methyl group or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about three carbon atoms. Typically, only one substituted dibromonorbornane dicarboximide compound is used to flame retard a polystyrenic foam, but two or more N-substituted dibromonorbornane dicarboximide compounds can be used to flame retard a polystyrenic foam, where "different compounds" means that R is not the same in the different compounds. Flame retardants of category (i) are compositions of the invention.

[0024] Suitable R groups include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, hexyl, isohexyl, 2,3-dibromopropyl, 3,4-dibromobutyl, 4,5-dibromopentyl, 5,6-dibromohexyl, 2,3,5,6-tetrabromohexyl, and the like. Preferred R groups include methyl and 2,3-dibromopropyl.

[0025] Some synthetic routes to N-substituted dibromonorbornane dicarboximide flame retardants used in the present invention are known; see in this connection U.S. Pat. No. 3,784,509. Generally, 5,6-dibromonorbornane-2,3-dicarboxylic anhydride can be made by reacting maleic anhydride with cyclopentadiene to form 5-norbornene-2,3-dicarboxylic anhydride, and brominating the 5-norbornene-2,3-dicarboxylic anhydride, or by reacting dibromocyclopentadiene with maleic anhydride. Bromination of the 5-norbornene-2,3-dicarboxylic anhydride is a preferred route. One way to form the N-substituted dibromonorbornane dicarboximide is via reaction of the 5,6-dibromonorbornane-2,3-dicarboxylic anhydride with ammonia or a primary amine to give the desired 5,6-dibromonorbornane-2,3-dicarboximide. If the hydrocarbyl group attached to the nitrogen is olefinic, bromine can be added to this olefinic group, resulting in a compound containing bromine on the norbornane ring and on the nitrogen substituent.

[0026] A process of this invention and a preferred method for producing N-substituted dibromonorbornane dicarboximide flame retardants comprises forming a 5-norbornene-2,3-dicarboximide by bringing together 5-norbornene-2,3-dicarboxylic anhydride and ammonia or a primary amine, forming an intermediate product, followed by removal of water to form 5-norbornene-2,3-dicarboximide. The 5-norbornene-2,3-dicarboximide is brominated to form a 5,6-dibromonorbornane-2,3-dicarboximide. This process is advantageous when bromination of an unsaturated group on the dicarboximide nitrogen is desired, since all of the bromination can occur in one step. Bromine is a preferred bromination agent in the process. Without wishing to be bound by theory, the

intermediate product is believed to be comprised of a 5-norbornene-3-aminocarbonyl-2-carboxylic acid.

[0027] In the processes of the invention, the group on the primary amine usually corresponds to the desired group on the nitrogen in the final product, *i.e.*, the primary amine has an amino group which is a methyl group, or a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms. The amino group is preferably a methyl group or a linear or branched substituted or unsubstituted aliphatic group having from two to about three carbon atoms. Examples of primary amines that can be used in the process include methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, tert-butylamine, pentylamine, isopentylamine, hexylamine, isohexylamine, allylamine, butenylamine, pentenylamine, hexenylamine, hexadienylamine, and the like. Preferred primary amines include methylamine and allylamine.

[0028] Another process of this invention and preferred method for producing N-substituted dibromonorbornane dicarboximide flame retardants comprises forming an N-substituted 5-norbornene-2,3-dicarboximide, followed by bromination of the 5-norbornene-2,3-dicarboximide to form a 5,6-dibromonorbornane-2,3-dicarboximide. The N-substituted 5-norbornene-2,3-dicarboximide is formed by bringing together 5-norbornene-2,3-dicarboxylic anhydride and ammonia or aqueous ammonium hydroxide in a liquid organic medium, forming an intermediate product, followed by removal of water to form 5-norbornene-2,3-dicarboximide. The dried N-H imide then may be deprotonated with an inorganic carbonate. The deprotonated imide, a 5-norbornene-2,3-dicarboximide salt, is brought together with a hydrocarbyl chloride, wherein the hydrocarbyl chloride is methyl chloride, or a linear or branched substituted or unsubstituted aliphatic chloride having from two to about six carbon atoms, to form an N-substituted 5-norbornene-2,3-dicarboximide. The N-substituted 5-norbornene-2,3-dicarboximide is brominated to form a 5,6-dibromonorbornane-2,3-dicarboximide. Bromine is a preferred bromination agent in this process. As for the above process, this process is advantageous when bromination of an unsaturated group on the dicarboximide nitrogen is desired, since all of the bromination can occur in one step. Again without wishing to be bound by theory, the intermediate product is believed to be comprised of a 5-norbornene-3-aminocarbonyl-2-carboxylic acid.

[0029] Alternatively, as the N-H imide (5-norbornene-2,3-dicarboximide) is commercially available, the above process can be performed starting from the N-H imide.

[0030] Another process of this invention is a method for producing an unsubstituted dibromonorbornane dicarboximide flame retardant. The method comprises brominating 5-norbornene-2,3-dicarboximide to form 5,6-dibromonorbornane-2,3-dicarboximide. Bromine is a preferred bromination agent in this process. If desired, the brominated N-H
5 imide can be deprotonated with an inorganic carbonate, and the deprotonated imide, a 5-norbornene-2,3-dicarboximide salt, is then brought together with a hydrocarbyl chloride, wherein the hydrocarbyl chloride is methyl chloride, or a linear or branched substituted or unsubstituted aliphatic chloride having from two to about six carbon atoms, to form an N-substituted 5-norbornene-2,3-dicarboximide. To N-substitute the imide in this process,
10 gentler conditions, such as lower temperatures, are recommended.

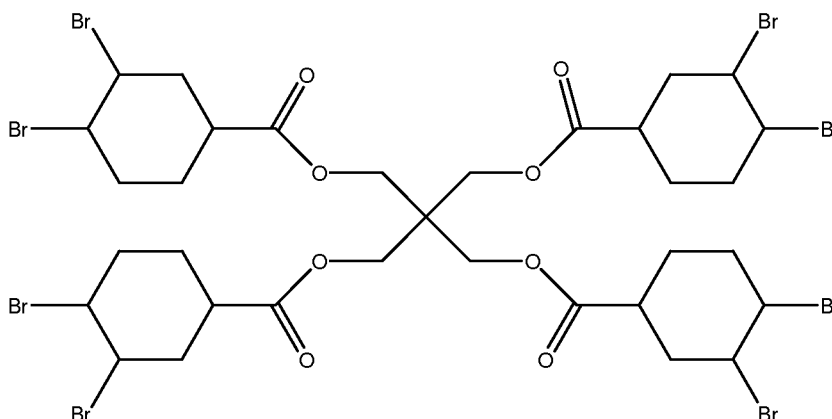
[0031] Various inorganic carbonates may be used in the process. Such inorganic carbonates include carbonates of the alkali metals, alkaline earth metals, zinc, and the like. Examples of suitable carbonates include lithium carbonate, sodium carbonate, potassium carbonate, magnesium carbonate, calcium carbonate, zinc carbonate, and the
15 like, or a mixture of any two or more inorganic carbonates. Alkali metal carbonates are preferred, and sodium carbonate and potassium carbonate are preferred alkali metal carbonates. The inorganic carbonate is typically introduced to the reaction vessel in solid form, preferably in anhydrous solid form. It is recommended and preferred that a phase transfer catalyst, normally a quaternary ammonium halide be employed in the process with
20 the inorganic carbonate. Tetrabutylammonium bromide is a common quaternary ammonium halide phase transfer catalyst.

[0032] The hydrocarbyl chlorides that can be used in the process are methyl chloride, or a linear or branched substituted or unsubstituted aliphatic chloride having from two to about six carbon atoms; preferably, the hydrocarbyl chloride is a linear or branched
25 substituted or unsubstituted aliphatic chloride having from two to about three carbon atoms. Suitable hydrocarbyl chlorides that can be used in the process include methyl chloride, ethyl chloride, propyl chloride, isopropyl chloride, butyl chloride, isobutyl chloride, tert-butyl chloride, pentyl chloride, isopentyl chloride, hexyl chloride, isohexyl chloride, allyl chloride, butenyl chloride, pentenyl chloride, hexenyl chloride, hexadienyl
30 chloride, and the like. Preferred hydrocarbyl chlorides include allyl chloride.

[0033] The liquid organic medium for this process is generally comprised of one or more solvents which are preferably polar, not water miscible, or more preferably, are both polar

and not water miscible. Suitable solvents can include chlorobenzene, ethyl acetate, acetone, acetonitrile, and the like.

[0034] The flame retardant of category (ii) utilized in the practice of this invention is a compound having the formula:



5

[0035] This flame retardant of category (ii) is a composition of the invention.

[0036] Synthesis of the brominated pentaerythritol tetracyclohexenate flame retardant via bromination of pentaerythritol tetracyclohexenate is an embodiment of this invention. Bromination can be carried out in any conventional manner; use of elemental bromine is preferred. Routes to pentaerythritol tetracyclohexenate are known; see in this connection

[0037] A process of this invention and a preferred method for producing the brominated pentaerythritol tetracyclohexenate comprises I) bringing together pentaerythritol tetraacrylate and 1,3-butadiene to form pentaerythritol tetracyclohexenate; and II) brominating at least a portion of the pentaerythritol tetracyclohexenate formed in I). Pentaerythritol tetraacrylate is commercially available, and the bromination can be carried out in any conventional manner; use of elemental bromine is preferred.

[0038] Another process of this invention and preferred method for producing the brominated pentaerythritol tetracyclohexenate comprises I) bringing together, in a liquid medium, pentaerythritol, at least one alkyl ester of 3-cyclohexene carboxylic acid, and a catalytic amount of lithium amide and/or sodium amide to form a reaction mixture, and substantially continuously removing alcohol formed in the reaction mixture, to form pentaerythritol tetracyclohexenate; and II) brominating at least a portion of the pentaerythritol tetracyclohexenate formed in I). The bromination can be carried out in any conventional manner; use of elemental bromine is preferred.

[0039] The alkyl ester of 3-cyclohexene carboxylic acid is normally a C₁-C₄ alkyl ester, and the alkyl ester of 3-cyclohexene carboxylic acid can be methyl 3-cyclohexene carboxylate, ethyl 3-cyclohexene carboxylate, propyl 3-cyclohexene carboxylate, isopropyl 3-cyclohexene carboxylate, butyl 3-cyclohexene carboxylate, isobutyl 3-cyclohexene carboxylate, tert-butyl 3-cyclohexene carboxylate, and the like. A preferred alkyl esters of 3-cyclohexene carboxylic acid is methyl 3-cyclohexene carboxylate. Mixtures of two or more alkyl esters of 3-cyclohexene carboxylic acid can be used, if desired.

[0040] Lithium amide and/or sodium amide is used in a catalytic amount in this process of the invention. Lithium amide is preferred. A catalytic amount of lithium amide and/or sodium amide is typically in the range of about 4 mole% to about 10 mole% relative to the pentaerythritol. Preferably, the amount of lithium amide and/or sodium amide relative to pentaerythritol is in the range of about 5 mole% to about 8 mole%.

[0041] The alcohol produced in step I) of the process is a normally a C₁-C₄ alcohol, and corresponds to the ester(s) used in the process. For example, using methyl 3-cyclohexene carboxylate will cause methanol to be formed.

[0042] Step I) of the process is usually conducted a temperature of at least about 140°C, in order to speed up the reaction as well as to facilitate the removal of the alcohol formed in the reaction mixture. Thus, the liquid medium is generally one or more organic solvents having boiling point of at least about 130°C. Preferred solvents are those that either co-distill or form an azeotrope with the alcohol produced in the reaction mixture. Suitable solvents include, but are not limited to, o-xylene, m-xylene, p-xylene, xylenes, ethylbenzene, chlorobenzene, diethylbenzene, amylbenzene, tetrahydronaphthalene, and the like. Mixtures of two or more solvents can be used as the liquid medium, provided that the boiling point of the liquid medium is at least about 130°C.

[0043] In an embodiment of this invention, the flame retardant compound is present in an amount of from about 0.1 to about 10 wt% of the extruded styrenic polymer foam composition. In another embodiment, the flame retardant compound is present in an amount of about 1 to about 7 wt% of the extruded styrenic polymer foam composition. In still another embodiment, the flame retardant compound is present in an amount of about 2 to about 5 wt% of the extruded styrenic polymer foam composition. In yet another embodiment, the flame retardant compound is present in an amount of about 3 to about 5 wt% of the extruded styrenic polymer foam composition.

[0044] In another embodiment of this invention, the flame retardant compound is present in an amount of from about 0.1 to about 10 wt% of the expanded styrenic polymer foam composition. In another embodiment, the flame retardant compound is present in an amount of about 0.5 to about 7 wt% of the expanded styrenic polymer foam composition.

5 In still another embodiment, the flame retardant compound is present in an amount of about 1 to about 2 wt% of the expanded styrenic polymer foam composition.

[0045] When the flame retardant compound is an N-substituted dibromonorbornane dicarboximide, the styrenic polymer foam compositions of this invention may be formed from a mixture having an initial shear viscosity that decreases less than about 15% after
10 about 32 minutes at 190°C. In another embodiment, when the flame retardant compound is an N-substituted dibromonorbornane dicarboximide, the styrenic polymer foam composition may be formed from a mixture having an initial shear viscosity that decreases less than about 10% after about 32 minutes at 175°C. In still another embodiment, the foam is formed from a composition in which the flame retardant is an N-substituted
15 dibromonorbornane dicarboximide has an initial shear viscosity that decreases less than about 2% after about 32 minutes at 190°C.

[0046] The styrenic polymer foam composition may be formed from a mixture in which the polystyrene has a molecular weight (M_w) of at least about 90% of the styrenic polymer in an identical composition without the flame retardant compound. In another aspect, the
20 styrenic polymer foam composition may be formed from a mixture in which the styrenic polymer has a molecular weight (M_w) of at least about 97% of the styrenic polymer in an identical composition without the flame retardant compound.

[0047] The styrenic polymer foam composition can have an average Yellowness Index of about 1 to about 10. In another embodiment, the styrenic polymer foam composition
25 may have an average Yellowness Index of about 1 to about 5, more preferably of about 1 to about 3, most preferably of about 1 to about 2, and in some embodiments the foam has an average Yellowness Index of about 1.

Foaming Agents

30 [0048] Any of a wide variety of known foaming agents or blowing agents can be used in producing the expanded or foamed flame resistant polymers of this invention. U.S. Pat. No. 3,960,792 gives a listing of some suitable materials. Generally speaking, volatile carbon-containing chemical substances are the most widely for this purpose. They

include, for example, such materials as aliphatic hydrocarbons including ethane, ethylene, propane, propylene, butane, butylene, isobutane, pentane, neopentane, isopentane, hexane, heptane and mixtures thereof; volatile halocarbons and/or halohydrocarbons, such as methyl chloride, chlorofluoromethane, bromochlorodifluoromethane, 1,1,1-trifluoroethane, 1,1,1,2-tetrafluoroethane, dichlorofluoromethane, dichlorodifluoromethane, chlorotrifluoromethane, trichlorofluoromethane, sym-tetrachlorodifluoroethane, 1,2,2-trichloro-1,1,2-trifluoroethane, sym-dichlorotetrafluoroethane; volatile tetraalkylsilanes, such as tetramethylsilane, ethyltrimethylsilane, isopropyltrimethylsilane, and n-propyltrimethylsilane; and mixtures of such materials. One preferred fluorine-containing blowing agent is 1,1-difluoroethane also known as HFC-152a (FORMACEL Z-2, E.I. duPont de Nemours and Co.) because of its reported desirable ecological properties. Water-containing vegetable matter such as finely-divided corn cob can also be used as blowing agents. As described in U.S. Pat. No. 4,559,367, such vegetable matter can also serve as fillers. Use of carbon dioxide as a foaming agent, or at least a component of the blowing agent, is particularly preferred because of its innocuous nature *vis-a-vis* the environment and its low cost. Methods of using carbon dioxide as a blowing agent are described, for example, in U.S. Pat. No. 5,006,566 wherein the blowing agent is 80 to 100% by weight of carbon dioxide and from 0 to 20% by weight of one or more halohydrocarbons or hydrocarbons that are gaseous at room temperature, in U.S. Pat. Nos. 5,189,071 and 5,189,072 wherein a preferred blowing agent is carbon dioxide and 1-chloro-1,1-difluoroethane in weight ratios of 5/95 to 50/50, and in U.S. Pat. No. 5,380,767 wherein preferred blowing agents comprise combinations of water and carbon dioxide. Other preferred blowing agents and blowing agent mixtures include nitrogen or argon, with or without carbon dioxide. If desired, such blowing agents or blowing agent mixtures can be mixed with alcohols, hydrocarbons or ethers of suitable volatility. See for example, U.S. Pat. No. 6,420,442.

Other components

[0049] Such ingredients as extrusion aids (*e.g.*, barium stearate or calcium stearate), peroxide or C-C synergists, acid scavengers (*e.g.*, magnesium oxide or tetrasodium pyrophosphate), dyes, pigments, fillers, stabilizers, antioxidants, antistatic agents, reinforcing agents, and the like can be included in the foam compositions of this invention. If desired, nucleating agents (*e.g.*, talc, calcium silicate, or indigo) to control cell size can

be included in the styrenic polymer compositions used in producing the flame retardant expanded or foamed styrenic polymers of this invention. Each of the particular ancillary materials selected for use in the foam compositions of this invention are used in conventional amounts, and should be selected such that they do not materially affect adversely the properties of the finished polymer foam composition for its intended utility.

[0050] As described above, in some preferred embodiments of this invention, no other flame retardant is employed. In other preferred embodiments of this invention, at least one synergist, such as dicumyl or dicumyl peroxide for expanded polystyrene or dicumyl for extruded polystyrene, or at least one thermal stabilizer, such as dibutyl tin maleate or hydrocalcite is included in the styrenic polymer foam composition. Examples of synergists that may be suitable for use with the present invention include, but are not limited to, dicumyl, dicumyl peroxide, ferric oxide, zinc oxide, zinc borate, and oxides of a Group V element, for example, bismuth, arsenic, phosphorus, and antimony. When a synergist is employed, the ratio of the total amount of synergist to the total amount of flame retardant compound is typically about 1:1 to about 1:7. In one embodiment of the present invention, the ratio of the total amount of synergist to the total amount of flame retardant compound is about 1:2 to about 1:4.

[0051] Examples of thermal stabilizers include, but are not limited to, zeolites, hydrotalcite, talc, organotin stabilizers, including butyl tin, octyl tin, and methyl tin mercaptides, butyl tin carboxylate, octyl tin maleate, dibutyl tin maleate, epoxy derivatives, polymeric acrylic binders, metal oxides, for example, ZnO, CaO, and MgO, mixed metal stabilizers, for example, zinc, calcium/zinc, magnesium/zinc, barium/zinc, and barium/calcium/zinc stabilizers, metal carboxylates, for example, zinc, calcium, barium stearates or other long chain carboxylates, metal phosphates, for example, sodium, calcium, magnesium, or zinc or any combination thereof. The amount of such thermal stabilizer, when employed, is typically in the range of about 1 to about 5 wt% based on the total weight of the polymer composition. It will be noted that both the expanded styrenic polymer compositions of this invention and the extruded styrenic polymer compositions of this invention can be devoid of synergists employed in unfoamed or unexpanded styrenic polymers such as antimony oxide.

[0052] The following examples are presented for purposes of illustration, and are not intended to impose limitations on the scope of this invention.

EXAMPLE 1

Synthesis of N-methyl-5,6-dibromonorbornane-2,3-dicarboximide

[0053] **2-methyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoisoindole-1,3-dione** (N-methyl-5-norbornene-2,3-dicarboximide). A 12 L round-bottom flask was charged with 5-norbornene-2,3-dicarboxylic anhydride (nadix anhydride, 880 g, 5.36 mol) and xylenes (4.5 L). The flask was fitted with a thermowell, a 3-way nitrogen gas line connected to a bubbler, a mechanical stirrer, and a cold finger condenser cooled with dry ice/isopropyl alcohol (IPA), and which condenser was connected to a cylinder of methylamine equipped with a regulator. Methylamine (170 g, 5.36 mol) was added to the flask via the condenser, condensed by passage of the gas over the condenser. The addition rate of the methylamine was controlled by the gas flow, which was regulated to keep the reaction temperature between 30 and 35 °C.

[0054] Once the reaction was complete (as verified by ¹H NMR spectroscopy), a Dean Stark trap was inserted between the reactor and the condenser, and a heating mantle was added. The temperature was slowly raised to reflux (108-135 °C, depending on the amount of water present) and water was collected in the trap. The dehydration step was complete after 90 minutes with 100 mL (104%) of water collected. A red-colored impurity was removed with an aqueous sodium bicarbonate wash (5%, 200 mL) at 60 °C, followed by an aqueous wash (200 mL) at 60 °C. The N-methyl imide compound was concentrated using rotary evaporation to give white solids. Purification by distillation (overhead approximately 130 °C/< 1mm) yielded 732g (77%) of white solids (mp 98-101 °C) and 140g of brown residue. GC analysis showed that the imide had a purity of 98.9 area%, with two minor impurities (0.3 and 0.8 area%) eluting within 30 seconds of the N-methyl imide. NMR (¹H, CDCl₃) δ 1.57 (1H, d), 1.75 (1H, d), 2.8 (3H, s), 3.30 (2H, q), 3.37 (2H, m), 6.1 (2H, t). ¹³C NMR (400 MHz, CDCl₃) δ 22.8, 43.4, 44.57, 50.8, 133.07, 176.37.

[0055] **5,6-dibromo-2-methylhexahydro-1H-4,7-methanoisoindole-1,3-dione** (N-methyl-5,6-dibromonorbornane-2,3-dicarboximide). A 5 L round bottom jacketed flask was charged with the N-methyl imide (400 g, 2.24 mol) and bromochloromethane (BCM, 2.2 L). The solution was stirred mechanically and cooled by a circulating bath set at 15 °C. Br₂ (359.9 g, 2.24 mol) was added dropwise from an addition funnel in 5 mL increments to keep the solution as saturated with bromine as possible without having the

temperature increase too rapidly. Once the reaction was complete (checked by GC), the circulating bath temperature was raised to 60 °C (to dissolve any precipitate in the reaction mixture), and 200 mL of aqueous sodium sulfite (10%) was added to the mixture. The mixture was stirred at room temperature for 10 minutes before separating the organic layer from the mixture. The organic layer was washed with 200 mL of aqueous sodium bicarbonate (5%).

[0056] The washed organic layer was returned to the reaction flask, and a distilling column was added. The solution was heated, and about 1 L of water/BCM azeotrope was collected. The slurry produced during the distillation was transferred to a 2 L Erlenmeyer flask and cooled in an ice bath for 1-2 hours. Filtration yielded 556g (64%) of colorless crystals having a purity of 91-93 area% by GC. Mass spectral analysis showed that the remaining materials were two minor isomers of the desired product. A portion of the product was purified by recrystallizing 100 g of the material from 500 mL of 75% v/v chloroform/methanol solution (mp 240–244 °C). Purity by GC ranged from 98 area% to 99 area%. ¹H NMR (400 MHz, d-6 DMSO) δ 1.8 (1H, d), 2.25 (1H, d), 2.8 (3H, s), 2.9 (2H, t), 3.35 (2H, d), 4.3 (2H, d). ¹³C NMR (400 MHz, d-6 DMSO): δ 24.9, 37.8, 47.6, 50.25, 53.9, 176.5.

EXAMPLE 2

Synthesis of N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide

[0057] **2-allyl-3a,4,7,7a-tetrahydro-1H-4,7-methanoisindole-1,3-dione** (N-allyl-5-norbornene-2,3-dicarboximide). A 5 L round bottom flask was charged with 5-norbornene-2,3-dicarboxylic anhydride (650 g, 3.96 mol) and toluene (2.6 L). The flask was fitted with a condenser, thermowell and a mechanical stirrer. Allylamine (226.2 g, 3.96 mol) was dropped into the solution from an addition funnel over a 45-minute period. Using an ice bath, the exothermic reaction was kept below 30 °C. Once the reaction was complete (monitored by ¹H NMR spectroscopy), a Dean-Stark trap was added, and the temperature was slowly raised to 104 °C using a heating mantle; water was collected in the trap. The dehydration step was complete after 70 minutes with 70 mL (97%) of water collected. Colored impurities were removed by an aqueous sodium bicarbonate wash (5%, 200 mL), followed by an aqueous wash (200 mL). The N-allyl imide was concentrated by rotary evaporation. A portion of the resulting oil was distilled at 135-145 °C at 1mm of

pressure. The remainder of the oil was stirred in hot hexane until homogenous, and allowed to cool to room temperature while stirring. The solids were colorless, rod-shaped crystals, mp 55-57 °C, with an isolated yield of 500 g (77% yield). ¹H NMR (400 MHz, CDCl₃): δ 1.5 (1H, d), 1.73 (1H, dt), 3.28 (2H, q), 3.4 (2H, m), 3.94 (2H, dt), 5.1 (2H, dd), 5.6 (1H, m), 6.05 (2H, t). ¹³C NMR (400 MHz, CDCl₃): δ 41.1, 45.3, 46.2, 52.6, 118.4, 131.3, 134.8, 177.6.

[0058] 5,6-dibromo-2-(2,3-dibromopropyl)hexahydro-1H-4,7-methanoisindole-1,3-dione (N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide). A 5 L round bottom jacketed flask was charged with the N-allyl imide (448 g, 2.2 mol) and chloroform (1.5 L; about 330 mL per 100 g of N-allyl imide). The solution was mechanically stirred and cooled to 15 °C by a circulating bath. Br₂ (704.3 g, 4.41 mol) was added dropwise from an addition funnel over a 2-hour period. Once the reaction was complete (checked by GC), 100 mL of 10 wt% aqueous sodium sulfite was added and the mixture was stirred at room temperature for 30-60 minutes. The slurry was filtered, and the filtrate was allowed to separate into layers. The organic layer was separated from the aqueous layer and recombined with the solids. The mixture was stirred for 15-20 minutes with 100 mL of aqueous sodium bicarbonate (5%). The slurry was filtered and the solids were dried. The solids were recrystallized by stirring about 400 g of the solid in 3 L of hot toluene at 90 °C, separating any remaining water, and allowing the solution to cool in an ice bath. The recrystallized solids were colorless crystals, mp 170-174 °C, with a yield of 987.26 g (86%). Purity by GC ranged from 91% to 93 % area. ¹H NMR (400 MHz, CDCl₃): δ 1.79 (1H, d), 2.59 (1H, d), 3.16 (2H, dd), 3.3 (2H, m), 3.36 (1H, t), 3.9 (1H, dd), 4.02 (2H, t), 4.25 (-CHBr-CHH'Br, 1H, dd), 4.41 (-CHBr-CHH'Br, 1H, dd), 4.68 (-CHBr-CHH'Br, 1H, m). ¹³C NMR (400 MHz, CDCl₃): δ 44.15, 38.1, 44.3, 46.4, 47.5, 47.8, 50.57, 51.45, 51.65, 174.89, 175.45.

EXAMPLE 3

Synthesis of the brominated pentaerythritol tetracyclohexenate

[0059] 3-Cyclohexene-1-carboxylic acid, 2,2-bis[[(3-cyclohexen-1-ylcarbonyl)oxy]-methyl]-1,3-propanediyl ester (pentaerythritol tetracyclohexenate). A 500 mL jacketed round bottom flask was charged with o-xylene (about 80 mL, 70 g), pentaerythritol (7.47 g, 54.9 mmol) and methyl 3-cyclohexene carboxylate (40.0 g, 285 mmol). The flask was

fitted with a Dean-Stark distillation bridge, thermocouple, nitrogen purge, and a mechanical stirrer. The circulating bath fluid was heated to 180 °C. After about 2 hours, when the reaction temperature reached about 136 °C, a catalytic amount of lithium amide (63 mg, 2.7 mmol) was added. The circulating bath fluid temperature was increased to 185 °C over the course of one hour to attain a reaction temperature of about 141 °C, where distillation of o-xylene/methanol was observed; the o-xylene/methanol was removed. Over the next 4.5 hours, two more 50 mg aliquots of lithium amide were added, along with 55 g of o-xylene to replace the solvent removed by distillation (about 46 g of o-xylene/methanol). Reaction progress was monitored by gas chromatography (about 5 area% of methyl 3-cyclohexene carboxylate remained). The reactor was cooled to about 24 °C. About 55 mL of toluene and about 55 mL of water were added; the mixture was allowed to separate into two phases. The organic phase was washed, separated, dried over sodium sulfate, and filtered. The solvent and excess 3-cyclohexene carbonate were removed by distillation and rotary evaporation. The reaction progress was monitored by gas chromatography (about 5 area% of methyl 3-cyclohexene carboxylate remained). The product crystallized after standing during 2 days to afford a white solid (26.5 g, 46.9 mmol) in about 85% yield (melting point (DSC): 67 °C; TGA 5 wt% loss: 311 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.68 (-CH-CHH'-CH₂-, 4H), 1.98 (-CH-CHH'-CH₂-, 4H), 2.09 (-CH-CH₂-CH₂-, 8H), 2.23 (-CH-CH₂-CH=CH-, 8H), 2.58 (-C=O-CH-, 4H), 4.15 (-C-CH₂-O-, 8H), 5.67 (-CH=CH-, 8H); ¹³C NMR (400 MHz, CDCl₃): δ 24.47 (-CH-CH₂-CH₂-), 25.12 (-CH-CH₂-CH₂-), 27.55 (-CH-CH₂-CH=CH-), 39.44 (-C=O-CH-), 42.5 (-C-CH₂-), 62.31 (-C-CH₂-O-), 125.10 (-CH-CH₂-CH=CH-), 126.93 (-CH-CH₂-CH=CH-), 175.35 (C=O).

[0060] 3,4-Dibromocyclohexyl-1-carboxylic acid, 2,2-bis[(3,4-dibromocyclohex-1-ylcarbonyl)oxy]methyl-1,3-propanediyl ester (brominated pentaerythritol tetracyclohexenate). A 500 mL jacketed round bottom flask was charged with about 90 g of dichloromethane and 10 g of ethanol. The flask was fitted with a thermocouple, nitrogen purge and a mechanical stirrer. The unsaturated 3-cyclohexene-1-carboxylic acid, 2,2-bis[(3-cyclohexen-1-ylcarbonyl)oxy]methyl-1,3-propanediyl ester (16.0 g, 28.3 mmol) was dissolved in the solvent mixture, and the circulating bath fluid was cooled to – 10 °C under low-light conditions. Bromine (21.5 g, 6.9 mL, 135 mmol, 4.75 eq) was added drop-wise over 25 minutes, maintaining the reaction temperature below 1 °C. After

the addition of bromine was complete, the solution was warmed to about 24°C over 10 minutes and stirred for an additional 30 minutes. Sodium sulfite (32 g of a 10 wt% aqueous solution) and sodium carbonate (32.4 g of a 10 wt% aqueous solution) were added and the reaction was stirred for about 15 minutes. The mixture was allowed to
 5 separate into two layers, and the pH of the aqueous layer was measured (pH ~9-10). The organic layer was separated, the solvent from was removed by rotary evaporation. The resultant solid was cooled and removed from the flask by scraping into a powder. The white powder was further dried in a vacuum oven at 40°C overnight to afford product (30.1 g, mmol) in about 88% yield (MW: 1208.26 g/mol; 52.9 wt% Br (theo.); 52.1 wt%
 10 Br (meas.); TGA 5 wt% loss: 276°C; 247 ppm bromide; ¹H NMR (400 MHz, CDCl₃): δ 1.92 (-CH-CH₂-CH₂-, 8H), 2.02 (-CH-CH₂-CHH'-, 4H), 2.18 (-CH-CHH'-CHBr-, 4H), 2.51 (-CH-CH₂-CHH'-, 4H), 2.60 (-CH-CHH'-CHBr-, 4H), 2.93 (-C=O-CH-, 4H), 4.17 (-C-CH₂-O-, 8H), 4.61 (-CH-CH₂-CHBr-CHBr-, 4H), 4.70 (-CH-CH₂-CHBr-CHBr-, 4H); ¹³C NMR (400 MHz, CDCl₃): δ 23.62 (-CH-CH₂-CH₂-), 28.46 (-CH-CH₂-CH₂-), 31.09 (-CH-CH₂-CH=CH-), 37.89 (-C=O-CH-), 42.79 (-C-CH₂-), 52.07 (-CHBr-CHBr-), 52.19 (-CHBr-CHBr-), 62.81 (-C-CH₂-O-), 174.08 (C=O).

EXAMPLE 4

[0061] A compression molded plaque was prepared by Brabender mixing 1.84 g of solid
 20 white powder flame retardant N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide with 48.16 g of STYRON[®] 678E general purpose polystyrene (GPPS) from The Dow Chemical Company, which polystyrene is a general purpose non-flame-retarded grade of unreinforced, crystal polystyrene having a melt flow index at 200°C, with 5 kg pressure of 10.5 grams per 10 minutes, and an LOI of 18.0. The mixer was
 25 heated to 150-160°C, and the flame retardant was added to the molten polystyrene incrementally during three minutes at 25-60 rpm. The mixture was blended an additional 5 minutes at 70 rpm. The resulting blended mixture was then compression molded at 150°C for 5 minutes. Bars for the LOI test were cut from the molds and tested according to the ASTM Standard Test method D 2863-87 (commonly referred to as the limiting
 30 oxygen index (LOI) test; in this test, the higher the LOI value, the more flame resistant the composition).

[0062] Another compression molded plaque was prepared as just described by Brabender mixing 2.36 g of solid white powder flame retardant N-methyl-5,6-dibromonorbornane-2,3-dicarboximide with 47.64 g of STYRON[®] 678E general purpose polystyrene.

- 5 [0063] Another compression molded plaque was prepared as just described by Brabender mixing 2.59 g of solid white powder flame retardant brominated pentaerythritol tetracyclohexenate with 57.41 g of STYRON[®] 678E general purpose polystyrene.

- [0064] N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide and N-methyl-5,6-dibromonorbornane-2,3-dicarboximide were prepared according to Examples 1 and 2. The brominated pentaerythritol tetracyclohexenate was prepared according to Example 3. No thermal stabilizer was added to any of the formulations. Results are summarized in Table 1.

TABLE 1

Run	Flame retardant	Loading	Bromine content	LOI
1	N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide	3.68 wt%	2.25 wt%	25.7
2	N-methyl-5,6-dibromonorbornane-2,3-dicarboximide	4.72 wt%	2.25 wt%	25.8
3	Brominated pentaerythritol tetracyclohexenate	4.32 wt%	2.25 wt%	23.3

15

EXAMPLE 5

- [0065] To illustrate flame retardant efficacy, various foam compositions containing N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide (compound I) and N-methyl-5,6-dibromonorbornane-2,3-dicarboximide (compound II) were subjected to ASTM Standard Test Method D 2863-87, commonly referred to as the limiting oxygen index (LOI) test. In this test, the higher the LOI value, the more flame resistant the composition.

- [0066] Compounds I and II were prepared according to Examples 1 and 2. The polystyrene used was PS-168, which is a general-purpose non-flame-retarded grade of unreinforced crystal polystyrene commercially available from Dow Chemical Company.

25

It has a weight average molecular weight of about 172,000 daltons and a number average molecular weight of about 110,000 daltons (measured by GPC). The molecular weight analyses were determined in tetrahydrofuran (THF) with a modular gel permeation chromatograph (Waters Corporation, #150-CV) equipped with a differential refractometer (Waters Corporation, #410) and a light scattering intensity detector (Precision Detectors, Inc., model PD-2000) and Ultrastyrigel Mixed B columns of 100, 103, 104, and 500 angstrom porosities (Polymer Laboratories). Polystyrene standards (Polymer Laboratories) were used in the determination of molecular weights.

[0067] Sample A was prepared by making a concentrate (11 wt% compound I), and then letting the concentrate down into a neat resin at a ratio of about 35 wt% concentrate to about 65 wt% PS-168 neat resin and extruding low density foam via carbon dioxide injection. The concentrate contained about 11 wt% compound I, about 0.5 wt% hydrotalcite thermal stabilizer, about 4.3 wt % Mistron Vapor Talc, about 1.5 wt% calcium stearate, and about 82.7 wt% Dow PS-168. The concentrates were produced on a Werner & Pfleiderer ZSK-30 co-rotating twin screw extruder at a melt temperature of about 175°C. A standard dispersive mixing screw profile was used at about 250 rpm and a feed rate of about 1 kg/hour. PS-168 resin concentrates were fed via a single screw gravimetric feeder, and the powder additives were pre-mixed and fed using a twin screw powder feeder.

[0068] The concentrate was then mixed into neat Dow polystyrene PS-168 using the same twin screw extruder at a ratio of about 35 weight% concentrate to about 65 weight% polystyrene to produce foam using the following conditions: temperatures of Zones 1 (about 175°C), 2 (about 160°C), 3 (about 130°C), and 4 (about 130°C), about 145°C die temperature, about 60 rpm screw speed, about 3.2 kg/hour feed rate, 40/80/150 screen pack, from about 290 to about 310 psig carbon dioxide pressure, about 160°C melt temperature, from about 63 to about 70% torque, and from about 2 to about 3 ft/minute takeoff speed.

[0069] The foam contained about 3.9 wt% flame retardant (about 2.35 wt% bromine), and about 1.5 wt% talc as a nucleating agent for the foaming process. Hydrotalcite (DHT-4A, Kyowa Chemical) in an amount of about 5 wt% of the flame retardant compound was also used to stabilize the flame retardant during the extrusion and foam-forming process. A standard two-hole stranding die (1/8 inch diameter holes) was used to produce the foams, with one hole plugged. The resulting 5/8 inch diameter foam rods had a very thin

surface skin (0.005 inches or less) and a fine closed cell structure. Carbon dioxide gas was injected into barrel #8 (the ZSK-30 is a 9-barrel extruder). The rods were foamed with carbon dioxide to a density of about 9.0 lbs/ft³ (0.14 specific gravity).

[0070] Sample B was prepared in the same manner as Sample A, except that the concentrate contained about 13.6 wt% N-methyl-5,6-dibromonorbornane-2,3-dicarboximide. Comparative sample K was prepared in the same manner as Sample A, except that the concentrate contained about 9 wt% SAYTEX[®] HP900SG (stabilized hexabromocyclo-dodecane, HBCD, Albemarle Corporation). Since the HP900SG flame retardant already contains 5 wt% hydrotalcite, no additional hydrotalcite was added in the preparation of Sample K.

[0071] Results are summarized in Table 2.

TABLE 2

Foam sample	Flame retardant	Loading	Bromine content	LOI
A	Compound I	3.85 wt%	2.35 wt%	25.0
B	Compound II	4.77 wt%	2.27 wt%	25.7
K	HBCD	2.99 wt%	2.24 wt%	26.1

[0072] The results in Table 2 indicate that the N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide and N-methyl-5,6-dibromonorbornane-2,3-dicarboximide are highly efficacious flame retardants in extruded polystyrene foams, comparable to commercially available HBCD.

EXAMPLE 6

[0073] The thermal stability of N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide (compound I) and N-methyl-5,6-dibromonorbornane-2,3-dicarboximide (compound II) used in accordance with the present invention was evaluated using the Thermal HBr Measurement Test. Compounds I and II were prepared according to Examples 1 and 2.

[0074] A sample of from about 0.5 to about 1.0 g flame retardant was weighed into a three neck 50 mL round bottom flask. Teflon tubing was then attached to one of the openings in the flask. Nitrogen was fed into the flask through the Teflon tubing at a flow rate of about 0.5 SCFH. A small reflux condenser was attached to another opening on the

flask. The third opening was plugged. An about 50 vol % solution of glycol in water at a temperature of about 85 °C was run through the reflux condenser. Viton tubing was attached to the top of the condenser and to a gas-scrubbing bottle. Two more bottles were attached in series to the first. All three bottles had about 90 mL of about 0.1 N NaOH solutions. After assembling the apparatus, the nitrogen was allowed to purge through the system for about 2 minutes. The round bottom flask was then placed into an oil bath at about 220 °C and the sample was heated for about 15 minutes. The flask was then removed from the oil bath and the nitrogen was allowed to purge for about 2 minutes. The contents of the three gas scrubbing bottles were transferred to a 600 mL beaker. The bottles and viton tubing were rinsed into the beaker. The contents were then acidified with about 1:1 HNO₃ and titrated with about 0.01 N AgNO₃. Samples were run in duplicate and an average of the two measurements was reported.

[0075] Results are summarized in Table 3. Lower thermal HBr values are preferred for a thermally stable flame retardant in extrudable polystyrene foams or extruded polystyrene foams. Comparative sample L is SAYTEX[®] HP900P (hexabromocyclododecane, HBCD, Albemarle Corporation).

TABLE 3

Foam sample	Flame retardant	HBr
A	N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide	1006 ppm
B	N-methyl-5,6-dibromonorbornane-2,3-dicarboximide	357 ppm
L	HBCD	50,000 ppm

[0076] The results in Table 3 indicate that the flame retardants of this invention are thermally stable, and so do not decompose to release excessive amounts of thermally cleaved HBr upon heating at typical operating temperatures for use in extruded polystyrene foams.

EXAMPLE 7

[0077] The melt stability of N-(2,3-dibromopropyl)-5,6-dibromonorbornane-2,3-dicarboximide (compound I) and N-methyl-5,6-dibromonorbornane-2,3-dicarboximide

(compound II) in polystyrene was also evaluated. Samples were prepared and subjected to ASTM Standard Test Method D 3835-90, commonly referred to as the Melt Stability Test.

[0078] Sample A containing about 11 weight % concentrate of compound I in polystyrene was heated in a barrel and extruded over time. A Dynisco-Kayeness Polymer Test Systems LCR 6052 Rheometer (Model D6052M-115, serial no. 9708-454)/WinKARS instrument/software package was used to measure the viscosity as a function of time in the heated barrel. Evaluations were conducted at a shear rate of 500 sec⁻¹ using a 20/1 L/d tungsten carbide die and a 9.55 mm barrel diameter, for dwell times of about 6.5, 13, 19.5, 25.9, and 32.4 minutes. For thermally stable materials, the viscosity should not substantially change over time.

[0079] Compounds I and II were prepared according to Examples 1 and 2. Samples A, B and K were prepared as described in Example 5 for production of ~10 wt% flame retardant concentrates (prior to formation of foams) in PS-168 polystyrene resin. The control (comparative) sample PS-168 is PS-168 polystyrene resin (without a flame retardant compound), as described in Example 5. Results are summarized in Table 4; values in the table are shear viscosities in Pa•csec.

TABLE 4

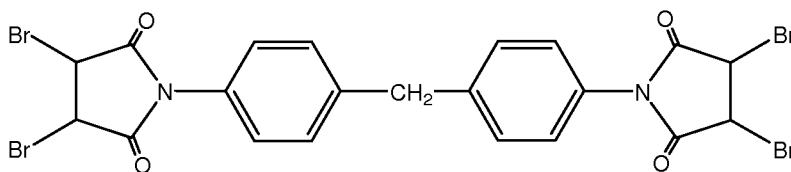
Sample	Flame retardant	6.5 min.	13 min.	19.5 min.	25.9 min.	32.4 min.
at 175 °C						
A	Compound I	485	477	478	464	480
B	Compound II	409	401	385	401	407
K	HBCD	488	478	464	465	480
PS-168	none	616	587	587	617	612
at 190 °C						
A	Compound I	245	242	241	245	246
B	Compound II	223	221	220	222	222
K	HBCD	271	265	265	268	266
PS-168	none	362	355	355	355	359

[0080] As can be seen from Table 4, the shear viscosity of Samples A and B remained stable (within 5% of its initial value) at 175°C and 190°C, demonstrating good retention of melt stability.

5

EXAMPLE 8

[0081] The impact of extrusion on the molecular weight of various flame retardant concentrates and foams was determined by evaluating samples using GPC before and after extrusion. Samples A, B and comparative sample K were prepared as described in Example 5 for production of ~10 wt% flame retardant concentrates (prior to formation of
10 foams) in PS-168 polystyrene resin. PS-168 is as described in Example 7. Comparative sample M was prepared by using a 30 wt% concentrate of compound III instead of the 11 wt% concentrate of compound I. Compound III, which is a brominated bis-1,1'-(methylenedi-4,1-phenylene)bismaleimide, has the following structure:



15 [0082] The concentrate contained about 30 wt% (1.11 kg) compound III and about 70 weight% (2.59 kg) of STYRON[®] 680 general purpose polystyrene (GPPS) from The Dow Chemical Company, which polystyrene is a general purpose non-flame-retarded grade of unreinforced, crystal polystyrene. The concentrate was produced on a Leistritz/Haake
20 Micro 18 counter-rotating twin-screw extruder at a melt temperature of about 170°C. A standard dispersive mixing screw profile was used at about 100 rpm and a feed rate of about 3 kg/hour. The polystyrene resin concentrate and the powder additives were pre-mixed and fed using a single-screw gravimetric feeder. The yellow-orange extruded strands exhibited slight foaming and odor, indicative of thermal release of HBr. Results are summarized in Table 5, where the MW is an abbreviation for weight average
25 molecular weight, and the reported difference is the difference of the post-extrusion molecular weight from that of the initial molecular weight.

TABLE 5

Sample	Flame retardant	Initial MW	Post-extrusion MW	Difference
A	Compound I	172,000 daltons	177,000 daltons	+3%
B	Compound II	172,000 daltons	171,000 daltons	-1%
K	HBCD	172,000 daltons	166,000 daltons	-3%
M	Compound III	240,000 daltons	120,000 daltons	-50%
PS-168	none	172,000 daltons	171,000 daltons	-1%

[0083] The results in Table 5 indicate that compounds I and II are highly stable and cause minimal, if any, degradation of the polystyrene. In contrast, compound III causes significant degradation of the polystyrene and is not suitable for producing a flame retardant extruded polystyrene foam.

EXAMPLE 9

[0084] The Yellowness Index (YI) is a value still used commonly and is particularly useful for detecting variation among very white objects, such as polystyrene foams, despite having been withdrawn in 1995 by ASTM. Yellowness index measurement capabilities, YI D1925 [C/2], are readily available on commercial instruments. When objects are being compared using the YI D1925 [C/2], they must be similar in transparency, opacity, thickness, shape, and other physical attributes.

[0085] A Hunter Lab ColorQUEST[®] Spectrocolorimeter (diffuse geometry) was used to measure the average YI value for various flame retardant foams. The average YI values given herein were obtained from a HunterLab ColorQUEST[®] XE Spectrometer (serial number: CQX2963) from Hunter Associates Laboratory, Inc., Reston, VA, using a 6.6 mm SAV (small area view) port aperture and a nominal diffuse/8° Sphere optical geometry, 10° Observer, D65 illuminant with a Didymium filter (78.12% transmission at 430 nm, 34.28% transmission at 570 nm). EasyMatch[®] QC software, version 3.61.00 (2004) was used to process the instrumental data. The data was processed for the 2 degree standard observer function and C illuminant for obtaining YI D1925 [C/2] values.

[0086] The spectrometer instrument was calibrated using calibrated tile set HCL-405 in “reflectance – specular included” (RSIN) standardization mode. The small area view

(SAV) was used, where the entire sample, cylindrical foams of about 1.5 cm in diameter and about 5 inches in length, covered the light emitting through the small aperture (hole diameter about 0.9 cm) of the external reflectance port. No sample cell or lens was used, and the UV filter was left out. The green tile ($X=19.35$, $Y=25.44$, $Z=21.23$, $L^* = 57.50$, $a^* = -22.42$, $b^* = 10.18$; Illuminant D65, 10° Observer, ASTM E308) is standardized once/week, and the value is maintained at ± 0.3 for X, Y, and Z.

[0087] The calibration procedure was as follows:

- 1) The cover plate (used for small area view) was installed at the external reflectance port.
- 2) To initiate calibration, the external reflectance port was covered with the black light trap, covering the area view, and was read by the detector.
- 3) The light trap was removed, and the reflectance port was covered with the white calibration tile ($X = 80.19$, $Y = 85.05$, $Z = 89.76$, $L^* = 93.90$, $a^* = -0.87$, $b^* = 1.05$; Illuminant D65, 10° Observer, ASTM E308; Serial No. CQX2963, Date 10/31/05) and read by the detector.

It should be noted that Dow's PS-168 (no flame retardant) also may be used as a reference standard, but similar values are obtained when white tile calibration is used, and a reference standard not used.

[0088] After calibration, the average YI of foams were measured using cylindrical samples having the dimensions described above. The foam "rod" was held with an end-on view to completely cover the small area view at the external reflectance port. Three separate foam samples were independently measured three times (with or without using a standard PS-168 reference foam) and averaged to arrive at the values discussed herein. The results of these measurements show that the flame retardant compounds of this invention can be extruded with little color imparted to the foam.

[0089] Samples A and B and comparative samples K and PS-168 were prepared as described above in Example 5. Results are summarized in Table 6.

TABLE 6

Foam sample	Flame retardant	Average YI	Visual color
A	Compound I	1	white
B	Compound II	5	white
K	HBCD	1	white
PS-168	none	1	white

[0090] The results in Table 6 indicate that compounds I and II are highly suitable for use in forming polystyrene foam. The lack of or minimal color change is demonstrative of high thermal stability with little or no polymer degradation.

EXAMPLE 10

[0091] Expandable polystyrene beads were prepared to demonstrate that the compositions of the present invention can successfully be used to form flame retardant polystyrene beads, which can then be used to form expanded polystyrene foams. Compounds I and II were prepared according to Example 1 and 2. Compound IV was prepared according to Example 3.

[0092] To form sample A, about 0.28 g of polyvinyl alcohol (PVA) in about 200 g of deionized water was poured into a 1-liter Buchi glass vessel. Separately, a solution was formed containing about 0.64 g of dibenzoyl peroxide (75% in water), about 0.22 g of dicumyl peroxide, and about 1.72 g of compound I in about 200 g of styrene. This latter solution was poured into the vessel containing the aqueous PVA solution. The liquid was mixed with an impeller-type stirrer set at 1000 rpm in the presence of a baffle to generate shear in the reactor. The mixture was then subjected to the following heating profile: from 20°C to 90°C in 45 minutes and held at 90°C for 4.25 hours (first stage operation); from 90°C to 130°C in 1 hour and held at 130°C for 2 hours (second stage operation); and from 130°C to 20°C in 1 hour.

[0093] At the end of the first stage, the reactor was pressurized with nitrogen (2 bars). Once cooled, the reactor was emptied and the mixture filtered. The flame retardant beads formed in the process were dried at 60°C overnight and sieved to determine bead size distribution. In this procedure, the sieves are stacked from the largest sieve size on top to the lowest sieve size on bottom, with a catch pan underneath. The sieves were vibrated at

a 50% power setting for 10 minutes, and the sieves were weighed individually subtracting the tare weight of the sieve screens). The weight percent of material at each sieve size was calculated based on the total mass of the material. A 90.71% conversion was achieved.

- [0094] Sample B was prepared similarly to sample A using 2.22 g of compound II.
- 5 Sample C was prepared similarly to sample A using 1.98 g of compound IV. Comparative sample D was prepared similarly to sample A using 1.40 g of SAYTEX[®] HP900P (hexabromocyclododecane, HBCD, Albemarle Corporation). Comparative sample E was prepared similarly to sample A using 2.10 g of ethylenebis(dibromonorbornane-dicarboximide) (SAYTEX[®] BN-451, Albemarle Corporation). Comparative sample F
- 10 was prepared similarly to sample A, but without added flame retardant. Results are summarized in Table 7.

TABLE 7

Sample	A	B	C	D	E	F
Flame retardant	Compound I	Compound II	Compound IV	HBCD	BN-451	none
Solubility in styrene at 25°C	>1 wt%	>1 wt%	>18 wt%	~8 wt%	<0.1 wt%	-
Loading	0.85 wt%	1.1 wt%	0.98 wt%	0.70 wt%	1.0 wt%	none
Yield	90.7 wt%	90.9 wt%	95.4 wt%	93.0 wt%	none	91.2 wt%
Particle size distribution of beads						
>2 mm	4.6%	3.6%	1.4%	9.3%	-	9.6%
>1.4 mm	25.5%	27.5%	32.3%	45.3%	-	50.7%
>1 mm	50.4%	50.2%	56.0%	39.1%	-	33.9%
>710 µm	15.2%	13.1%	9.7%	3.3%	-	3.7%
>500 µm	3.0%	2.9%	0.3%	1.2%	-	0.9%
>250 µm	1.3%	2.7%	0.3%	1.9%	-	1.3%

- 15 [0095] The results in Table 7 indicate that the flame retardant compounds of the present invention may be used to form polystyrene beads, which can then be used to form expanded polystyrene foams.

COMPARATIVE EXAMPLE

- 20 [0096] An aqueous suspension polymerization of styrene towards formation of expandable polystyrene beads was attempted with N,N'-ethylenebis(5,6-dibromo-2,3-

norbornanedicarboximide) (BN-451; Saytex[®] BN-451, Albemarle Corporation), which has a styrene solubility of less than about 0.1 wt% at about 25°C. About 0.28 g of polyvinyl alcohol (PVA) in 200 g of deionized water was poured into a 1-liter Büchi glass vessel. Separately, a mixture was prepared containing about 0.64 g of dibenzoyl peroxide (about 75 wt% in water), and about 2.10 g of BN-451 in about 200 g of styrene. Insoluble BN-451 particles were apparent in this latter mixture, which was poured into the vessel containing the aqueous PVA solution. The liquid was mixed with an impeller-type stirrer set at about 1000 rpm in the presence of a baffle to generate shear in the reactor. The mixture was then subjected to the following heating profile: from about 20°C to about 90°C in about 45 minutes and held at about 90°C for about 4.25 hours (first stage operation).

[0097] The second stage of the reaction (heating from about 90°C to about 130°C in about 1 hour and hold at about 130°C for about 2 hours) was not attempted. Typically, after about 2 hours, formation of very small beads begins when a stable suspension polymerization occurs. Failure of the aqueous suspension polymerization during the first stage was observed within about 2 hours at about 90°C, evidenced by rapid increase in viscosity and formation of a large mass of polystyrene. Thus, the procedure was halted after about 2 hours heating at about 90°C. The results of this evaluation indicate that the composition of this formulation cannot be used to form flame retardant polystyrene beads.

[0098] Components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component, a solvent, or *etc.*). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution as such changes, transformations, and/or reactions are the natural result of bringing the specified components together under the conditions called for pursuant to this disclosure. Thus the components are identified as ingredients to be brought together in connection with performing a desired operation or in forming a desired composition. Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first

contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. The fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, blending or mixing operations, if
5 conducted in accordance with this disclosure and with ordinary skill of a chemist, is thus of no practical concern.

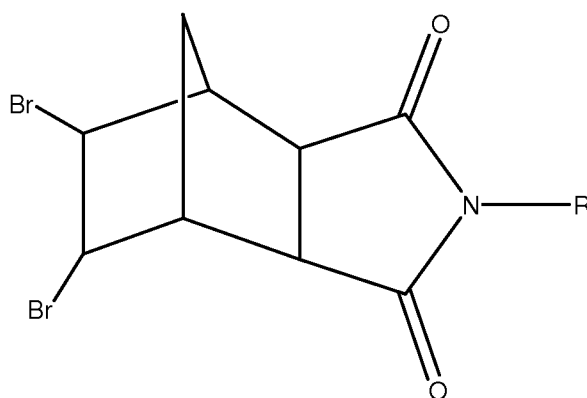
[0099] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a claim to a single element to which the article refers. Rather, the article "a"
10 or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0100] Each and every patent or other publication or published document referred to in any portion of this specification is incorporated *in toto* into this disclosure by reference, as if fully set forth herein.

15 [0101] This invention is susceptible to considerable variation in its practice. Therefore the foregoing description is not intended to limit, and should not be construed as limiting, the invention to the particular exemplifications presented hereinabove.

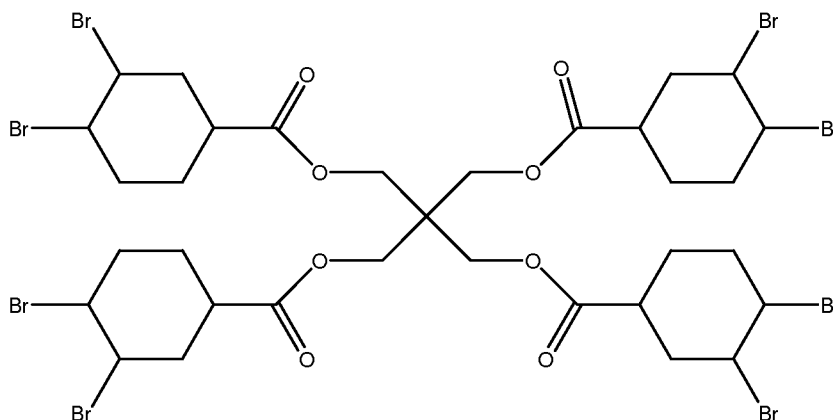
CLAIMS:

1. A flame retardant styrenic polymer foam composition which comprises a styrenic polymer and flame retardant amount of flame retardant resulting from inclusion in the foam recipe before or during formation of the foam
- 5 (i) at least one compound having the formula:



where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or

- (ii) a compound having the formula:



or

- 15 (iii) a combination of (i) and (ii).

2. A flame retardant styrenic polymer foam composition as in Claim 1 wherein said styrenic polymer foam composition is either a) in the form of expandable styrenic polymer beads or granules or b) in the form of an extruded styrenic polymer

foam, with the proviso that for compound (i), when said styrenic polymer foam composition is b), R is not hydrogen.

3. A composition as in Claim 2 wherein no other flame retardant is employed.

4. A composition as in Claim 3 wherein at least one synergist or at least one
5 thermal stabilizer is included in said composition.

5. A composition as in Claim 1 which has at least one of the following features:

the flame retardant is included in the foam recipe in an amount of about 0.1 to about 10 wt% of the foam;

10 said styrenic polymer foam composition has an average Yellowness Index of about 1 to about 10;

said styrenic polymer is crystal polystyrene.

6. A composition as in Claim 1 in which compound (i) has been included, wherein R is a methyl group, a linear or branched substituted or unsubstituted aliphatic
15 group having from two to about three carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about three carbon atoms.

7. A composition as in Claim 6 wherein R is a methyl group or a 2,3-dibromopropyl group.

8. A composition as in Claim 2 wherein said styrenic polymer foam
20 composition is in the form of expandable styrenic polymer beads or granules, and wherein said composition has at least one of the following features:

the flame retardant is included in the foam recipe in an amount of about 0.5 to about 7 wt% of the foam;

25 the flame retardant has a minimum solubility in styrene at about 25 °C of about 0.5 wt% to about 8 wt%;

the flame retardant has a minimum solubility in styrene at about 40 °C of about 0.5 wt% to about 10 wt%;

the styrenic polymer of said expandable styrenic beads or granules is composed of an average of at least 80 wt% of polymerized styrene.

30 9. A composition as in Claim 2 wherein said styrenic polymer foam composition is in the form of an extruded styrenic polymer foam, and wherein said composition has at least one of the following features:

the flame retardant is included in the foam recipe in an amount of about 1 to about 7 wt % of the foam;

the extruded polystyrene foam has an average Yellowness Index of about 1 to about 5;

5 the styrenic polymer of said extruded styrenic polymer foam is composed of at least 80 wt% of polymerized styrene.

10. A composition as in Claim 9 in which compound (i) has been included, and wherein said composition has at least one of the following characteristics:

(a) the flame retardant styrenic polymer foam composition is formed from a mixture having an initial shear viscosity that decreases less than about 15% after about 32 minutes at 190°C;

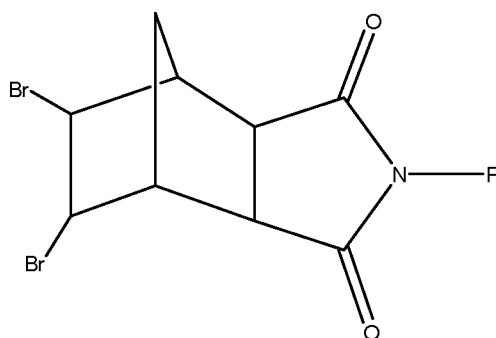
(b) the flame retardant styrenic polymer foam composition is formed from a mixture having an initial shear viscosity that decreases less than about 10% after about 32 minutes at 175°C;

15 (c) the flame retardant styrenic polymer foam composition is formed from a composition in which the styrenic polymer has a molecular weight (M_w) of at least about 90% of the styrenic polymer in an identical composition without the flame retardant compound; or

(d) the flame retardant styrenic polymer foam composition has an average Yellowness Index of about 1 to about 5.

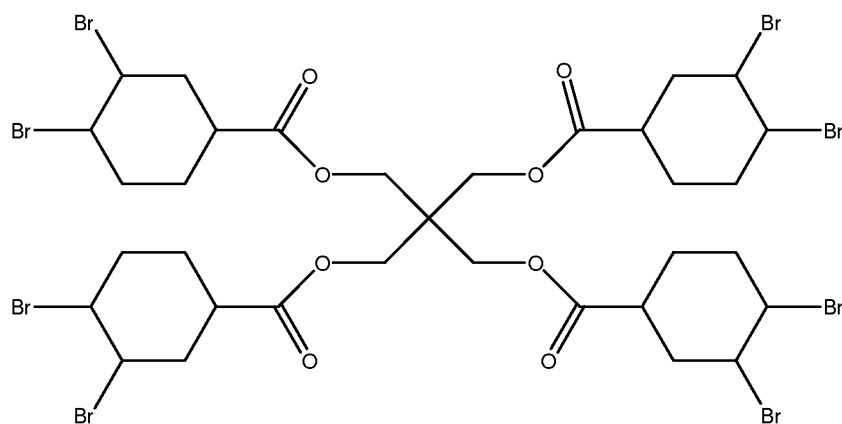
20 11. A method of preparing a flame retardant styrenic polymer foam composition as in Claim 1, said method comprising including in the foam recipe of said composition before or during formation of the foam

(i) at least one flame retardant compound having the formula:



where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or

- 5 (ii) a flame retardant compound having the formula:



or

- (iii) a combination of (i) and (ii).

12. A method as in Claim 11 wherein expandable styrenic beads or granules
10 are prepared from a suspension-polymerizable mixture comprised of at least one styrenic monomer.

13. A method as in Claim 17 wherein at least 80 wt% of said styrenic monomer is styrene.

14. A method as in Claim 11 wherein larger expanded beads or granules of at
15 least one styrenic polymer are prepared, which method comprises expanding smaller beads or granules formed from a suspension polymerization recipe.

15. A method as in Claim 14 wherein said smaller styrenic beads or granules and said larger styrenic beads or granules are composed of at least 80 wt% of polymerized styrene.

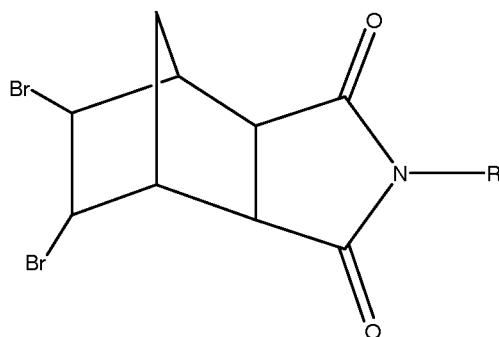
20 16. A method as in Claim 11 wherein said method comprises molding expanded beads or granules of at least one styrenic polymer.

17. A method as in Claim 11 wherein an extruded styrenic foam is prepared from a foamable molten styrenic polymer mixture, with the proviso that for compound (i), R is not hydrogen.

18. A method as in Claim 17 wherein said styrenic polymer is composed of at least 80 wt% of polymerized styrene.

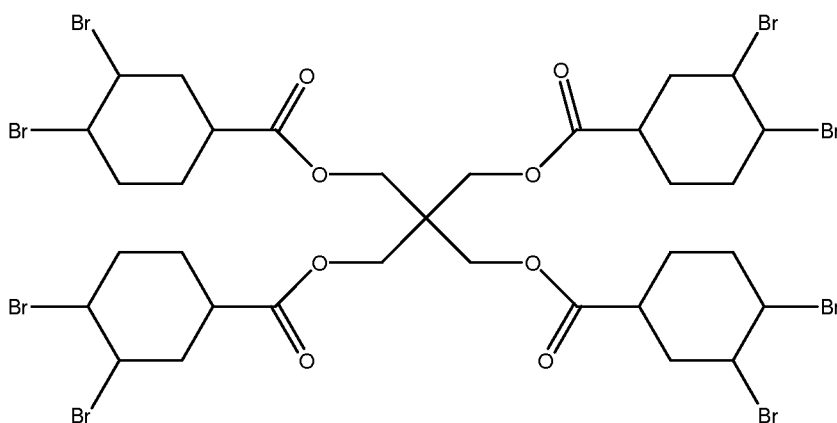
19. A flame retardant styrenic polymer foam recipe in which was included a flame retardant amount of flame retardant, said flame retardant at least prior to inclusion
5 being

(i) at least one compound having the formula:



where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a
10 halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or

(ii) a compound having the formula:



or

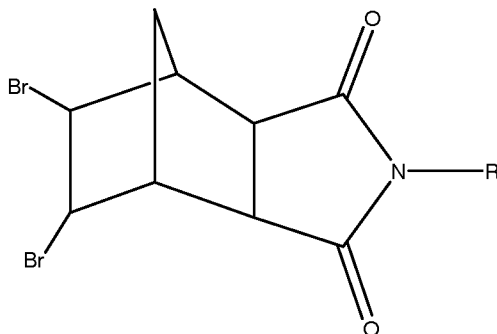
15 (iii) a combination of (i) and (ii).

20. A recipe as in Claim 19 in which compound (i) has been included, wherein R is a methyl group, a linear or branched substituted or unsubstituted aliphatic group

having from two to about three carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about three carbon atoms.

21. A recipe as in Claim 19 wherein R is a methyl group or a 2,3-dibromopropyl group.

5 22. A process for forming a compound having the formula:



where R is hydrogen, a methyl group, a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, or a halogenated linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, which process comprises

- 10 I) a) bringing together 5-norbornene-2,3-dicarboxylic anhydride and ammonia or a primary amine, wherein said primary amine has an amino group which is a methyl group, or a linear or branched substituted or unsubstituted aliphatic group having from two to about six carbon atoms, to form an intermediate product, and removing water from at least a portion of the
- 15 intermediate product to form a 5-norbornene-2,3-dicarboximide; or
- b) (i) bringing together, in a liquid organic medium, 5-norbornene-2,3-dicarboxylic anhydride and ammonia or aqueous ammonium hydroxide, to form an intermediate product, and removing water from at least a portion of the intermediate product to form 5-norbornene-2,3-dicarboximide,
- 20 (ii) bringing together an inorganic carbonate and at least a portion of the dried 5-norbornene-2,3-dicarboximide from (i) to form a 5-norbornene-2,3-dicarboximide salt, and
- (iii) contacting at least a portion of the 5-norbornene-2,3-dicarboximide salt formed in (ii) with a hydrocarbyl chloride, wherein said hydrocarbyl
- 25 chloride is methyl chloride, or a linear or branched substituted or

unsubstituted aliphatic chloride having from two to about six carbon atoms, to form a 5-norbornene-2,3-dicarboximide; or

- c) (i) bringing together an inorganic carbonate and 5-norbornene-2,3-dicarboximide to form a 5-norbornene-2,3-dicarboximide salt, and
5 (ii) contacting at least a portion of the 5-norbornene-2,3-dicarboximide salt formed in (i) with a hydrocarbyl chloride, wherein said hydrocarbyl chloride is methyl chloride, or a linear or branched substituted or unsubstituted aliphatic chloride having from two to about six carbon atoms, to form a 5-norbornene-2,3-dicarboximide; and

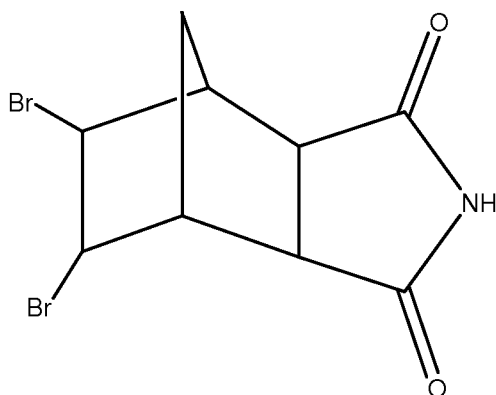
10 II) brominating at least a portion of the 5-norbornene-2,3-dicarboximide formed in I).

23. A process as in Claim 22 wherein in I), procedure a) is carried out, and wherein said primary amine has an amino group which is a methyl group or a linear or branched substituted or unsubstituted aliphatic group having from two to about three carbon atoms.

15 24. A process as in Claim 23 wherein said primary amine is methylamine or allylamine.

25. A process as in Claim 22 wherein in I), procedure b) is carried out, and wherein a phase transfer catalyst is present in (iii).

26. A process for forming a compound having the formula:

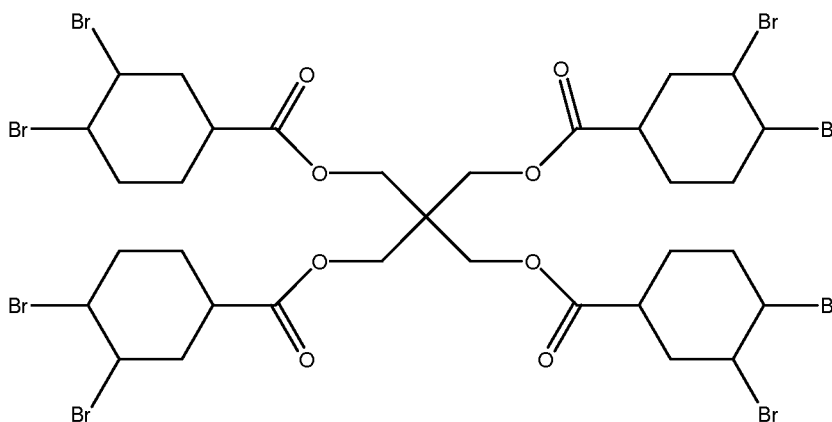


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which process comprises brominating the 5-norbornene-2,3-dicarboximide to form 5,6-dibromonorbornane-2,3-dicarboximide.

27. A process as in Claim 26 which further comprises
- (i) bringing together an inorganic carbonate and at least a portion of the 5,6-dibromonorbornane-2,3-dicarboximide from Claim 26 to form a 5,6-dibromonorbornane-2,3-dicarboximide salt, and
- 5 (ii) contacting at least a portion of the 5,6-dibromonorbornane-2,3-dicarboximide salt formed in (i) with a hydrocarbyl chloride, wherein said hydrocarbyl chloride is methyl chloride, or a linear or branched substituted or unsubstituted aliphatic chloride having from two to about six carbon atoms, to form an N-substituted 5,6-dibromonorbornane-2,3-dicarboximide.
- 10 28. A process as in Claim 26 wherein a phase transfer catalyst is present in (i).
29. A process as in Claim 25 or 28 wherein said hydrocarbyl chloride is methyl chloride or a linear or branched substituted or unsubstituted aliphatic chloride having from two to about three carbon atoms and/or wherein said inorganic carbonate is an alkali metal carbonate.
- 15 30. A process as in Claim 29 wherein said hydrocarbyl chloride is methyl chloride or allyl chloride.

31. A composition which is a compound having the formula:



32. A process for forming a compound of Claim 31, which process comprises
- 20 brominating pentaerythritol tetracyclohexenate.
33. A process for forming a compound of Claim 31, which process comprises
- I) a) bringing together pentaerythritol tetraacrylate and 1,3-butadiene to form pentaerythritol tetracyclohexenate; or
- b) bringing together, in a liquid medium, pentaerythritol, at least one alkyl
- 25 ester of 3-cyclohexene carboxylic acid, and a catalytic amount of lithium

amide and/or sodium amide to form a reaction mixture, and substantially continuously removing alcohol formed in the reaction mixture, to form pentaerythritol tetracyclohexenate; and

- II) brominating at least a portion of the pentaerythritol tetracyclohexenate formed in
5 I).

34. A process as in Claim 33 wherein in I), procedure a) is carried out.

35. A process as in Claim 33 wherein in I), procedure b) is carried out, and wherein said alkyl ester of 3-cyclohexene carboxylic acid is methyl 3-cyclohexene carboxylate.