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(54) Title: FLAME RETARDANT COATINGS

(57) Abstract: Provided are flame retardant coating compositions and articles coated therewith, which compositions comprise (A) a coating and (B) an effective flame retarding amount of a mixture of (i) at least one compound selected from the group consisting of the (a) sterically hindered nitroxyl stabilizers, (b) sterically hindered hydroxylamine stabilizers and (c) sterically hindered alkoxyamine stabilizers and (ii) at least one conventional flame retardant selected from the group consisting of (d) organohalogen flame retardants, (e) organophosphorous flame retardants, (f) isocyanurate flame retardants and (g) melamine based flame retardants. In flame retardant coating compositions that comprise at least one ethylenically unsaturated, polymerizable monomer, which monomer contains a sterically hindered amine moiety, the conventional flame retardant is an optional component. The coated articles are for example iron, steel, stainless steel, aluminum and other non-ferrous metals, wood, plywood, paper, cardboard, chip board, particle board, plastics, thermoplastics, epoxies, neoprene, rubber, composites, fiberglass reinforced composites, polyesters, polymeric foam, masonry, fabric or textiles, optical fibers, wire and cable constructions and circuit boards.



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FLAME RETARDANT COATINGS

The instant invention pertains to flame retardant coatings that comprise at least one sterically hindered nitroxyl, hydroxylamine or alkoxyamine compound, and at least one conventional flame retardant. In flame retardant coating compositions that comprise at least one ethylenically unsaturated, polymerizable monomer, which monomer contains a sterically hindered amine moiety, the conventional flame retardant is an optional component.

Background of the Invention

U.S. Pat. No. 5,096,950 discloses the co-use of certain NOR (N-alkoxy) hindered amines with a brominated Sb_2O_3 -containing flame retardant in polypropylene.

U.S. Pat. No. 5,393,812 discloses polyolefin compositions which are made flame retardant by a combination of a halogenated hydrocarbyl phosphate or phosphonate ester flame retardant in combination with a alkoxyamine functional hindered amine.

U.S. Pat. No. 5,844,026 discloses polyolefin compositions comprising certain NOR hindered amines and certain conventional flame retardants.

U.S. Pat. No. 6,117,995 discloses that certain N-alkoxy hindered amines may be used as flame retardants for organic polymers.

U.S. Pat. No. 6,271,377 discloses polyolefin compositions that comprise N-hydroxyalkoxy hindered amines and a halogenated flame retardant.

U.S. Pat. No. 6,309,987 and equivalent WO 99/54530 teach polyolefin non-woven flame retardant fabrics that comprise N-alkoxyamines.

A Revolutionary UV Stable Flame Retardant System for Polyolefins - R. Srinivasan, A. Gupta and D. Horsey, *Int. Conf. Addit. Polyolefins* **1998**, 69-83, teaches polyolefins

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comprising certain NOR hindered amines with halogen and phosphorus containing conventional flame retardants.

Advances in a Revolutionary Flame Retardant System for Polyolefins - R. Srinivasan, B. Rotzinger, *Polyolefins 2000, Int. Conf. Polyolefins 2000*, 571-581, teaches polyolefins comprising certain NOR hindered amines with brominated and phosphorus containing flame retardants.

N. Kaprinidis and R. King, in an abstract posted on the Society of Plastics Engineers website, posted Sep. 2001, discuss the use of NOR hindered amines as flame retardants in polyolefins. The abstract is for a paper submitted to the Polymer Modifiers and Additives Division subsection to be presented at the Polyolefins 2002 conference in Houston, TX, Feb. 24, 2002. The website is www.PMAD.org.

EP 0792911 A2, discloses polyolefin compositions that comprise alkoxyamine functional hindered amines and tris(trihalogenopentyl) phosphate flame retardants.

WO 99/00450, copending U.S. application Nos. 09/502,239, filed Nov. 3, 1999, and 09/714,717, filed Nov. 16, 2000, disclose the use of certain N-alkoxy hindered amines as flame retardants.

EP 568354, U.S. Pat. No. 6,084,008 and U.S. Pat. No. 5,723,515 describe fire-resistant coatings.

Ethylenically unsaturated, polymerizable monomers containing a sterically hindered amine moiety are disclosed for example in U.S. Pat. Nos. 4,983,737, 5,047,489 and 5,077,340.

The flame retardant (FR) market today is comprised of products which function to interfere with the combustion process by chemical and/or physical means. Mechanistically these FRs have been proposed to function during combustion of an article in either the gas phase, the condensed phase or both. The organohalogens are proposed to generate halogen species (e.g. HX) which interfere in the gas phase with free radical organic "fuel" from the polymer substrate. Synergists are proposed to react with HX to form additional

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chemical species which interfere with combustion in the gas phase, such as reaction of antimony oxide with HX to form antimony halide and water vapor. Antimony compounds such as antimony trioxide also act as radical scavengers forming antimony halides. Thus, they can inhibit the propagation of the fire.

Although antimony compounds are efficient in terms of cost performance, they recently raised concern because of the toxicity of the byproducts which are formed during combustion in the presence of a halogenated flame retardant. Antimony oxides often contain trace amounts of arsenic compounds which are suspected carcinogens. Because of these ecological concerns, there is a movement to replace antimony trioxide in the present commercial flame retardant applications. However, it is very difficult to find an effective synergist which is both environmentally friendly and efficient as far as cost performance is concerned.

Another reason to add flame retardant additives is to prevent dripping during the application of the fire. During combustion, parts of the polymer separate from the matrix in the shape of droplets. Often, the droplets are flaming and impose tremendous danger for fire spread. It is common to add fillers such as talc in large amounts to the polymer, with negative consequences on the mechanical properties. Other fillers sometimes used include calcium carbonate, magnesium carbonate, zinc borate, silicates, silicones, glass fibres, glass bulbs, asbestos, kaolin, mica, barium sulfate, calcium sulfate, metal oxides, hydrates and hydroxides such as zinc oxide, magnesium hydroxide, alumina trihydrate, silica, calcium silicate, magnesium silicate.

It has been found that coatings with good flame retardant properties are prepared when the coatings comprise at least one compound selected from the group consisting of the sterically hindered nitroxyl, hydroxylamine and alkoxyamine additives and at least one certain conventional flame retardant. It has further been found that coatings with good flame retardant properties are prepared from coating compositions that comprise (i) at least one compound selected from the group consisting of ethylenically unsaturated, polymerizable monomers, which monomers contain a sterically hindered amine moiety and optionally (ii) at least one certain conventional flame retardant. With the use of these flame retardant additives, antimony compounds and fillers may be largely reduced or replaced. As the instant sterically hindered amine additives are active as stabilizers, the coating compositions

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of the invention are efficiently protected from the deleterious effects of light, oxygen and/or heat.

Detailed Disclosure

The instant invention pertains to flame retardant coating compositions which comprise

(A) a coating and

(B) an effective flame retarding amount of a mixture of

(i) at least one compound selected from the group consisting of the

- (a) sterically hindered nitroxyl stabilizers,
- (b) sterically hindered hydroxylamine stabilizers and
- (c) sterically hindered alkoxyamine stabilizers and

(ii) at least one conventional flame retardant selected from the group consisting of

- (d) organohalogen flame retardants,
- (e) organophosphorus flame retardants,
- (f) isocyanurate flame retardants and
- (g) melamine based flame retardants.

The instant invention further pertains to flame retardant coating compositions which comprise

(A) a resin binder and

(B) an effective flame retarding amount of

(i) at least one ethylenically unsaturated, polymerizable monomer, which monomer contains a sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety, and

optionally

(ii) at least one conventional flame retardant selected from the group consisting of

- (a) organohalogen flame retardants,
- (b) organophosphorus flame retardants,
- (c) isocyanurate flame retardants and
- (d) melamine based flame retardants.

The additive combination of components (i) and (ii) is synergistic towards providing flame retardancy to coatings.

Coatings

The coating component (A) of the present invention is a coating layer. It is for example a cured paint, varnish, adhesive or sealant layer. Alternatively, it is a thin plastic layer, for example an extruded thermoplastic coating as further described herein.

A paint or varnish formulation comprises resin, solvent, pigments, fillers, surfactants, and other typical components.

The present fire retardant coatings are suitable for example in the fields of construction, transportation, telecommunications, utilities, marine, chemical, petroleum, manufacturing and military, the hygiene sector, the medical sector, the textile and clothing industry, automobile applications, packaging, pharmacy, electrical engineering, electronics and domestic appliances.

Suitable substrates for the present coatings are for example iron, steel, stainless steel, aluminum and other non-ferrous metals, wood, plywood, paper, cardboard, chip board, particle board, plastics, PVC (polyvinyl chloride), thermoplastics, thermoplastic polyolefin, epoxies, neoprene, rubber, composites and the like.

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The present coating materials can be used on most substrates and in severe climatic and environmental conditions where heat, light, oxygen and humidity are potential degradants. The coatings are suitable for the interior and exterior of homes, roofs, factories, commercial buildings, airplanes, vehicles, ships, boats, sailboats and the like.

Plastics and composites are suitable substrates according to this invention, for example fiberglass reinforced composites, polyesters, polymeric foam and thermoplastic resins such as polyolefins and thermoplastic polyolefins (TPO).

The coatings of this invention are suitable for use in painted automotive thermoplastic olefin structures.

The present coatings are advantageously used in marine applications such as bulkheads, piers, docks, cabin penetration barriers, cables, conduits, cargo areas, cabins and floors and off-shore drilling applications.

The present coatings may be employed in transportation applications, for example in autos, buses, trucks, cargo ships and airplanes, for coating vehicular undercarriages, exhaust systems, gas tanks, fire walls, engine compartments, catalytic converters, hoods, cargo liner patches, airport loading bridges, etc.

The present coatings are advantageously employed in the telecommunications, computer, utilities, petroleum and chemical industries, for example in cable and conduit wraps, optical fiber coatings, grease filled wire and cable, communications towers, fire penetration barriers, seals, pipeline wraps, storage tanks, reactors, ovens, distillation columns, furnaces and the like.

The coatings of this invention are suitable as coatings for circuit boards, for example radiation-curable coatings for circuit boards.

The present coatings are suitable as a cable coating to serve as a fire-stop for electrical, control and communications cables, for example cables grouped together in cable trays and raceways, junction boxes, cable trenches and similar applications.

Suitable optical fiber coatings are disclosed for example in U.S. Pat. Nos. 6,187,835, 6,350,790, 6,197,422 and 6,362,249, the disclosures of which are hereby incorporated by reference.

Coating Compositions comprising ethylenically unsaturated (B)

The coating composition is for example a curable paint, varnish, adhesive or sealant composition. The present compositions are for example thermally or radiation (ultraviolet light, UV) curable. Alternatively, it is a curable film composition, for example a thermoplastic coating composition for extrusion films as further described herein.

A paint or varnish formulation comprises resin, solvent, pigments, fillers, surfactants, and other typical components.

The present fire retardant coating compositions are suitable for coatings for example in the fields of construction, transportation, telecommunications, utilities, marine, chemical, petroleum, manufacturing and military, the hygiene sector, the medical sector, the textile and clothing industry, automobile applications, packaging, pharmacy, electrical engineering, electronics and domestic appliances.

Suitable substrates for the present coating compositions are for example iron, steel, stainless steel, aluminum and other non-ferrous metals, wood, plywood, paper, cardboard, chip board, particle board, plastics, PVC (polyvinyl chloride), thermoplastics, thermoplastic polyolefin, epoxies, neoprene, rubber, composites, glass, glass fiber, plastic fiber and the like.

The present coating compositions can be used on most substrates and in severe climatic and environmental conditions where heat, light, oxygen and humidity are potential degradants. The coatings are suitable for the interior and exterior of homes, roofs, factories, commercial buildings, airplanes, vehicles, ships, boats, sailboats and the like.

Plastics and composites are suitable substrates according to this invention, for example fiberglass reinforced composites, polyesters, polymeric foam and thermoplastic resins such as polyolefins and thermoplastic polyolefins (TPO).

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General Uses

The coatings/coating compositions of this invention are suitable for architectural paints, for example flat, low, semi or high gloss finishes, for example as the primer or final coat.

The present coating compositions may be advantageously applied to exterior siding, interior structures, roofing, garages, ceilings, penetration barriers, PVC wrappings and the

like. They may be employed in private homes, hotels and offices, for example as applied to wallpaper, paneling, drywall, wallboard, wainscoting, trusses, flooring and subflooring, studs, architectural millwork and trim, tiles, exterior decks, ceiling tiles, kitchen cabinets, kitchen hoods, carpet backing, interior walls, doors, file cabinets, office furniture, safes, barriers and the like.

The present coating compositions may be applied to structural steel, columns, beams, steel decking, bar joists, hung ceilings in commercial buildings, high-rise office buildings and apartment complexes, bridges and tunnels and the like.

In reference to steel and other metal substrates, such substrates may be primed metal, structural steel, aluminum, metal alloys, structural steel beams and columns, coil coating substrates, steel honeycomb structures in junction boxes, insulated steel, stainless steel piping, vessels and tanks.

The coating compositions of this invention are suitable for application masonry such as brick, concrete, cement block and platerboard.

Suitable wood substrates are for example dimensional lumber, plywood, particle board, OOSB board, unfinished interior wood, plywood acoustical board, insulation board, cellulose board, fiberboard, excelsior (wood wool), wood shavings, cedar shakes, unsheathed shingles, shakes, siding, telephone poles, posts, paper, paperboard, cardboard, corrugated sheets, etc.

The present flame retardant additives may be applied to wood as a stain component, as a sanding sealer component, as part of a topcoat, by pressure or vacuum impregnation or as saturants. The present flame retardant additives as applied to wood may be combined with a preservative; they may be incorporated into wood composite products during manufacture, by pressure impregnation, or may be applied as part of a paint or surface coating.

The present flame retardant additives as applied to paper may be sprayed on at the wet end of a paper machine or may be added in the size press or water boxes on the dry end; or may be applied with a coater or with a multi-station printing press.

The present coating compositions may further comprise foaming agents, blowing agents, charring agents and binding agents, thixotropic agents, spumific agents, dipentaerythritol and other additives for examples as disclosed in U.S. Pat. No. 5,723,515, the disclosure of which is hereby incorporated by reference.

Textiles are suitable coating substrates according to this invention, for example textile backcoatings, welding curtains, canopies, dividers, awnings, tents, nylon rope, netting, carpet backing, wall coverings, decorative products, natural fibers, synthetic fibers, upholster, carpeting, draperies, stage curtains, mattresses, hospital fabrics and woven and nonwoven fabrics.

The present coating compositions may form coatings that are part of a composite construction with textile character, for example constructions which comprise a textile fabric and a polyolefin film coating and/or extrusion coating, for example as disclosed in U.S. Pat. No. 6,235,658, the disclosure of which is hereby incorporated by reference. The present coatings may be polyolefin coatings as disclosed in U.S. Pat. No. 6,251,995, the disclosure of which is hereby incorporated by reference.

The textile fabric may be woven, knitted or nonwoven fabrics based on polyethylene, polypropylene, polyethylene terephthalate, polyamide, cellulose or cotton. The polyolefin film or extrusion coating is for example about 3 to about 200 microns thick.

The instant invention also pertains to abrasion-resistant coating compositions suitable for coating over polycarbonates. Such coatings as described in U.S. Patent No. 5,214,085 comprise a silyl acrylate, aqueous colloidal silica, a photoinitiator and optionally a polyfunctional acrylate as well as UV absorbers. Such present coatings, in addition to flame retardancy, provide resistance to degradation after prolonged outdoor exposure to sunlight, moisture and heat. Resistance is provided against yellowing, delamination and formation of microcracks and decreasing transparency.

Sealants and adhesive compositions, for example sealant and adhesive layer compositions, also fall under the present definition of "flame retardant coating compositions".

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For example, such as mastics, latex adhesives, binders, caulks, putties, mortars and sealants.

Adhesive compositions are for example laminating adhesives, pressure-sensitive adhesives (PSA) and structural adhesives. UV (ultraviolet light) curable adhesives are also a subject of this invention. UV curable adhesives are for example photonic adhesives which are for example for cables, connectors, amplifiers, splices, etc. Photonic adhesives fall under the class of structural adhesives.

The present coating compositions may be employed to form layers of laminated articles, as film and/or as adhesive layers. For example, coatings and layers as disclosed in U.S. Pat. Nos. 6,187,845, 6,191,199 and 6,268,415, the disclosures of which are hereby incorporated by reference. Such coatings, films and adhesive layers are for example solar control films, films and glazings, UV absorbing glasses and glass coatings, windscreens, retroreflective sheetings and signs, solar reflectors, optical films and the like.

The present coating compositions may be used to form clear coats or pigmented coats. They may be waterborne systems or solvent borne or may be a powder coating composition or a gel coat formulation.

The present coating compositions may be ambient cured, radiation cured (for example with the influence of a photoinitiator), oven cured or cured (crosslinked) with the aid of a catalyst, for example an acid catalyst.

Where a photoinitiator is employed, they are for example mono- or bisacylphosphine oxide photoinitiators or α -hydroxy ketone photoinitiators. These photoinitiators are described for example in U.S. Patent No. 5,942,290, incorporated herein by reference.

The present coating compositions are based for example on alkyd resins; chlorinated alkyd resins; polyurethane resins; thermoplastic acrylic resins; acrylic alkyls; acrylic resins; latex emulsions; acrylic alkyd or polyester resins optionally modified with silicon, isocyanates, ketimines or oxazolidines; phenol-formaldehyde resins; resorcinol-formaldehyde resins; epoxy resins; epoxide resins crosslinked with carboxylic acids, anhydrides, polyamines or mercaptans; or acrylic and polyester resin systems modified with reactive groups in the

backbone thereof and crosslinked with epoxide. For example, coatings based on resins of vinyl acetate-acrylate copolymer emulsions, solutions of vinyltoluene-2-ethylhexyl acrylate copolymers and polyurethane.

Epoxy binders are widely used in coating compositions and are suitable for the present invention. Epoxies are for example aliphatic, aromatic, cyclic, acyclic, alicyclic or heterocyclic. Such resins may be polyglycidyl ethers derived from such polyhydric alcohols as ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butylene glycol, 1,5-pentanediol, 1,2,6-hexanetriol, glycerol, trimethylolpropane, bisphenol-A and bisphenol-F. Epoxide resins may also be polyglycidyl ethers of polycarboxylic acids, for example materials produced by the reaction of an epoxy compound such as epichlorohydrin with an aliphatic or aromatic polycarboxylic acid such as oxalic acid, succinic acid, glutaric acid, terephthalic acid, 2,6-naphthalene dicarboxylic acid and dimerized linoleic acid.

Epoxy resins are also derived from the epoxidation of an olefinically unsaturated alicyclic material. Among these are the epoxy alicyclic ethers and esters well known in the art. Epoxy resins also include those containing oxyalkylene groups. Such groups can be pendant from the backbone of the epoxide resin or they can be included as part of the backbone. The proportion of oxyalkylene groups in the epoxy resin depends upon a number of factors, among them the size of the oxyalkylene group and the nature of the epoxy resin.

Additionally, epoxy resins encompass the epoxy novolac resins. These resins are prepared by reacting an epichlorohydrin with the condensation product of an aldehyde with a monohydric or polyhydric phenol. One example is the reaction product of epichlorohydrin with a phenol-formaldehyde condensate. A mixture of epoxy resins can also be used herein.

Materials such as epoxidized soybean oil, dimer acid based materials, such as EMPOL 1010 resin which is commercially available from Emery Chemicals, and rubber modified polyepoxide resins, such as the product prepared from a polyglycidyl ether of bisphenol A, e.g. EPON 828 from Shell Chemical, and an acid functional polybutadiene.

Crosslinkable polyurethanes, polyesters, polyvinyls, polysulfides, urea and formaldehyde are examples of resins which are suitable for this invention.

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The instant invention also pertains to radiation-curable (UV-curable) coating systems comprising ethylenically unsaturated acrylic resins, polyurethane acrylates, epoxy acrylates, polyester acrylates, unsaturated polyester/styrene resins and silyl acrylates. The ethylenically unsaturated polymerizable compounds can contain one or more than one olefinic double bond. They may be low molecular (monomeric) or high molecular (oligomeric) compounds. Radiation cured coatings are described for example in U.S. Pat. No. 6,376,584, filed Feb. 27, 2001, hereby incorporated by reference. Unsaturated monomers are typically alkyl- or hydroxyalkyl acrylates or methacrylates, styrene, ethylene glycol diacrylate, propylene glycol diacrylate, neopentyl glycol diacrylate, hexamethylene glycol diacrylate or bisphenol A diacrylate, 4,4'-bis(2-acryloyloxyethoxy)diphenylpropane, trimethylolpropane triacrylate, pentaerythritol triacrylate or tetraacrylate, styrene, hexamethylene glycol or bisphenol A diacrylate, 4,4'-bis(2-acryloyloxyethoxy)diphenylpropane or trimethylolpropane triacrylate. Oligomeric polyunsaturated compounds are for instance polyester acrylates or unsaturated polyester resins which are prepared from maleic acid, fumaric acid, phthalic acid and one or more than one diol, and which typically have molecular weights from about 500 to 3000. Unsaturated carboxylic acids are for example acrylic acid and methacrylic acid.

Powder coating compositions for example comprise glycidyl methacrylate with selected alcohol components.

The present coating compositions are for example enamel compositions with high solids content based on crosslinkable acrylic, polyester, urethane, or alkyd resins curable with an additional acid catalyst. These acid catalyzed stoving lacquers are based for example on hot crosslinkable acrylic, polyester, polyurethane, polyamide or alkyd resins.

The present coating compositions are suitable for multi-layer systems, for example the flame retardant additive combinations of this invention may be present in one or more than one layer of a multi-layer coating system.

The present coating compositions may be applied to the substrate by any conventional manner, for example by brush, roller, spray, dipping, electrostatic deposition, extrusion/coextrusion, troweling (mastics) and the like.

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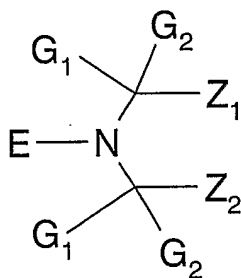
The present coating compositions may be intumescent or non-intumescent.

The present coating compositions are employed to form, of course, thin layers. The layers are for example from about 5 microns to about 10 mil thick, for instance from about 10 microns to about 7 mil thick, or from about 1 mil to about 5 mil thick. They are for instance about 10 microns, or about 1, 2, 3, 4, 5 or 6 mil thick. There are 26 microns per mil.

The present coating compositions provide coatings that are themselves flame retardant and provide flame retardancy to the entire article of which they are a part (for instance a coated plastic part).

Sterically Hindered Compounds of Component (i)

The present sterically hindered stabilizers of component (i) are well known in the art, and are for example of the formula



where

G₁ and G₂ are independently alkyl of 1 to 8 carbon atoms or are together pentamethylene,

Z₁ and Z₂ are each methyl, or Z₁ and Z₂ together form a linking moiety which may additionally be substituted by an ester, ether, amide, amino, carboxy or urethane group, and

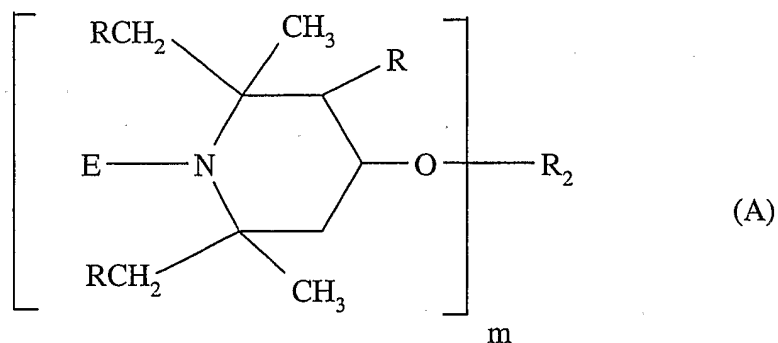
E is oxyl, hydroxyl, alkoxy, cycloalkoxy, aralkoxy, aryloxy, $-O-CO-OZ_3$, $-O-Si(Z_4)_3$, $-O-PO(OZ_5)_2$ or $-O-CH_2-OZ_6$ where Z_3 , Z_4 , Z_5 and Z_6 are selected from the group consisting of hydrogen, an aliphatic, araliphatic and aromatic moiety; or E is $-O-T-(OH)_b$,

T is a straight or branched chain alkylene of 1 to 18 carbon atoms, cycloalkylene of 5 to 18 carbon atoms, cycloalkenylene of 5 to 18 carbon atoms, a straight or branched chain alkylene of 1 to 4 carbon atoms substituted by phenyl or by phenyl substituted by one or two alkyl groups of 1 to 4 carbon atoms;

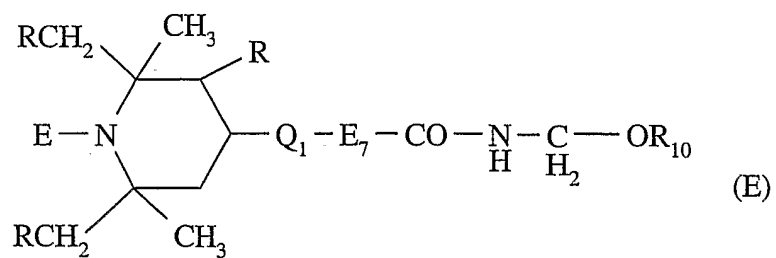
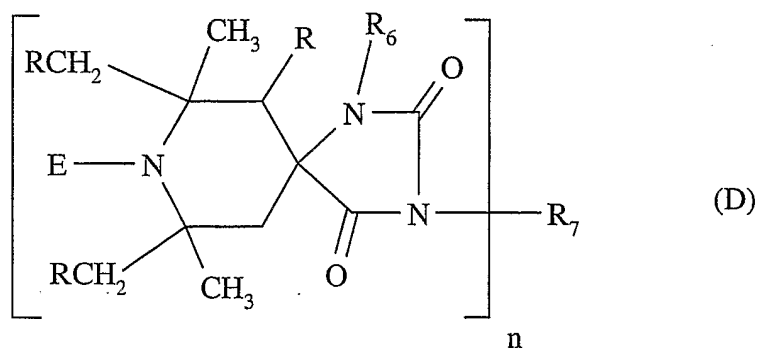
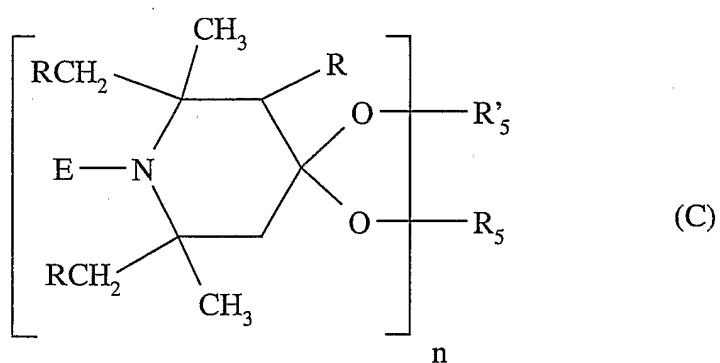
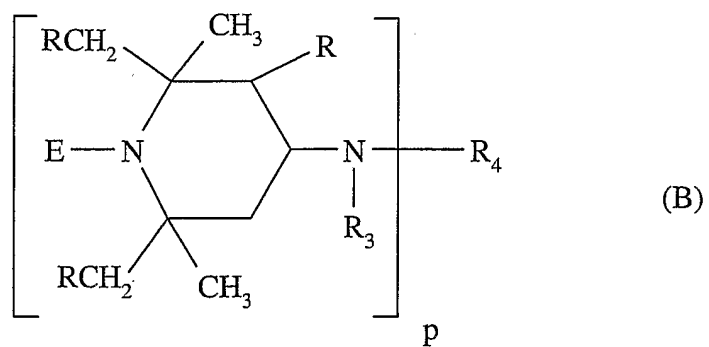
b is 1, 2 or 3 with the proviso that b cannot exceed the number of carbon atoms in T, and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T.

E is for example oxyl, hydroxyl, alkoxy, cycloalkoxy or aralkoxy. For instance, E is methoxy, propoxy, cyclohexyloxy or octyloxy.

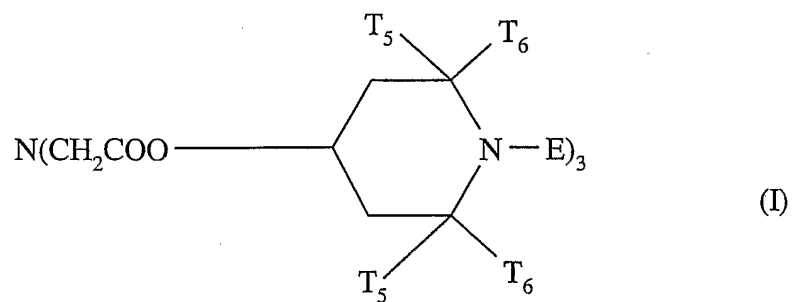
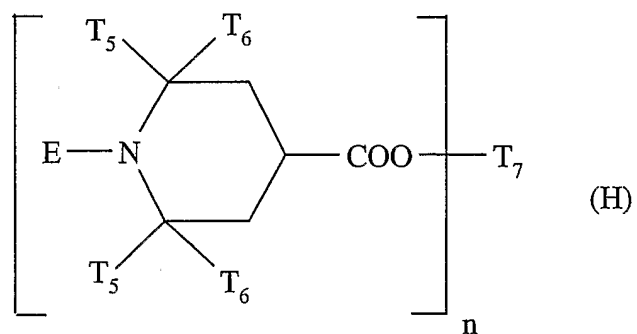
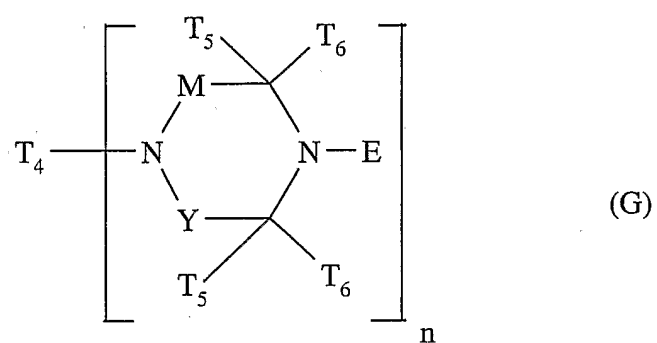
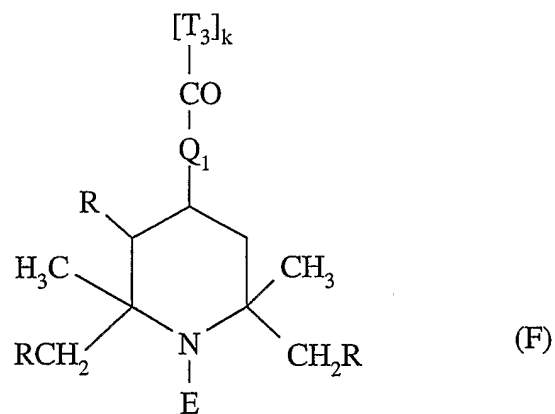
The present sterically hindered stabilizers of component (i) are for example of the formula A-R



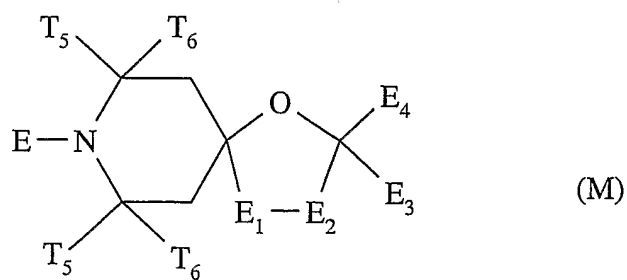
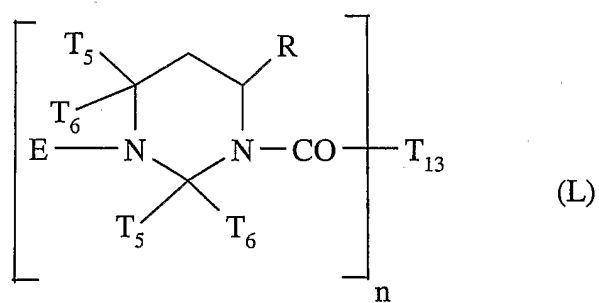
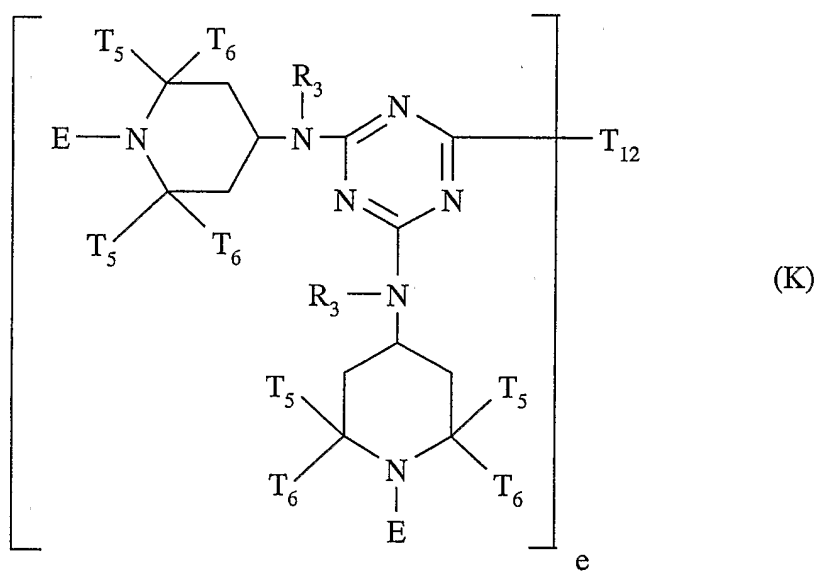
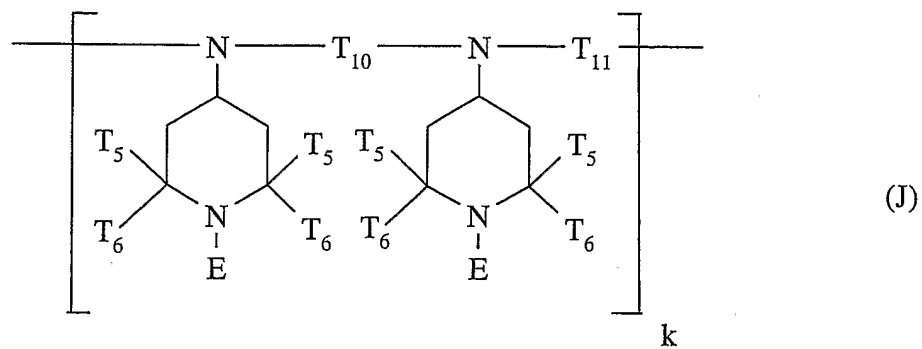
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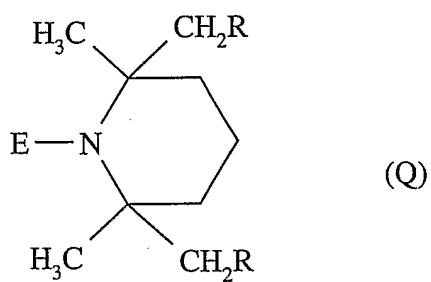
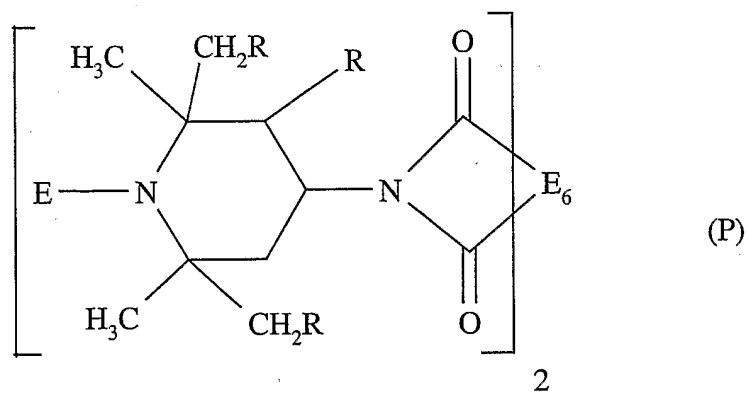
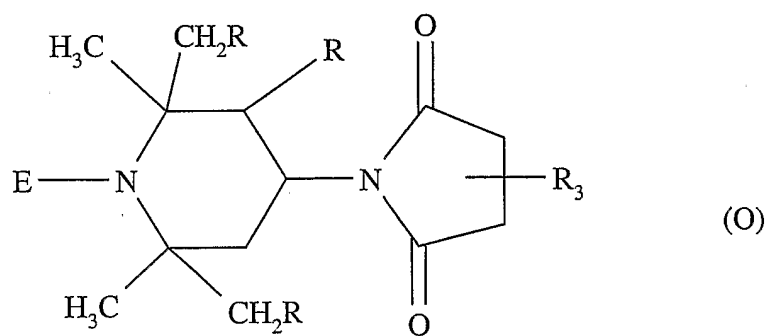
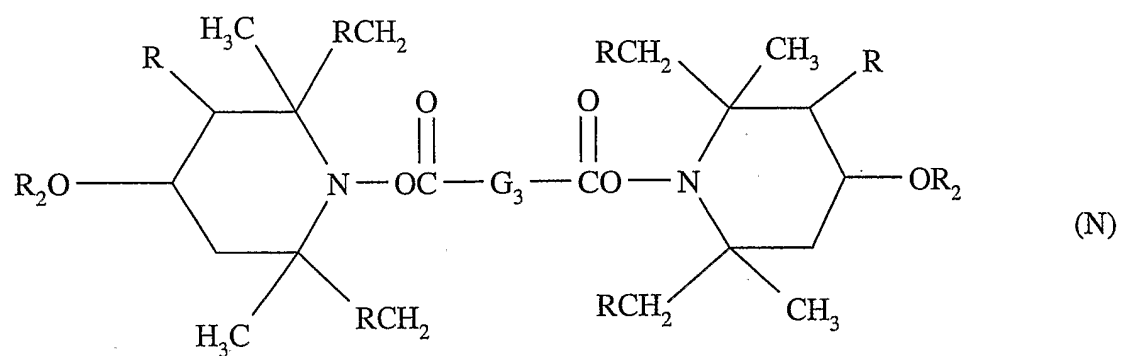


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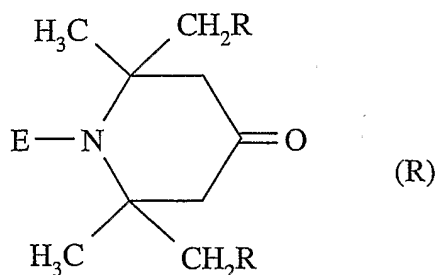


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wherein

E is oxyl, hydroxyl, alkoxy of 1 to 18 carbon atoms, cycloalkoxy of 5 to 12 carbon atoms or aralkoxy of 7 to 15 carbon atoms, or E is $-O-T-(OH)_b$,

T is a straight or branched chain alkylene of 1 to 18 carbon atoms, cycloalkylene of 5 to 18 carbon atoms, cycloalkenylene of 5 to 18 carbon atoms, a straight or branched chain alkylene of 1 to 4 carbon atoms substituted by phenyl or by phenyl substituted by one or two alkyl groups of 1 to 4 carbon atoms;

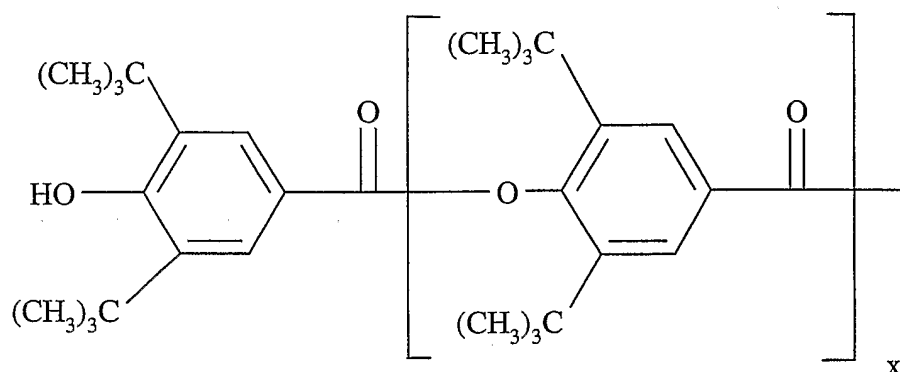
b is 1, 2 or 3 with the proviso that b cannot exceed the number of carbon atoms in T, and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T;

R is hydrogen or methyl,

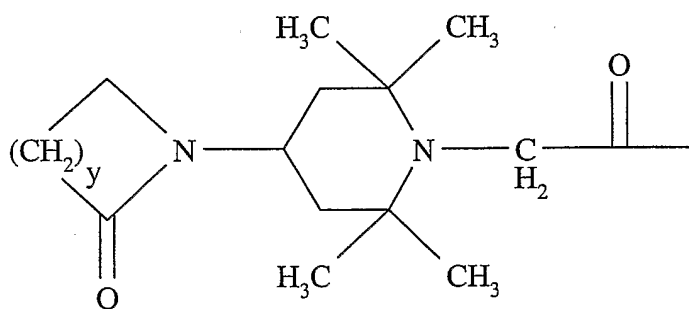
m is 1 to 4,

when m is 1,

R_2 is hydrogen, C_1 - C_{18} alkyl or said alkyl optionally interrupted by one or more oxygen atoms, C_2 - C_{12} alkenyl, C_6 - C_{10} aryl, C_7 - C_{18} aralkyl, glycidyl, a monovalent acyl radical of an aliphatic, cycloaliphatic or aromatic carboxylic acid, or a carbamic acid, for example an acyl radical of an aliphatic carboxylic acid having 2-18 C atoms, of a cycloaliphatic carboxylic acid having 5-12 C atoms or of an aromatic carboxylic acid having 7-15 C atoms, or



wherein x is 0 or 1,

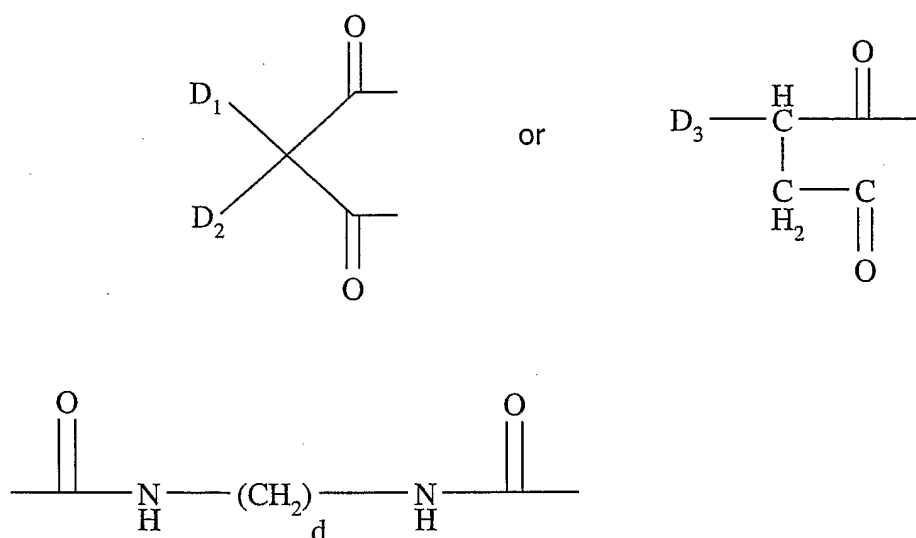


wherein y is 2-4;

when m is 2,

R₂ is C₁-C₁₂alkylene, C₄-C₁₂alkenylene, xylylene, a divalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid or of a dicarbamic acid, for example an acyl radical of an aliphatic dicarboxylic acid having 2-18 C atoms, of a cycloaliphatic or aromatic dicarboxylic acid having 8-14 C atoms, or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 C atoms;

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wherein D₁ and D₂ are independently hydrogen, an alkyl radical containing up to 8 carbon atoms, an aryl or aralkyl radical including 3,5-di-*t*-butyl-4-hydroxybenzyl radical, D₃ is hydrogen, or an alkyl or alkenyl radical containing up to 18 carbon atoms, and d is 0-20;

when m is 3, R₂ is a trivalent acyl radical of an aliphatic, unsaturated aliphatic, cycloaliphatic, or aromatic tricarboxylic acid;

when m is 4, R₂ is a tetravalent acyl radical of a saturated or unsaturated aliphatic or aromatic tetracarboxylic acid including 1,2,3,4-butanetetracarboxylic acid, 1,2,3,4-but-2-ene-tetracarboxylic, and 1,2,3,5- and 1,2,4,5-pentanetetracarboxylic acid;

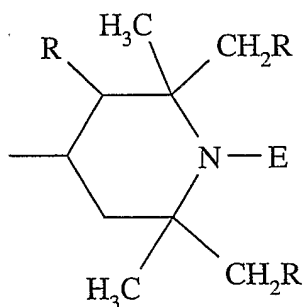
p is 1, 2 or 3,

R₃ is hydrogen, C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₉aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl;

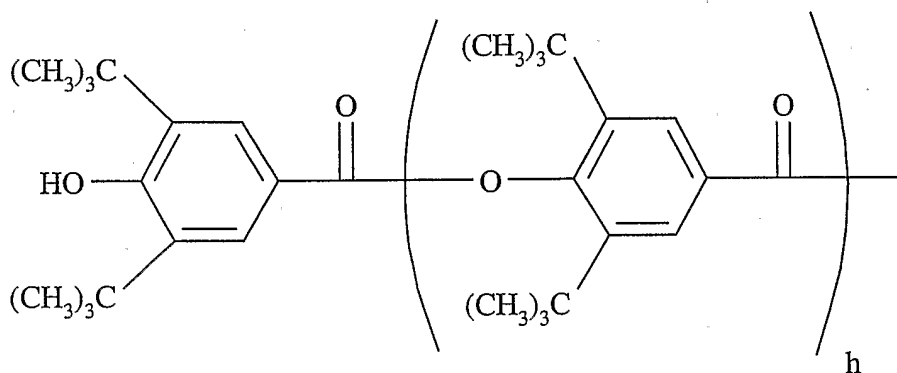
when p is 1,

R₄ is hydrogen, C₁-C₁₈alkyl, C₅-C₇cycloalkyl, C₂-C₈alkenyl, unsubstituted or substituted by a cyano, carbonyl or carbamide group, aryl, aralkyl, or it is glycidyl, a group of the formula -CH₂-CH(OH)-Z or of the formula -CO-Z or -CONH-Z wherein Z is hydrogen, methyl or phenyl; or a group of the formulae

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or



where h is 0 or 1,

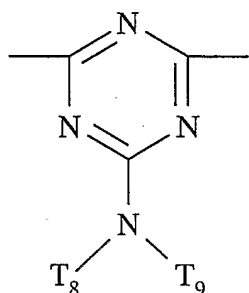
R_3 and R_4 together, when p is 1, can be alkylene of 4 to 6 carbon atoms or 2-oxo-polyalkylene the cyclic acyl radical of an aliphatic or aromatic 1,2- or 1,3-dicarboxylic acid,

when p is 2,

R_4 is a direct bond or is C_1 - C_{12} alkylene, C_6 - C_{12} arylene, xylylene, a $-CH_2CH(OH)-CH_2$ group or a group $-CH_2-CH(OH)-CH_2-O-X-O-CH_2-CH(OH)-CH_2-$ wherein X is C_2 - C_{10} alkylene, C_6 - C_{15} arylene or C_6 - C_{12} cycloalkylene; or, provided that R_3 is not alkanoyl, alkenoyl or benzoyl, R_4 can also be a divalent acyl radical of an aliphatic, cycloaliphatic or aromatic dicarboxylic acid or dicarbamic acid, or can be the group $-CO-$; or

R_4 is

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where T_8 and T_9 are independently hydrogen, alkyl of 1 to 18 carbon atoms, or T_8 and T_9 together are alkylene of 4 to 6 carbon atoms or 3-oxapentamethylene, for instance T_8 and T_9 together are 3-oxapentamethylene;

when p is 3,

R_4 is 2,4,6-triazinyl,

n is 1 or 2,

when n is 1,

R_5 and R'_5 are independently C_1 - C_{12} alkyl, C_2 - C_{12} alkenyl, C_7 - C_{12} aralkyl, or R_5 is also hydrogen, or R_5 and R'_5 together are C_2 - C_8 alkylene or hydroxyalkylene or C_4 - C_{22} acyloxyalkylene;

when n is 2,

R_5 and R'_5 together are $(-CH_2)_2C(CH_2)_2$;

R_6 is hydrogen, C_1 - C_{12} alkyl, allyl, benzyl, glycidyl or C_2 - C_6 alkoxyalkyl;

when n is 1,

R_7 is hydrogen, C_1 - C_{12} alkyl, C_3 - C_5 alkenyl, C_7 - C_9 aralkyl, C_5 - C_7 cycloalkyl, C_2 - C_4 hydroxyalkyl, C_2 - C_6 alkoxyalkyl, C_6 - C_{10} aryl, glycidyl, a group of the formula $-(CH_2)_t-COO-Q$ or of the formula $-(CH_2)_t-O-CO-Q$ wherein t is 1 or 2, and Q is C_1 - C_4 alkyl or phenyl; or

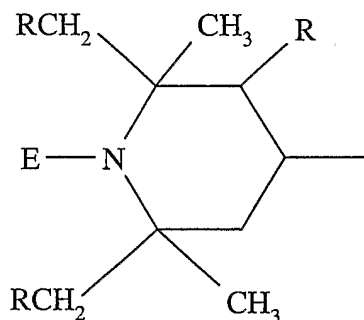
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when n is 2,

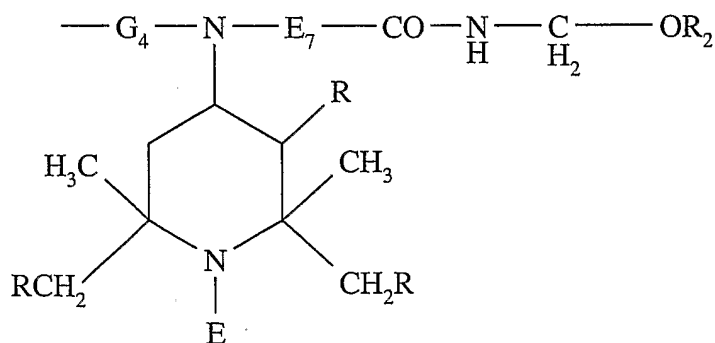
R_7 is C_2 - C_{12} alkylene, C_6 - C_{12} arylene, a group $-\text{CH}_2\text{CH}(\text{OH})-\text{CH}_2-\text{O}-\text{X}-\text{O}-\text{CH}_2-\text{CH}(\text{OH})-\text{CH}_2-$ wherein X is C_2 - C_{10} alkylene, C_6 - C_{15} arylene or C_6 - C_{12} cycloalkylene, or a group $-\text{CH}_2\text{CH}(\text{OZ}')\text{CH}_2-(\text{OCH}_2-\text{CH}(\text{OZ}')\text{CH}_2)_2-$ wherein Z' is hydrogen, C_1 - C_{18} alkyl, allyl, benzyl, C_2 - C_{12} alkanoyl or benzoyl;

Q_1 is $-\text{N}(\text{R}_8)-$ or $-\text{O}-$; E_7 is C_1 - C_3 alkylene, the group $-\text{CH}_2-\text{CH}(\text{R}_9)-\text{O}-$ wherein R_9 is hydrogen, methyl or phenyl, the group $-(\text{CH}_2)_3-\text{NH}-$ or a direct bond;

R_{10} is hydrogen or C_1 - C_{18} alkyl, R_8 is hydrogen, C_1 - C_{18} alkyl, C_5 - C_7 cycloalkyl, C_7 - C_{12} aralkyl, cyanoethyl, C_6 - C_{10} aryl, the group $-\text{CH}_2-\text{CH}(\text{R}_9)-\text{OH}$ wherein R_9 has the meaning defined above; a group of the formula



or a group of the formula



wherein G_4 is C_2 - C_6 alkylene or C_6 - C_{12} arylene; or R_8 is a group $-\text{E}_7-\text{CO}-\text{NH}-\text{CH}_2-\text{OR}_{10}$;

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Formula F denotes a recurring structural unit of a polymer where T_3 is ethylene or 1,2-propylene, is the repeating structural unit derived from an alpha-olefin copolymer with an alkyl acrylate or methacrylate; for example a copolymer of ethylene and ethyl acrylate, and where k is 2 to 100;

T_4 has the same meaning as R_4 when p is 1 or 2,

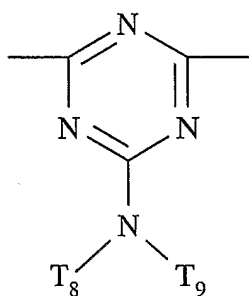
T_5 is methyl,

T_6 is methyl or ethyl, or T_5 and T_6 together are tetramethylene or pentamethylene, for instance T_5 and T_6 are each methyl,

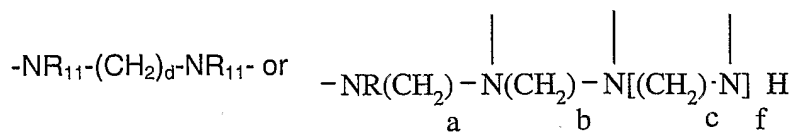
M and Y are independently methylene or carbonyl, and T_4 is ethylene where n is 2;

T_7 is the same as R_7 , and T_7 is for example octamethylene where n is 2,

T_{10} and T_{11} are independently alkylene of 2 to 12 carbon atoms, or T_{11} is

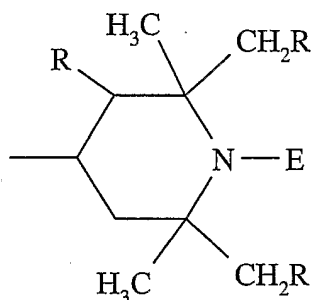


T_{12} is piperazinyl,



where R_{11} is the same as R_3 or is also

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a, b and c are independently 2 or 3, and f is 0 or 1, for instance a and c are each 3, b is 2 and f is 1; and

e is 2, 3 or 4, for example 4;

T_{13} is the same as R_2 with the proviso that T_{13} cannot be hydrogen when n is 1;

E_1 and E_2 , being different, each are -CO- or -N(E_5)- where E_5 is hydrogen, C_1 - C_{12} alkyl or C_4 - C_{22} alkoxy carbonyl alkyl, for instance E_1 is -CO- and E_2 is -N(E_5)-,

E_3 is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl, said phenyl or said naphthyl substituted by chlorine or by alkyl of 1 to 4 carbon atoms, or phenylalkyl of 7 to 12 carbon atoms, or said phenylalkyl substituted by alkyl of 1 to 4 carbon atoms,

E_4 is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl or phenylalkyl of 7 to 12 carbon atoms, or

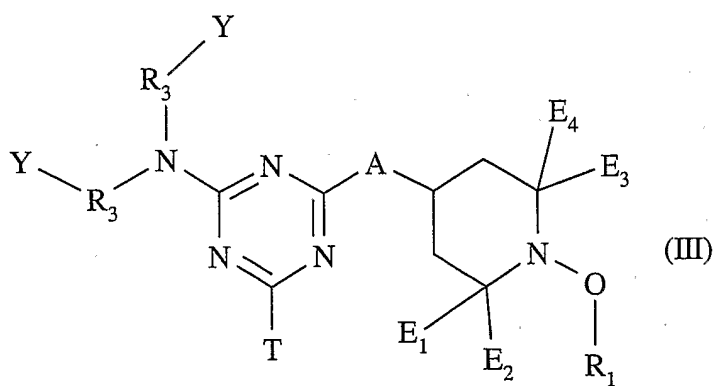
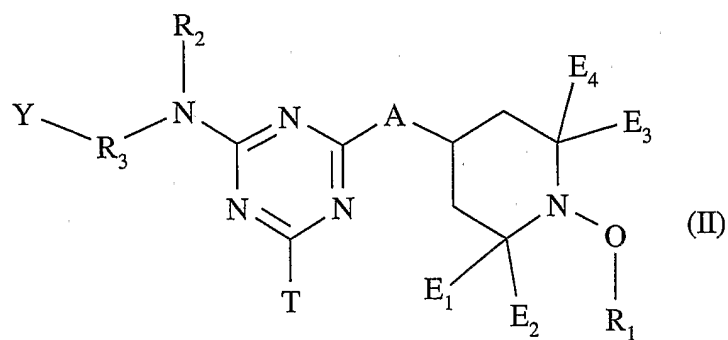
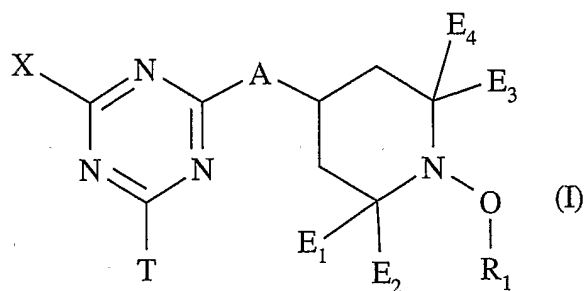
E_3 and E_4 together are polymethylene of 4 to 17 carbon atoms, or said polymethylene substituted by up to four alkyl groups of 1 to 4 carbon atoms, for example methyl,

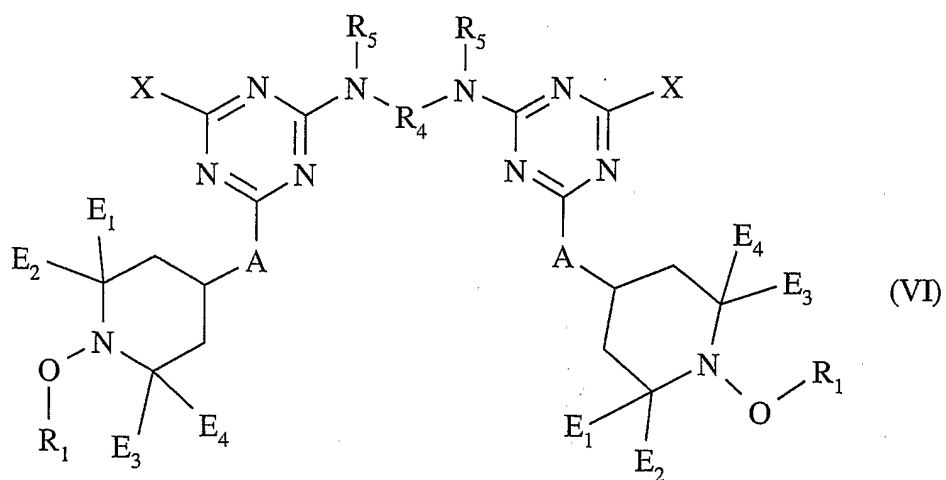
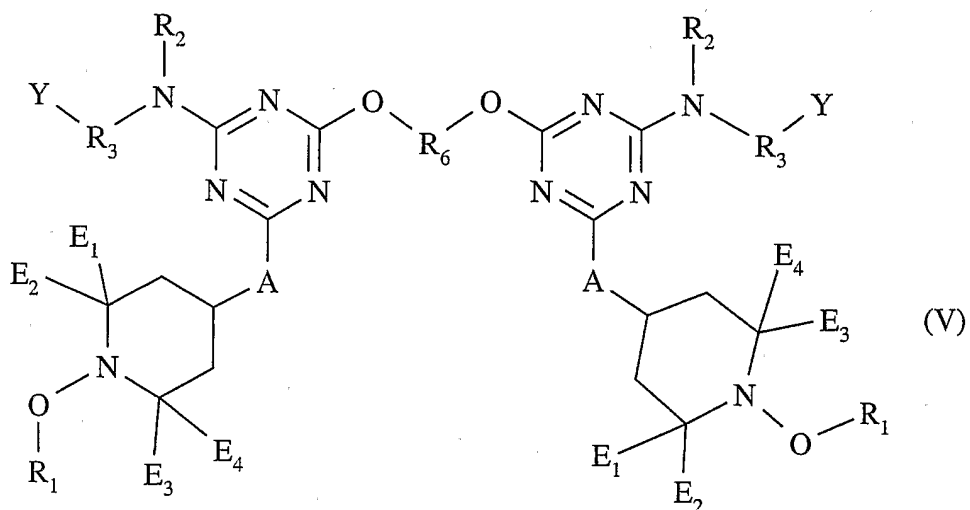
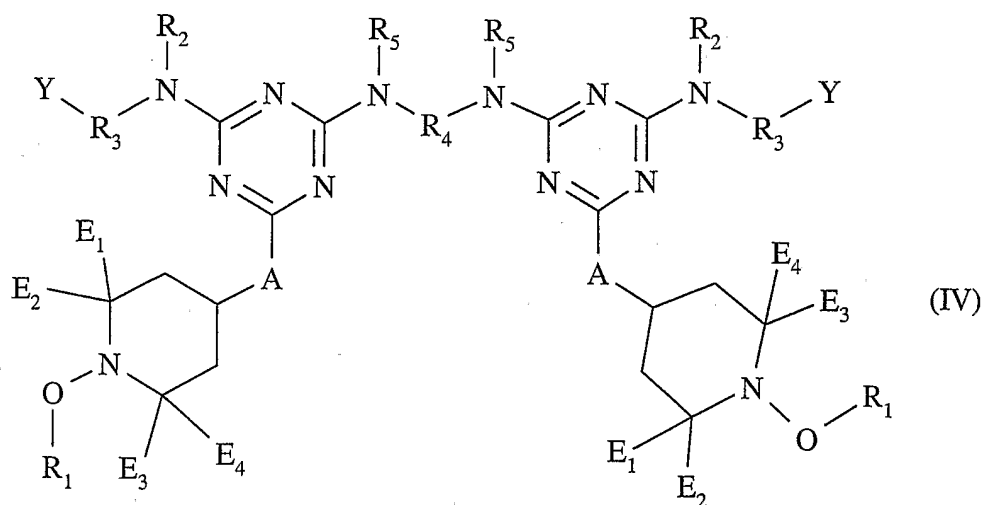
E_6 is an aliphatic or aromatic tetravalent radical,

R_2 of formula (N) is a previously defined when m is 1;

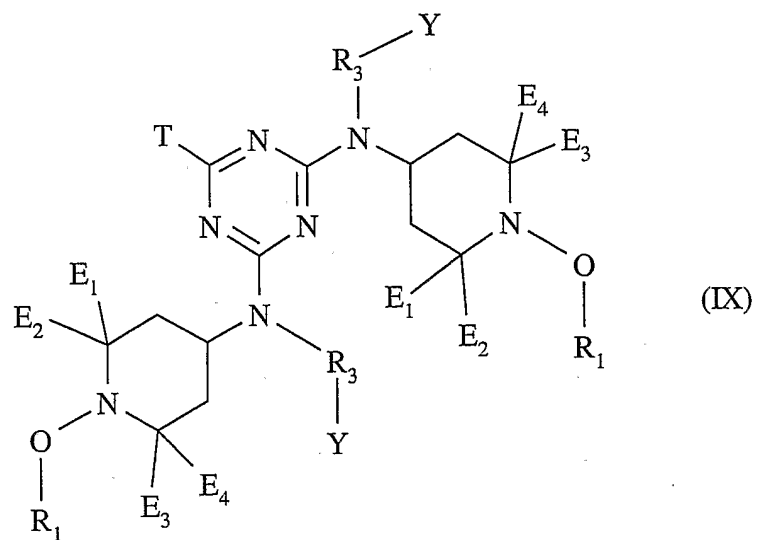
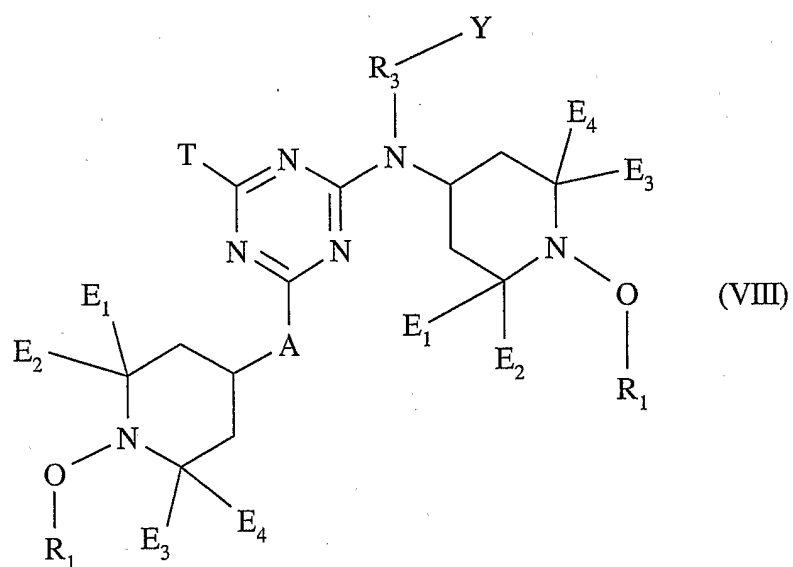
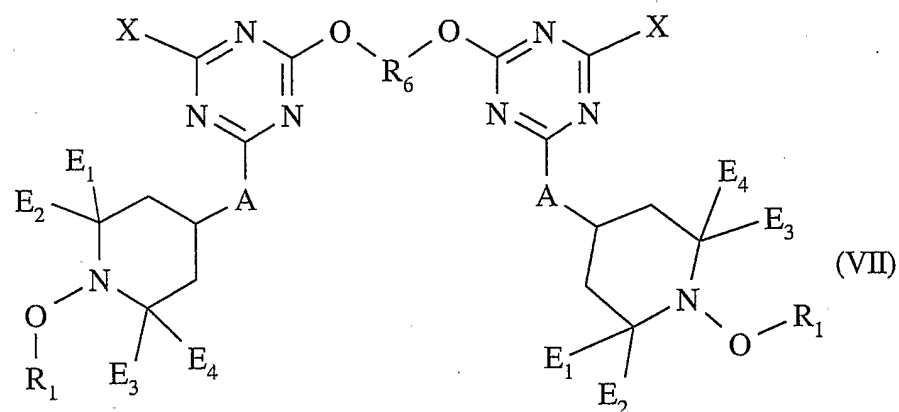
G_1 a direct bond, C_1 - C_{12} alkylene, phenylene or -NH- G' -NH wherein G' is C_1 - C_{12} alkylene; or

wherein the hindered amine compound is a compound of the formula I, II, III, IV, V, VI, VII, VIII, IX, X or XI

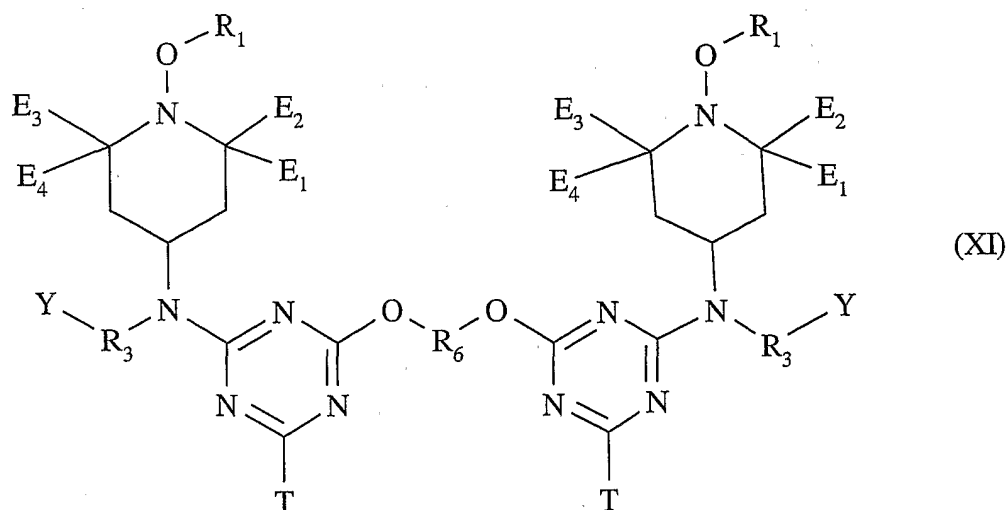
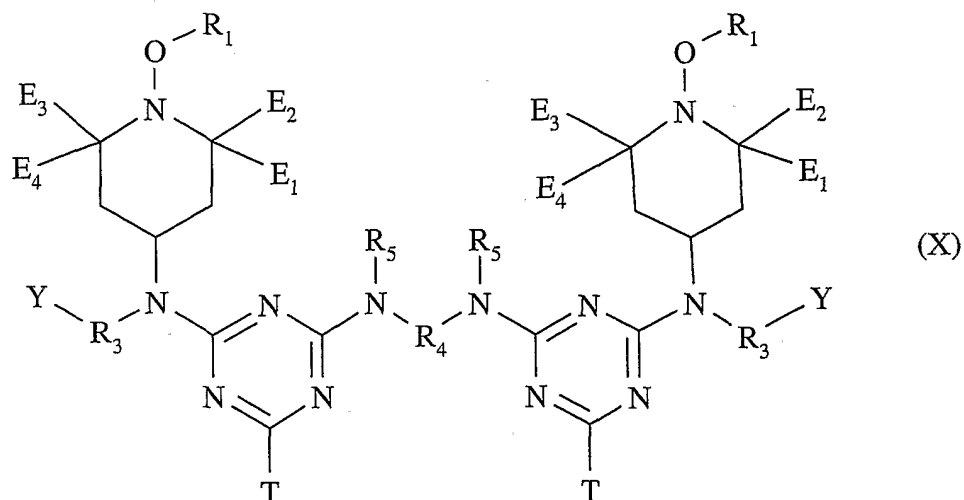




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wherein

E_1 , E_2 , E_3 and E_4 are independently alkyl of 1 to 4 carbon atoms, or E_1 and E_2 are independently alkyl of 1 to 4 carbon atoms and E_3 and E_4 taken together are pentamethylene, or E_1 and E_2 ; and E_3 and E_4 each taken together are pentamethylene,

R_1 is alkyl of 1 to 18 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, a bicyclic or tricyclic hydrocarbon radical of 7 to 12 carbon atoms, phenylalkyl of 7 to 15 carbon atoms, aryl of 6 to 10 carbon atoms or said aryl substituted by one to three alkyl of 1 to 8 carbon atoms,

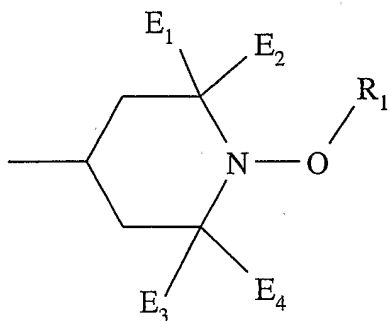
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R_2 is hydrogen or a linear or branched chain alkyl of 1 to 12 carbon atoms,

R_3 is alkylene of 1 to 8 carbon atoms, or R_3 is $-\text{CO}-$, $-\text{CO}-R_4-$, $-\text{CONR}_2-$, or $-\text{CO}-\text{NR}_2-R_4-$

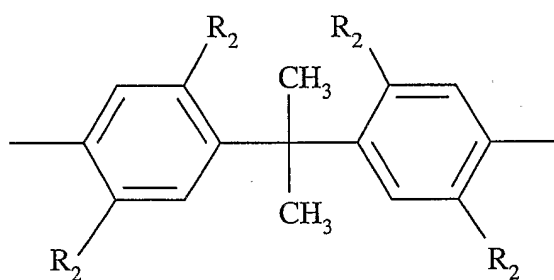
R_4 is alkylene of 1 to 8 carbon atoms,

R_5 is hydrogen, a linear or branched chain alkyl of 1 to 12 carbon atoms, or



or when R_4 is ethylene, two R_5 methyl substituents can be linked by a direct bond so that the triazine bridging group $-\text{N}(R_5)-R_4-\text{N}(R_5)-$ is a piperazin-1,4-diyl moiety,

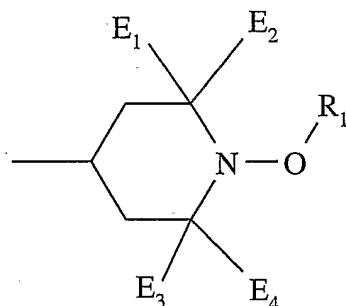
R_6 is alkylene of 2 to 8 carbon atoms or R_6 is



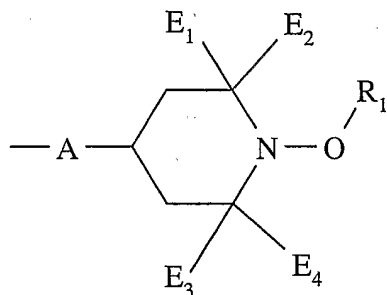
with the proviso that Y is not $-\text{OH}$ when R_6 is the structure depicted above,

A is $-\text{O}-$ or $-\text{NR}_7-$ where R_7 is hydrogen, a straight or branched chain alkyl of 1 to 12 carbon atoms, or R_7 is

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T is phenoxy, phenoxy substituted by one or two alkyl groups of 1 to 4 carbon atoms, alkoxy of 1 to 8 carbon atoms or $-N(R_2)_2$ with the stipulation that R_2 is not hydrogen, or T is

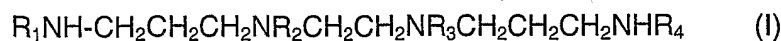


X is $-NH_2$, $-NCO$, $-OH$, $-O$ -glycidyl, or $-NHNH_2$, and

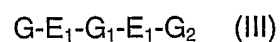
Y is $-OH$, $-NH_2$, $-NHR_2$ where R_2 is not hydrogen; or Y is $-NCO$, $-COOH$, oxiranyl, $-O$ -glycidyl, or $-Si(OR_2)_3$; or the combination R_3-Y- is $-CH_2CH(OH)R_2$ where R_2 is alkyl or said alkyl interrupted by one to four oxygen atoms, or R_3-Y- is $-CH_2OR_2$;

or

wherein the hindered amine compound is a mixture of N,N',N'' -tris[2,4-bis[(1-hydrocarbyloxy-2,2,6,6-tetramethylpiperidin-4-yl)alkylamino]-s-triazin-6-yl]-3,3'-ethylenediiminodipropylamine; N,N',N'' -tris[2,4-bis[(1-hydrocarbyloxy-2,2,6,6-tetramethylpiperidin-4-yl)alkylamino]-s-triazin-6-yl]-3,3'-ethylenediiminodipropylamine, and bridged derivatives as described by formulas I, II, IIA and III



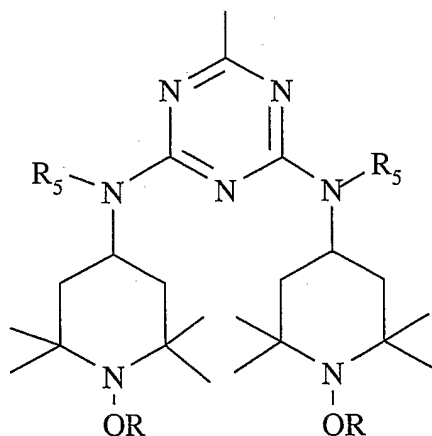
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where in the tetraamine of formula I

R_1 and R_2 are the s-triazine moiety E; and one of R_3 and R_4 is the s-triazine moiety E with the other of R_3 or R_4 being hydrogen,

E is



R is methyl, propyl, cyclohexyl or octyl, for instance cyclohexyl,

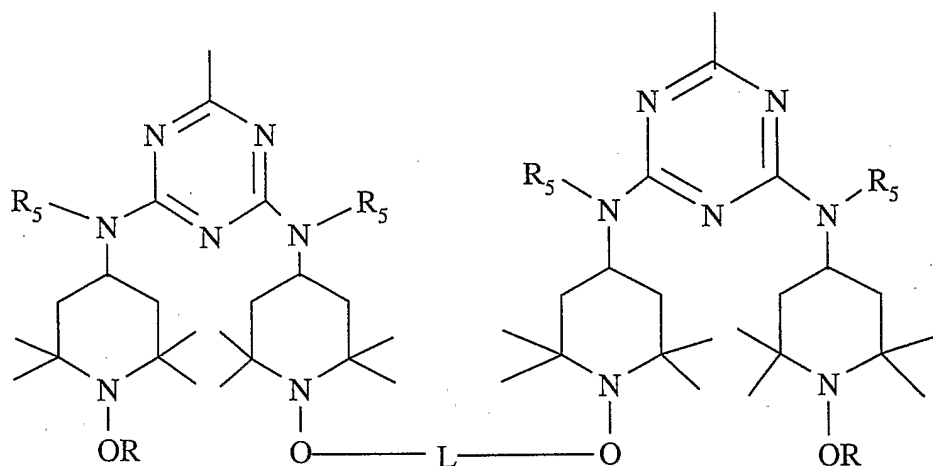
R_5 is alkyl of 1 to 12 carbon atoms, for example n-butyl,

where in the compound of formula II or IIA when R is propyl, cyclohexyl or octyl,

T and T_1 are each a tetraamine substituted by R_1 - R_4 as is defined for formula I, where

(1) one of the s-triazine moieties E in each tetraamine is replaced by the group E_1 which forms a bridge between two tetraamines T and T_1 ,

E_1 is



or

(2) the group E_1 can have both termini in the same tetraamine T as in formula IIA where two of the E moieties of the tetraamine are replaced by one E_1 group, or

(3) all three s-triazine substituents of tetraamine T can be E_1 such that one E_1 links T and T_1 and a second E_1 has both termini in tetraamine T,

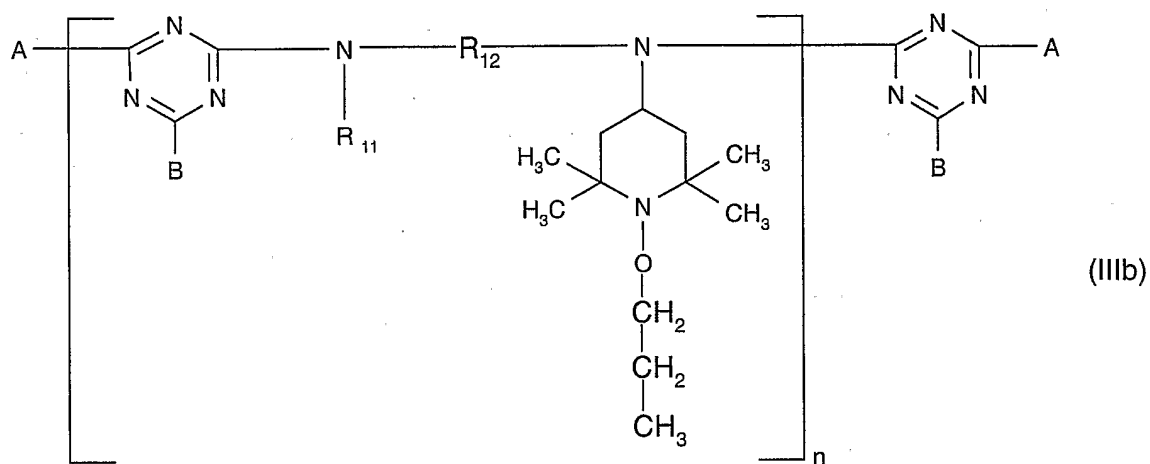
L is propanediyl, cyclohexanediyl or octanediyl;

where in the compound of formula III

G, G_1 and G_2 are each tetraamines substituted by R_1 - R_4 as defined for formula I, except that G and G_2 each have one of the s-triazine moieties E replaced by E_1 , and G_1 has two of the triazine moieties E replaced by E_1 , so that there is a bridge between G and G_1 and a second bridge between G_1 and G_2 ;

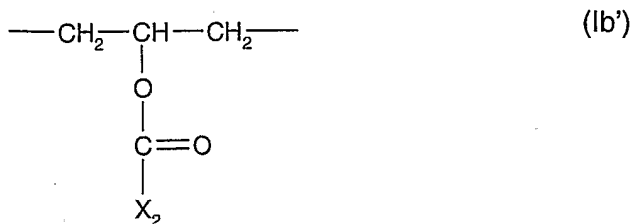
which mixture is prepared by reacting two to four equivalents of 2,4-bis[(1-hydrocarbyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine with one equivalent of N,N'-bis(3-aminopropyl)ethylenediamine;

or the hindered amine is a compound of the formula IIIb

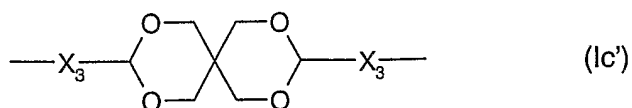


in which the index n ranges from 1 to 15;

R_{12} is C_2 - C_{12} alkylene, C_4 - C_{12} alkenylene, C_5 - C_7 cycloalkylene, C_5 - C_7 cycloalkylene-di(C_1 - C_4 alkylene), C_1 - C_4 alkylenedi(C_5 - C_7 cycloalkylene), phenylenedi(C_1 - C_4 alkylene) or C_4 - C_{12} alkylene interrupted by 1,4-piperazinediyl, -O- or $>N-X_1$ with X_1 being C_1 - C_{12} acyl or (C_1 - C_{12} alkoxy)carbonyl or having one of the definitions of R_{14} given below except hydrogen; or R_{12} is a group of the formula (Ib') or (Ic');



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with m being 2 or 3,

X₂ being C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl which is unsubstituted or substituted by 1, 2 or

3

C₁-C₄alkyl; phenyl which is unsubstituted or substituted by 1, 2 or 3 C₁-C₄alkyl or

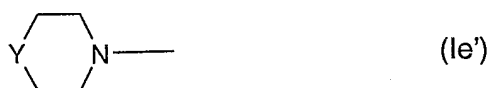
C₁-C₄alkoxy; C₇-C₉phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3

C₁-C₄alkyl; and

the radicals X₃ being independently of one another C₂-C₁₂alkylene;

R₁₃, R₁₄ and R₁₅, which are identical or different, are hydrogen, C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C₁-C₄alkyl; C₃-C₁₈alkenyl, phenyl which is unsubstituted or substituted by 1, 2 or 3 C₁-C₄alkyl or C₁-C₄alkoxy; C₇-C₉phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3 C₁-C₄alkyl; tetrahydrofurfuryl or

C₂-C₄alkyl which is substituted in the 2, 3 or 4 position by -OH, C₁-C₈alkoxy, di(C₁-C₄alkyl)amino or a group of the formula (Ie');

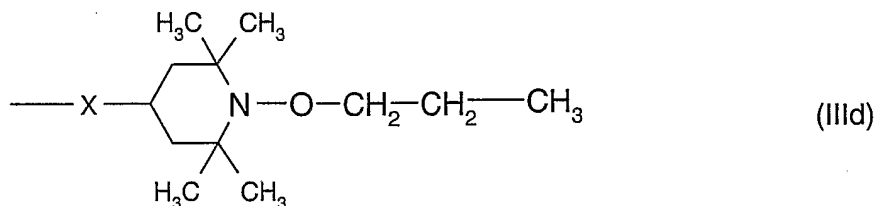


with Y being -O-, -CH₂-, -CH₂CH₂- or >N-CH₃,

or -N(R₁₄)(R₁₅) is additionally a group of the formula (Ie');

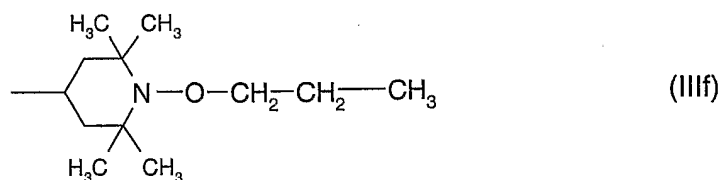
the radicals A are independently of one another -OR₁₃, -N(R₁₄)(R₁₅) or a group of the formula (IIId);

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X is -O- or >N-R₁₆;

R₁₆ is hydrogen, C₁-C₁₈alkyl, C₃-C₁₈alkenyl, C₅-C₁₂cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C₁-C₄alkyl; C₇-C₉phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3 C₁-C₄alkyl; tetrahydrofurfuryl, a group of the formula (IIIIf),



or C₂-C₄alkyl which is substituted in the 2, 3 or 4 position by -OH, C₁-C₈alkoxy, di(C₁-C₄alkyl)amino or a group of the formula (Ie');

R₁₁ has one of the definitions given for R₁₆; and

the radicals B have independently of one another one of the definitions given for A.

If R₂ is a monovalent acyl radical of a carboxylic acid, it is for example an acyl radical of acetic acid, stearic acid, salicylic acid, benzoic acid or β-(3,5-di-tert-butyl-4-hydroxyphenyl) propionic acid.

If R₂ is a divalent acyl radical of a dicarboxylic acid, it is for example an acyl radical of oxalic acid, adipic acid, succinic acid, suberic acid, sebacic acid, phthalic acid dibutylmalonic acid, dibenzylmalonic acid or butyl-(3,5-di-tert-butyl-4-hydroxybenzyl)-malonic acid, or bicycloheptenedicarboxylic acid, with succinates, sebacates, phthalates and isophthalates being specific examples.

If R_2 is a divalent acyl radical of a dicarbamic acid, it is for example an acyl radical of hexamethylenedicarbamic acid or of 2,4-toluylenedicarbamic acid.

The hindered alkoxyamine stabilizers of component (c) are well known in the art, also known as N-alkoxy hindered amines and NOR hindered amines or NOR hindered amine light stabilizers or NOR HALS.

They are disclosed for example in U.S. Pat. Nos. 5,004,770, 5,204,473, 5,096,950, 5,300,544, 5,112,890, 5,124,378, 5,145,893, 5,216,156, 5,844,026, 5,439,958, 5,021,481, 6,117,995, 6,271,377, and U.S. application Ser. Nos. 09/505,529, filed Feb. 17, 2000, 09/794,710, filed Feb. 27, 2001, 09/714,717, filed Nov. 16, 2000, 09/502,239, filed Nov. 3, 1999 and 60/312,517, filed Aug. 15, 2001. The relevant disclosures of these patents and applications are hereby incorporated by reference.

U.S. Pat. No. 6,271,377, and U.S. application Ser. Nos. 09/505,529, filed Feb. 17, 2000, and 09/794,710, filed Feb. 27, 2001, cited above disclose hindered hydroxyalkoxyamine stabilizers. For the purposes of this invention, the hindered hydroxyalkoxyamine stabilizers are considered a subset of the hindered alkoxyamine stabilizers and are part of present component (c). Hindered hydroxyalkoxyamine stabilizers are also known as N-hydroxyalkoxy hindered amines, or NORol HALS.

Typical nitroxyls of component (a) include bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-ethoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-propoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-acetamido-1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-ethylhexanoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-*t*-butyl-benzoate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) *n*-butylmalonate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) isophthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) terephthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) hexahydroterephthalate, *N,N'*-

bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipamide, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)caprolactam, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)dodecylsuccinimide, 2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-s-triazine, 4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one), 2-oxyl-1,1,3,3-tetramethyl-2-isobenzazole, 1-oxyl-2,2,5,5-tetramethylpyrrolidine, and N,N-bis-(1,1,3,3-tetramethylbutyl)nitroxide.

Nitroxyl stabilizers of component (a) are for example bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-ethoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-propoxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 4-acetamido-1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine, and 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one.

A specific embodiment is where the nitroxyl stabilizers of component (a) are bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate and 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine.

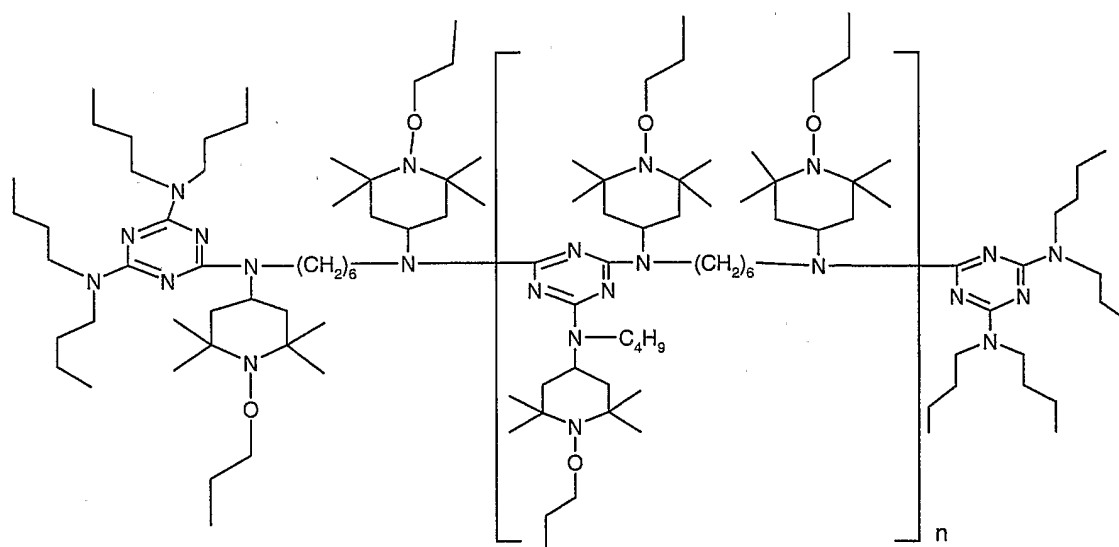
Hydroxylamine stabilizers of component (b) are for example those disclosed in U.S. Patent Nos. 4,831,134, 4,590,231, 4,668,721, 4,691,015, 4,831,134, 5,006,577, and 5,064,883, the relevant parts of which are incorporated herein by reference.

Specific examples of suitable compounds of present component (i) include:

- (a) the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine [CAS Reg. No. 191680-81-6];
- (b) 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine;
- (c) bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (d) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxyethylamino-s-triazine);
- (e) bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
- (h) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine;
- (i) 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine;

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- (j) 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine;
- (k) 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine;
- (l) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (m) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
- (n) 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino}-6-(2-hydroxyethylamino)-s-triazine; and
- (o) the compound of formula



in which n is from 1 to 15;

or the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine; or

the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine.

Compound (o) is disclosed in example 2 of U.S. Patent No. 6,117,995.

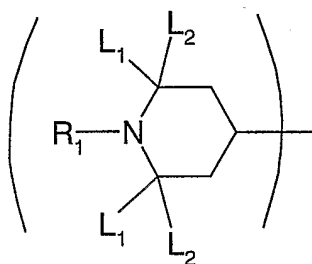
The sterically hindered alkoxyamine or hydroxyalkoxyamine is for example the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine [CAS Reg. No. 191680-81-6]; bis(1-octyloxy-

2,2,6,6-tetramethylpiperidin-4-yl) sebacate; or the compounds (i), (j), (k) or (o); or mixtures of said hindered alkoxyamines and hydroxyalkoxyamines.

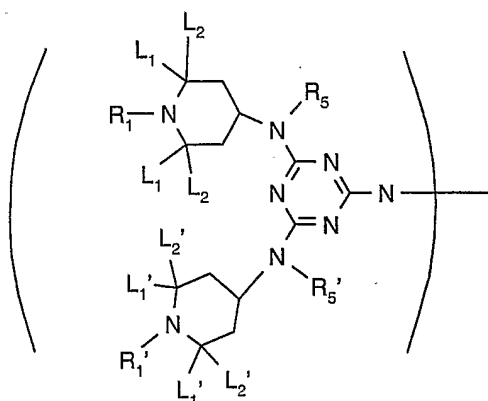
Polymerizable Sterically Hindered Compounds of Component (i)

The present ethylenically unsaturated, polymerizable monomers containing a sterically hindered amine moiety are disclosed for example in U.S. Pat. Nos. 4,983,737, 5,047,489 and 5,077,340, the relevant disclosures of which are hereby incorporated by reference.

The present hindered amine moieties are substituted on the 1-N atom with an oxyl, hydroxyl or hydrocarbyloxy group, said moiety independently having the formula



or

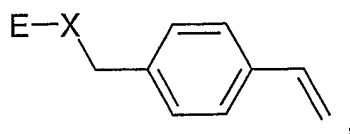
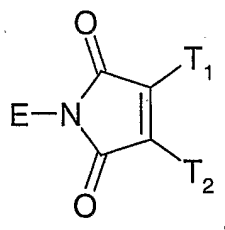
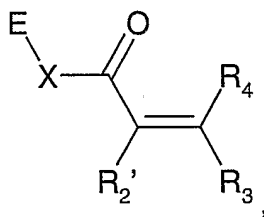
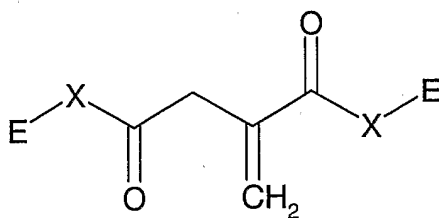
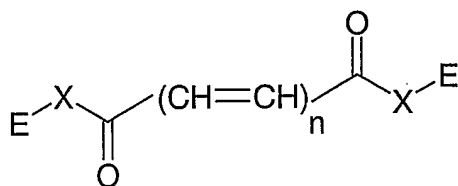


where

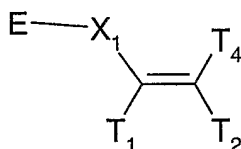
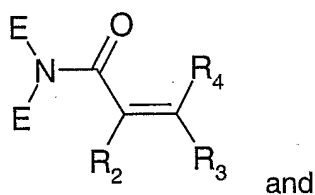
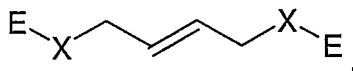
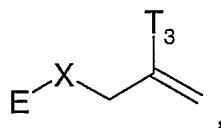
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L_1 , L_1' , L_2 and L_2' are independently alkyl of 1 to 4 carbon atoms, or L_1 and L_2 or L_1' and L_2' together are pentamethylene, and

said monomer is selected from the group consisting of formulae



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where

E is independently a sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety,

R₁ is oxyl, hydroxyl, straight or branched chain alkoxy of 1 to 36 carbon atoms, straight or branched chain alkenyloxy of 2 to 18 carbon atoms, straight or branched chain alkynyloxy of 2 to 18 carbon atoms, aralkoxy of 7 to 15 carbon atoms, cycloalkoxy of 5 to 12 carbon atoms, cycloalkenyloxy of 5 to 12 carbon atoms, a radical of a saturated or unsaturated bicyclic or tricyclic hydrocarbyloxy of 7 to 12 carbon atoms, or aryloxy of 6 to 10 carbon atoms or said aryloxy substituted by alkyl,

or R₁ is -O-T-(OH)_b,

R₁' is independently defined as for R₁,

T is a straight or branched chain alkylene of 1 to 18 carbon atoms, cycloalkylene of 5 to 18 carbon atoms, cycloalkenylene of 5 to 18 carbon atoms, a straight or branched chain alkylene of 1 to 4 carbon atoms substituted by phenyl or by phenyl substituted by one or two alkyl groups of 1 to 4 carbon atoms;

b is 1, 2 or 3 with the proviso that b cannot exceed the number of carbon atoms in T, and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T,

X is a direct bond, -O(polyoxyalkyleneO)- of 2 to 12 carbon atoms, -O-, -NH- or -NG-, where G is alkyl of 1 to 8 carbon atoms,

X₁ is a direct bond or -O-,

n is 1 or 2,

T₁, T₂ and T₄ are independently hydrogen, halogen, alkyl of 1 to 18 carbon atoms or aryl of 6 to 10 carbon atoms,

T₃ is hydrogen or methyl, and

R₂ is hydrogen or alkyl of 1 to 12 carbon atoms,

R₂' is hydrogen, alkyl of 1 to 12 carbon atoms or cyano,

R₃ and R₄ independently are hydrogen, alkyl of 1 to 12 carbon atoms, -COOH, or -COOG₁ where G₁ is straight or branched chain alkyl of 1 to 12 carbon atoms,

R₅ is straight or branched chain alkyl of 1 to 8 carbon atoms and

R₅' is independently defined as for R₅.

R_1 and R_1' are for example oxyl, hydroxyl, alkoxy, cycloalkoxy or aralkoxy. For instance, R_1 is methoxy, propoxy, cyclohexyloxy or octyloxy.

For example, L_1 , L_2 , L_1' and L_2' are each methyl.

For instance, R_1 and R_1' are alkoxy of 1 to 18 carbon atoms, alkenyloxy of 2 to 3 carbon atoms, propargyloxy, benzyloxy or cyclohexyloxy.

G is for example alkyl of 1 to 4 carbon atoms.

For instance, T_1 and T_2 are both hydrogen.

For example, T_3 is hydrogen.

For instance, R_2 , R_3 and R_4 are each hydrogen or R_3 and R_4 are hydrogen and R_2 and R_2' are methyl.

When R_1 and R_1' are alkoxy, they are for example, methoxy, ethoxy, butoxy, amyloxy, octyloxy, nonyloxy, dodecyloxy, tetradecyloxy, octadecyloxy, eicosyloxy, tricosyloxy, tricontyloxy or 2-hydroxy-2-methylpropoxy.

When R_1 and R_1' are alkenyloxy, they are for example, vinyloxy, allyloxy, octenyloxy or oleyloxy.

When R_1 and R_1' are alkynyloxy, they are for example propargyloxy.

When R_1 and R_1' are cycloalkoxy, they are for example, cyclopentyloxy, cyclohexyloxy, cyclooctyloxy, cyclododecyloxy or 1-hydroxycyclohexyloxy.

Each of the present polymerizable monomers contains an ethylenically unsaturated group allowing the monomer to polymerize using free radical initiation, photoinitiation, group transfer polymerization, graft polymerization, or cationic or anionic polymerization. More than one of the present monomers may be employed together.

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The present sterically hindered piperidine ring systems may also be substituted with for example hindered piperazine, piperazinone, morpholinone, oxazolidine ring systems and the like.

There are several synthetic procedures which can be used to prepare the instant polymerizable monomers containing a sterically hindered amine moiety.

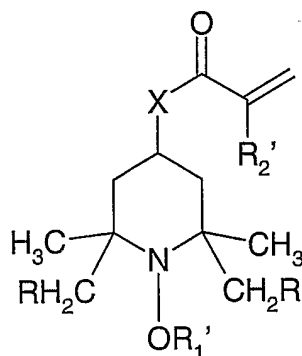
These include:

- (a) transesterification using a 4-hydroxy-2,2,6,6-tetramethylpiperidine and a lower alkyl ester of a unsaturated acid such as acrylic, fumaric, muconic or the like;
- (b) esterification using a 4-hydroxy-2,2,6,6-tetramethylpiperidine and an acid chloride such as acryloyl or methacryloyl chloride;
- (c) amidation using a 4-amino-2,2,6,6-tetramethylpiperidine and an acid chloride such as acryloyl or methacryloyl chloride;
- (d) imidation using a 4-amino-2,2,6,6-tetramethylpiperidine and a cyclic anhydride such as maleic anhydride followed by cyclization of the intermediate maleamic acid;
- (e) halide displacement using an unsaturated benzyl or allyl halide with the alkali metal alcoholate of 4-hydroxy-2,2,6,6-tetramethylpiperidine; and
- (f) catalytic oxidation of a preformed 4-acyloxy-2,2,6,6-tetramethylpiperidine with tert-butyl hydroperoxide or hydrogen peroxide in the presence of molybdenum trioxide catalyst and hydrocarbon solvent.

The intermediates needed to prepare the instant compounds are largely items of commerce or can be made by conventional methods known in the art.

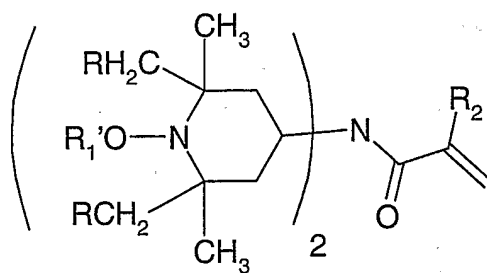
Polymerizable monomers containing a sterically hindered amine moiety of the instant invention include the following:

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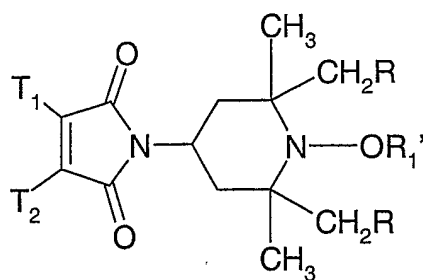
R	R ₁ '	X	R ₂ '
H	allyl	O	H
H	allyl	NH	methyl
H	cyclohexyl	O	methyl
H	methyl	O	H
H	methyl	N(n-butyl)	H
methyl	octyl	O	H
H	methyl	NH	H
H	methyl	NH	methyl
H	cyclohexyl	N(n-butyl)	methyl
H	cyclohexyl	NH	methyl
H	octadecyl	O	methyl
H	benzyl	O	H
H	octyl	O	methyl
methyl	octyl	O	methyl
H	octyl	NH	H
H	octyl	N(n-butyl)	methyl
H	octyl	NH	methyl

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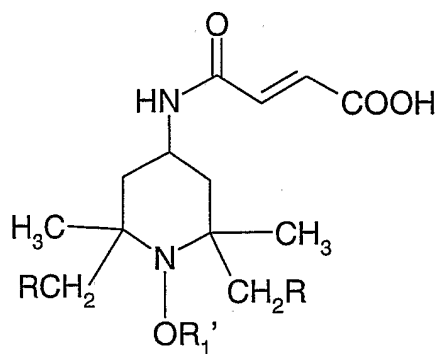
R	R ₁ '	R ₂
H	cyclohexyl	methyl
H	methyl	H
H	methyl	methyl
H	cyclohexyl	H
H	octyl	H
H	octyl	methyl
methyl	octyl	methyl
H	allyl	H
H	allyl	methyl
H	octadecyl	H
H	octadecyl	methyl

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R	R ₁ '	T ₁	T ₂
H	methyl	H	H
H	cyclohexyl	H	dodecyl
H	methyl	H	dodecyl
H	octyl	H	H
H	octyl	methyl	methyl
methyl	octyl	methyl	methyl
H	octyl	H	dodecyl
H	allyl	H	H
H	allyl	H	methyl
H	octadecyl	H	H

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R

 R_1'

H

methyl

H

cyclohexyl

H

octyl

H

octadecyl

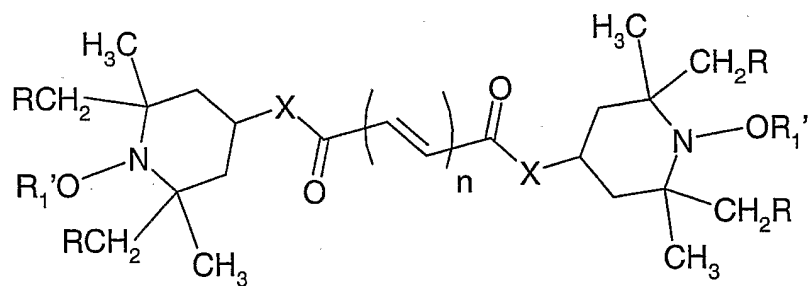
methyl

octyl

H

allyl

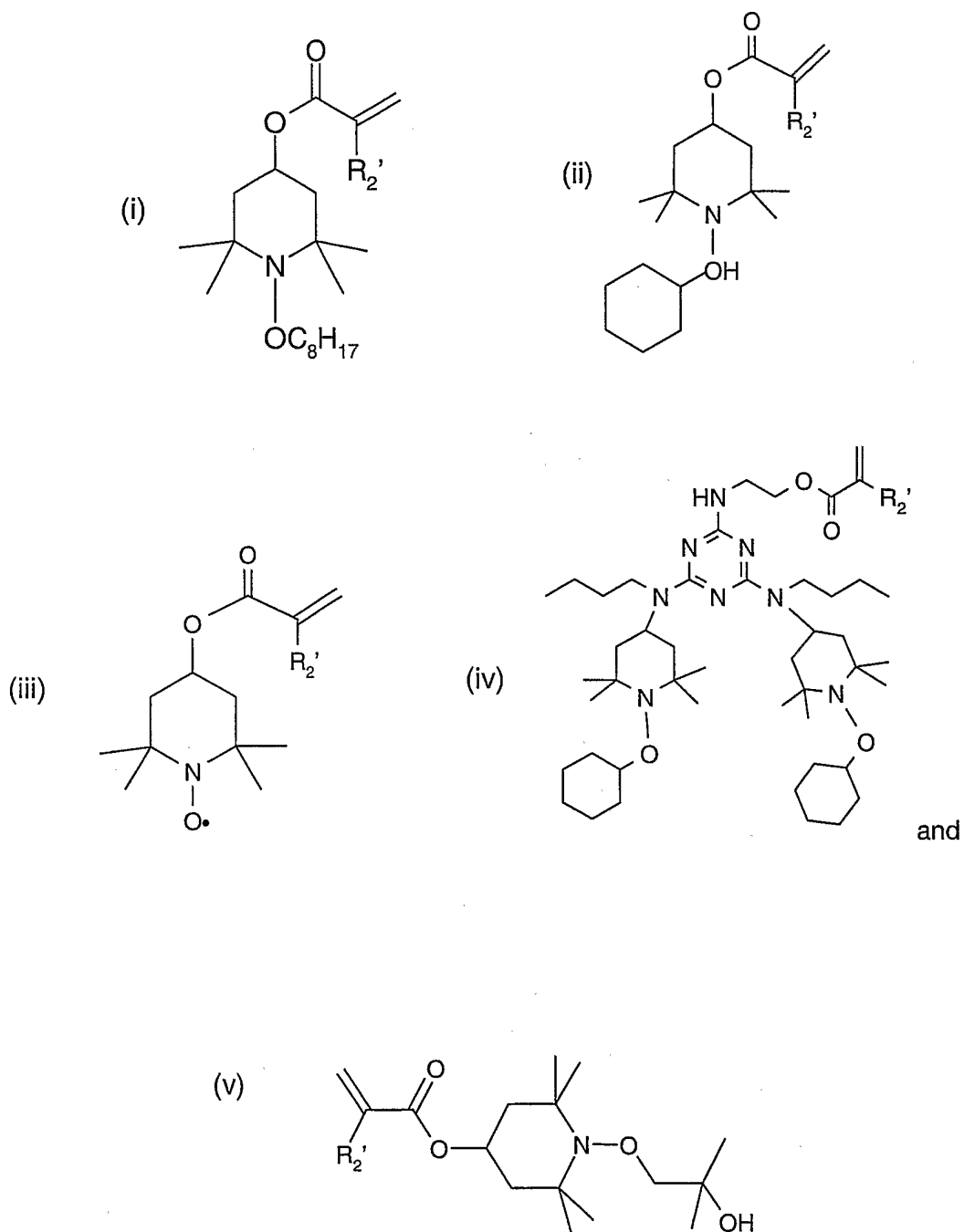
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R	R ₁ '	N	X
H	cyclohexyl	1	O
H	cyclohexyl	2	O
H	methyl	1	O
methyl	octyl	1	O
methyl	octyl	2	O
H	octyl	1	O
H	octyl	2	O
H	allyl	1	O
H	octadecyl	1	O
H	cyclohexyl	1	NH
H	cyclohexyl	1	N(n-butyl)
H	methyl	1	NH
H	methyl	1	N(n-butyl)
H	octyl	1	NH
H	octyl	1	N(n-butyl)
H	allyl	1	N(n-butyl)
H	octadecyl	1	N(n-butyl)

In the above examples, -OR₁' may also independently be oxyl, hydroxyl, 2-hydroxy-2-methylpropoxy, 1-hydroxycyclohexyloxy, cyclohexyloxy or propoxy.

The present ethylenically unsaturated, polymerizable monomers containing a sterically hindered amine moiety are for example selected from the group consisting of



where

R_2 is hydrogen or methyl.

The compositions of the present invention may further advantageously include hydrocarbyloxy hindered amine compounds that are not ethylenically unsaturated monomers.

Specific examples of suitable additional hindered amine compounds include compounds (a) – (o) further above; the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine; and the oligomeric compound which is the condensation product of 4,4'-hexamethylene-bis(amino-2,2,6,6-tetramethylpiperidine) and 2,4-dichloro-6-[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-s-triazine end-capped with 2-chloro-4,6-bis(dibutylamino)-s-triazine.

These additional hindered amine compounds are disclosed for example in U.S. Pat. No. 6,472,456 and 6,117,995, the relevant disclosures of which are hereby incorporated by reference. The last named compound is disclosed in example 2 of U.S. Patent No. 6,117,995.

Alkyl is a straight or branched chain and is for example methyl, ethyl, n-propyl, n-butyl, sec-butyl, tert-butyl, n-hexyl, n-octyl, 2-ethylhexyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Cycloalkyl groups are for example of from 5 to 7 carbon atoms and include cyclopentyl and cyclohexyl; typical cycloalkenyl groups include cyclohexenyl.

Aralkyl groups include for example benzyl, alpha-methyl-benzyl, alpha,alpha-dimethylbenzyl or phenethyl.

Aryl is for instance phenyl, naphthyl and biphenyl.

Alkoxy, aryloxy and cycloalkoxy groups are defined as for the present alkyl, aryl and cycloalkyl groups.

Halogen is for instance chloro and bromo.

Conventional Flame Retardants

Oganohalogen flame retardants are for example:

Chloroalkyl phosphate esters (ANTIBLAZE[®] AB-100, Albright & Wilson; FYROL[®] FR-2, Akzo Nobel),

tris(2-chloroethyl)phosphate

polybrominated diphenyl oxide (DE-60F, Great Lakes Corp.),

decabromodiphenyl oxide (DBDPO; SAYTEX[®] 102E),

tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate (PB 370[®], FMC Corp.),

tris(2,3-dibromopropyl)phosphate

tris(2,3-dichloropropyl)phosphate,

chlrendic acid,

tetrachlorophthalic acid,

tetrabromophthalic acid,

bis-(N,N'-hydroxyethyl)tetrachlorophenylene diamine,

poly-β-chloroethyl triphosponate mixture

bis(2,3-dibromopropyl ether) of bisphenol A (PE68),

brominated epoxy resin,

ethylene-bis(tetrabromophthalimide) (SAYTEX[®] BT-93),

bis(hexachlorocyclopentadieno)cyclooctane (DECLORANE PLUS[®]),

chlorinated paraffins,

octabromodiphenyl ether,

hexachlorocyclopentadiene derivatives,

1,2-bis(tribromophenoxy)ethane (FF680),

tetrabromo-bisphenol A (SAYTEX[®] RB100),

ethylene bis-(dibromo-norbornanedicarboximide) (SAYTEX[®] BN-451),

bis-(hexachlorocyclopentadieno) cyclooctane,

PTFE

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tris-(2,3-dibromopropyl)-isocyanurate, and
ethylene-bis-tetrabromophthalimide.

The organophosphorus flame retardants are for example:

Tetraphenyl resorcinol diphosphite (FYROLFLEX[®] RDP, Akzo Nobel),
triphenyl phosphate,
trioctyl phosphate,
tricresyl phosphate,
tetrakis(hydroxymethyl)phosphonium sulfide,
diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate,
hydroxyalkyl esters of phosphorus acids,
ammonium polyphosphate (APP) or (HOSTAFLAM[®] AP750),
resorcinol diphosphate oligomer (RDP),
phosphazene flame retardants and
ethylenediamine diphosphate (EDAP).

Isocyanurate flame retardants include polyisocyanurate, esters of isocyanuric acid and isocyanurates. For example, an hydroxyalkyl isocyanurate such as tris-(2-hydroxyethyl)isocyanurate, tris(hydroxymethyl)isocyanurate, tris(3-hydroxy-n-propyl)isocyanurate or triglycidyl isocyanurate.

The melamine based flame retardants are for example:

melamine cyanurate,
melamine borate,
melamine phosphates,
melamine polyphosphates and
melamine pyrophosphates.

Boric acid may be included as a flame retardant.

Especially preferred conventional flame retardants are

chloroalkyl phosphate esters,
polybrominated diphenyl oxide,
decabromodiphenyl oxide,
tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate,
bis(2,3-dibromopropyl ether) of bisphenol A,
brominated epoxy resin,
ethylene-bis(tetrabromophthalimide),
bis(hexachlorocyclopentadieno)cyclooctane,
chlorinated paraffins,
1,2-bis(tribromophenoxy)ethane,
tetrabromo-bisphenol A,
ethylene bis-(dibromo-norbornanedicarboximide),
bis-(hexachlorocyclopentadieno) cyclooctane,
tris-(2,3-dibromopropyl)-isocyanurate,
ethylene-bis-tetrabromophthalimide
tris-(2-hydroxyethyl)isocyanurate,
tris(hydroxymethyl)isocyanurate,
tris(3-hydroxy-n-propyl)isocyanurate,
triglycidyl isocyanurate,
melamine cyanurate,
melamine borate,
melamine phosphates,
melamine polyphosphates and melamine pyrophosphates.

The halogenated flame retardants useful in the present invention may be selected from organic aromatic halogenated compounds such as halogenated benzenes, biphenyls, phenols, ethers or esters thereof, bisphenols, diphenyloxides, aromatic carboxylic acids or polyacids, anhydrides, amides or imides thereof; organic cycloaliphatic or polycycloaliphatic halogenated compounds; and organic aliphatic halogenated compounds such as halogenated paraffins, oligo- or polymers, alkylphosphates or alkylisocyanurates. These components are largely known in the art, see e.g. US patents Nos. 4,579,906 (e.g. col. 3, lines 30-41), 5,393,812; see also *Plastics Additives Handbook*, Ed. by H. Zweifel, 5th Ed., Hanser Publ., Munich 2001, pp. 681-698.

The phosphazene flame retardants are well known in the art. They are disclosed for example in EP1104766, JP07292233, DE19828541, DE1988536, JP11263885, U.S. Pat. Nos. 4,107,108, 4,108,805 and 4,079,035 and 6,265,599. The relevant disclosures of the U.S. Patents are hereby incorporated by reference.

PTFE, polytetrafluoroethylene (for example Teflon® 6C; E. I. Du Pont), may be advantageously added to the present compositions as an additional flame retardant, as disclosed in U.S. application 60/312,517, filed Aug. 15, 2001.

Advantageously, the present compositions may contain only minor amounts of antimony compounds such as Sb_2O_3 , e.g. less than about 1%, for instance less than about 0.1% by weight of component (A); for example, the present compositions are essentially free of antimony.

Flame-retardant fillers are not required in order to improve the flame retardant properties and achieve a higher rating, e.g. in the UL-94 burning test (*infra*). Consequently, the compositions of the present invention may contain only minor amounts of flame-retardant fillers, e.g. less than about 3%, for instance less than about 1%, for example less than about 0.1% by weight of component (A); for example, the present compositions are essentially free of flame-retardant fillers.

Flame-retardant fillers are known in the art and are selected from the group consisting of magnesium hydroxide, alumina trihydrate and zinc borate. Coatings may contain flame-retardant fillers such as vermiculite or Portland cement. Flame-retardant fillers are inorganic compounds employed for flame-retardant properties, and at high enough levels to be considered "filler".

If conventional fillers such as talc, calcium carbonate and the like are normally employed for instance for flow properties in order to reduce the spread of flaming droplets (not flame-retardant per se), such conventional fillers may also be reduced with the use of the present compositions. For instance, the present compositions may contain only minor amounts of conventional fillers, for example less than about 3%, for instance less than 1%,

for example less than about 0.1% by weight component (A); for example, the present compositions are essentially free of conventional fillers.

Further, the present invention allows for conventional fillers to take the place of more expensive flame-retardant fillers.

The compositions of this invention may further advantageously include nano-scaled fillers. Nano-scaled fillers are also referred to as "nanoclays" are disclosed for example in U.S. Pat. Nos. 5,853,886 and 6,020,419, the relevant disclosures of which are hereby incorporated by reference.

Nano-scaled fillers of the present invention are for example phyllosilicates or smectite clays, for example organophilic phyllosilicates, naturally occurring phyllosilicates, synthetic phyllosilicates or a mixture of such phyllosilicates. The present nano-scaled fillers are for example montmorillonites, bentonites, beidellites, hectorites, saponites or stevensites.

The resulting stabilized compositions of the invention may optionally also contain various conventional additives, for example in amounts from about 0.01 to about 10%, for instance from about 0.025 to about 4%, for example from about 0.1 to about 2% by weight of component (A), such as the materials listed below, or mixtures thereof.

1. Antioxidants

1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures thereof.

1.2. Alkylthiomethylphenols, for example 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol, 2,6-di-dodecylthiomethyl-4-nonylphenol.

1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate, bis-(3,5-di-tert-butyl-4-hydroxyphenyl) adipate.

1.4. Tocopherols, for example α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures thereof (Vitamin E).

1.5. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis-(3,6-di-sec-amylphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)disulfide.

1.6. Alkylidenebisphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2'-ethylenebis(4,6-di-tert-butylphenol), 2,2'-ethylenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α,α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis-(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis-(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

1.7. O-, N- and S-benzyl compounds, for example 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

1.8. Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)-malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, didodecylmercaptoethyl-2,2-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butyl-4-hydroxybenzyl)malonate.

1.9. Aromatic hydroxybenzyl compounds, for example 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

1.10. Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)isocyanurate.

1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, the calcium salt of the monoethyl ester of 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid.

1.12. Acylaminophenols, for example 4-hydroxylauranilide, 4-hydroxystearanilide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

1.13. Esters of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-

nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.14. Esters of β -(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.15. Esters of β -(3,5-dicyclohexyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane.

1.17. Amides of β -(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamide, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)-hydrazide, N,N'-bis[2-(3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionyloxy)ethyl]oxamide (Nau-gard®XL-1 supplied by Uniroyal).

1.18. Ascorbic acid (vitamin C)

1.19. Aminic antioxidants, for example N,N'-di-isopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylaminophenol, 4-nonanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopropyl/isohexyldiphenylamines, a mixture of mono- und dialkylated tert-butyldiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-benzothiazine, phenothiazine, a mixture of mono- und dialkylated tert-butyl/tert-octylphenothiazines, a mixture of mono- und dialkylated tert-octyl-phenothiazines, N-allylphenothiazin, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethyl-piperid-4-yl)-hexamethylenediamine, bis(2,2,6,6-tetramethylpiperid-4-yl)sebacate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol.

2. UV absorbers and light stabilizers

2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chloro-benzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole,

2-(3',5'-bis-(α,α -dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)-carbonyl]ethyl)-2'-hydroxyphenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)-5-chloro-benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxycarbonyl)ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl]ethyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxycarbonyl)ethyl)phenyl)benzotriazole, 2,2'-methylene-bis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-yl]phenol]; the transesterification product of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl)ethyl)-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; $\left[R-CH_2CH_2-COO-CH_2CH_2 \right]_2$ where $R = 3'$ -tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl, 2-[2'-hydroxy-3'-(α,α -dimethylbenzyl)-5'-(1,1,3,3-tetramethylbutyl)-phenyl]-benzotriazole; 2-[2'-hydroxy-3'-(1,1,3,3-tetramethylbutyl)-5'-(α,α -dimethylbenzyl)-phenyl]benzotriazole.

2.2. 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

2.3. Esters of substituted and unsubstituted benzoic acids, as for example 4-tertbutyl-phenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

2.4. Acrylates, for example ethyl α -cyano- β,β -diphenylacrylate, isooctyl α -cyano- β,β -diphenylacrylate, methyl α -carbomethoxycinnamate, methyl α -cyano- β -methyl-p-methoxy-cinnamate, butyl α -cyano- β -methyl-p-methoxy-cinnamate, methyl α -carbomethoxy-p-methoxycinnamate and N-(β -carbomethoxy- β -cyanovinyl)-2-methylindoline.

2.5. Nickel compounds, for example nickel complexes of 2,2'-thio-bis-[4-(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N-cyclohexyldiethanolamine, nickel dibutyldithiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-

butylbenzylphosphonic acid, nickel complexes of ketoximes, e.g. of 2-hydroxy-4-methylphenyl undecylketoxime, nickel complexes of 1-phenyl-4-lauroyl-5-hydroxypyrazole, with or without additional ligands.

2.6. Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitritotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyl-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)-malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decan-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis-(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyl-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136504-96-6]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimid, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimid, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4,5]decane, a reaction product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro [4,5]decane und epichlorohydrin, 1,1-bis(1,2,2,6,6-pentamethyl-4-piperidyloxycarbonyl)-2-(4-methoxyphenyl)ethene, N,N'-bis-formyl-N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine, diester of 4-methoxy-methylene-malonic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetrame-

thyl-4-piperidyl)]siloxane, reaction product of maleic acid anhydride- α -olefin-copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine.

2.7. Oxamides, for example 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, mixtures of o- and p-methoxy-disubstituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxy-propyloxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxy-phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxy-propoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxy)phenyl-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxy-propoxy)phenyl]-1,3,5-triazine, 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine, 2-[2-hydroxy-4-[3-(2-ethylhexyl-1-oxy)-2-hydroxypropyloxy]phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine.

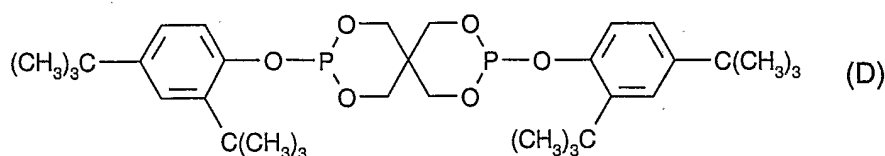
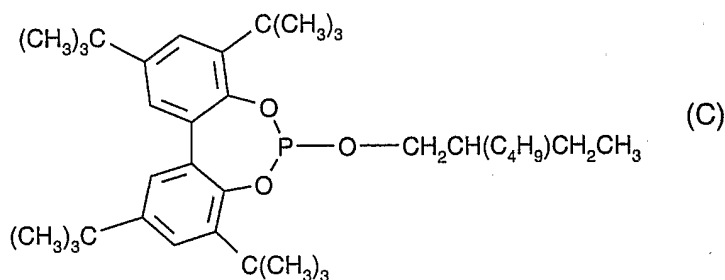
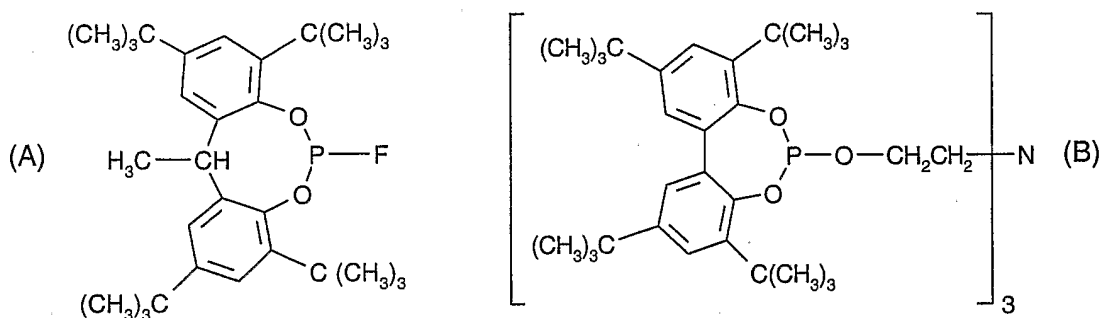
3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyl adipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl

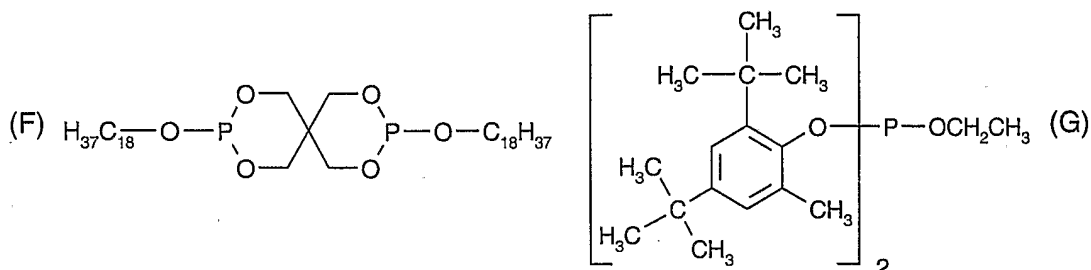
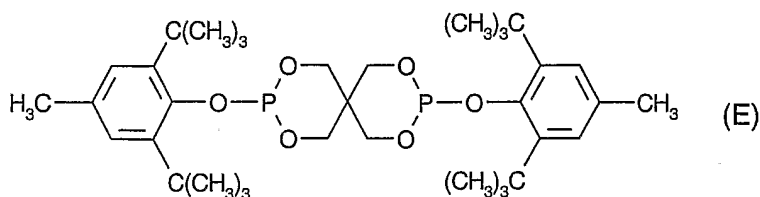
pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-pentaerythritol diphosphite, diisodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl)pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)pentaerythritol diphosphite, tris(aryl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2''-nitrido[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane.

Specific examples are the following phosphites:

Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos[®]168, Ciba-Geigy), tris(nonylphenyl) phosphite,



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5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-diethylhydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

6. Nitrones, for example, N-benzyl-alpha-phenyl-nitrone, N-ethyl-alpha-methyl-nitrone, N-octyl-alpha-heptyl-nitrone, N-lauryl-alpha-undecyl-nitrone, N-tetradecyl-alpha-tridcyl-nitrone, N-hexadecyl-alpha-pentadecyl-nitrone, N-octadecyl-alpha-heptadecyl-nitrone, N-hexadecyl-alpha-heptadecyl-nitrone, N-ocatadecyl-alpha-pentadecyl-nitrone, N-heptadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-hexadecyl-nitrone, nitrone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

7. Thiosynergists, for example, dilauryl thiodipropionate or distearyl thiodipropionate.

8. Peroxide scavengers, for example esters of β -thiodipropionic acid, for example the lauryl, stearyl, myristyl or tridecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

9. Polyamide stabilisers, for example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

10. Basic co-stabilisers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or zink pyrocatecholate.

11. Nucleating agents, for example, inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, for example, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, diphenylacetic acid, sodium succinate or sodium benzoate; polymeric compounds such as ionic copolymers (ionomers). Specific examples are 1,3:2,4-bis(3',4'-dimethylbenzylidene)sorbitol, 1,3:2,4-di(paramethyldibenzylidene)sorbitol, und 1,3:2,4-di(benzylidene)sorbitol.

12. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.

13. Other additives, for example, plasticisers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, antistatic agents and blowing agents.

14. Benzofuranones and indolinones, for example those disclosed in U.S. 4,325,863; U.S. 4,338,244; U.S. 5,175,312; U.S. 5,216,052; U.S. 5,252,643; DE-A-4316611; DE-A-4316622; DE-A-4316876; EP-A-0589839 or EP-A-0591102 or 3-[4-(2-acetoxyethoxy)phenyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-ethoxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,5-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,5-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,4-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(2,3-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

15. Amine oxides, for example amine oxide derivatives as disclosed in U.S. Patent Nos. 5,844,029 and 5,880,191, didecyl methyl amine oxide, tridecyl amine oxide, tridodecyl amine oxide and trihexadecyl amine oxide. U.S. Patent Nos. 5,844,029 and 5,880,191 disclose the use of saturated hydrocarbon amine oxides towards the stabilization of thermoplastic resins. It is disclosed that the thermoplastic compositions may further contain a stabilizer or mixture of stabilizers selected from phenolic antioxidants, hindered amine light stabilizers, ultraviolet light absorbers, organic phosphorus compounds, alkaline metal salts of fatty acids and thiosynergists.

Specific examples of additives are phenolic antioxidants (item 1 of the list), further sterically hindered amines (item 2.6 of the list), light stabilizers of the benzotriazole and/or o-hydroxyphenyltriazine class (items 2.1 and 2.8 of the list), phosphites and phosphonites (item 4 of the list) and peroxide-destroying compounds (item 5.) of the list.

Additional specific examples of additives (stabilizers) which are benzofuran-2-ones, such as described, for example, in US-A-4,325,863, US-A-4,338,244 or US-A-5,175,312.

The instant compositions can additionally contain another UV absorber selected from the group consisting of the s-triazines, the oxanilides, the hydroxybenzophenones, benzoates and the α -cyanoacrylates. Particularly, the instant composition may additionally contain an effective stabilizing amount of at least one other 2-hydroxyphenyl-2H-benzotriazole; another tris-aryl-s-triazine; or hindered amine or mixtures thereof. For example, additional components are selected from pigments, dyes, plasticizers, antioxidants, thixotropic agents, levelling assistants, basic costabilizers, further light stabilizers like UV absorbers and/or sterically hindered amines, metal passivators, metal oxides, organophosphorus compounds, hydroxylamines, and mixtures thereof, especially pigments, phenolic antioxidants, calcium stearate, zinc stearate, UV absorbers of the 2-(2'-hydroxyphenyl)benzotriazole and 2-(2-Hydroxyphenyl)-1,3,5-triazine classes, and sterically hindered amines.

The present compositions may also comprise a spumific agent. Examples are a combination of tris(2-hydroxyethyl)isocyanurate and ammonium polyphosphate, melamine, methyolated melamine, hexamethoxymethyl melamine, melamine monophosphate,

melamine biphosphate, melamine polyphosphate, melamine pyrophosphate, urea, dimethylurea, dicyandiamide, guanlyurea phosphate, glycine or amine phosphate. The foregoing release nitrogen gas when they decompose upon exposure to heat. Compounds which release carbon dioxide or water vapor upon exposure to heat can also be employed.

The present compositions may comprise a carbonific material (a poly-hydro compound) such as pentaerythritol, dipentaerythritol, tripentaerythritol, pentaerythritol polyurethanes, phenol triethylene glycol, resorcinol, inositol, sorbitol, dextrin and starch.

The present compositions may comprise silica.

The additives of the invention and optional further components may be added to the coating formulation individually or mixed with one another. If desired, the individual components can be mixed with one another before incorporation into the coating for example by dry blending, compaction or in the melt.

Component (i) is advantageously contained in the composition of the invention in an amount from about 0.1% to about 10% by weight based on the coating component (A); for example from about 0.25% to about 8% by weight; for instance from about 0.5% to about 3% by weight. For instance, component (i) is present from about 0.25% to about 10% or from about .5% to about 10% by weight based on (A). For example, component (i) is present from about 0.1% to about 8% or from about 0.1% to about 3% by weight based on (A).

Component (ii) is advantageously contained in the composition of the invention in an amount from about 0.5% to about 45% by weight of the coating (A); for instance about 3% to about 40%; for example about 5% to about 35% by weight of component (A). For example, component (ii) is employed from about 0.5% to about 10% by weight, from about 1% to about 10%, from about 3% to about 10% or from about 5% to about 10% by weight, based on the weight of the polymeric substrate. For example, component (ii) is employed from about 0.5% to about 8%, from about 0.5% to about 6%, from about 0.5% to about 5%, or from about 0.5% to about 3% by weight, based on the weight of the polymeric substrate, e.g. the resin binder (A).

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The ratio (parts by weight) of component (i) to component (ii) is for example between about 1:5 to about 1:200, for instance from about 1:50 to about 1:100, or about 1:10 to about 1:25. For example the ratio of component (i) to component (ii) is from about 1:10 to about 1:200, from about 1:25 to about 1:200, from about 1:50 to about 1:200 or from about 1:100 to about 1:200. For example, the weight ratio of component (i) to component (ii) is from about 1:5 to about 1:100, from about 1:5 to about 1:50, from about 1:5 to about 1:25, or from about 1:5 to about 1:10.

The amount of the optional conventional flame retardants employed also depends on the effectiveness of the specific compound(s), the specific coating and application type; for example, an amount of 5 to 15 % by weight of the compound tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate may be as efficient as an amount of 30 to 45% by weight of the compound decabromodiphenyl oxide in respect of the flame retardancy of the final composition. Isocyanurate flame retardants are normally employed between about 1 and about 10% by weight based on (A), for example between about 3 and about 6% by weight.

The coating compositions of the present invention are themselves flame retardant, and likewise provide flame retardancy to the substrates and articles on which they are coated. Accordingly, a further subject of the present invention is a flame retardant coated article comprising

- (A) a coating and
- (B) an effective flame retarding amount of a mixture of
 - (i) at least one compound selected from the group consisting of the
 - (a) sterically hindered nitroxyl stabilizers,
 - (b) sterically hindered hydroxylamine stabilizers and
 - (c) sterically hindered alkoxyamine stabilizers and
 - (ii) at least one conventional flame retardant selected from the group consisting of

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- (d) organohalogen flame retardants,
- (e) organophosphorus flame retardants
- (f) isocyanurate flame retardants and
- (g) melamine based flame retardants.

A further subject of the present invention is a flame retardant coated article comprising

a substrate coated with a flame retardant coating composition comprising

(A) a resin binder and

(B) an effective flame retarding amount of

(i) at least one ethylenically unsaturated, polymerizable monomer, which monomer contains a sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety, and

optionally

(ii) at least one conventional flame retardant selected from the group consisting of

- (a) organohalogen flame retardants,
- (b) organophosphorus flame retardants,
- (c) isocyanurate flame retardants and
- (d) melamine based flame retardants.

The effective flame retarding amount of component (B) is that needed to show flame retarding efficacy as measured by one of the standard methods used to assess flame retardancy. These include the NFPA 701 Standard Methods of Fire Tests for Flame-Resistant Textiles and Films, 1989 and 1996 editions; the UL 94 Test for Flammability of Plastic Materials for Parts in Devices and Appliances, 5th Edition, October 29, 1996; Limiting

Oxygen Index (LOI), ASTM D-2863; and Cone Calorimetry, ASTM E-1354. Ratings according to the UL 94 V test are as compiled in the following table:

Rating	Afterflame time	Burning drips	Burn to Clamp
V-0	< 10 s	no	no
V-1	< 30 s	no	no
V-2	< 30 s	yes	no
Fail	< 30 s		yes
Fail	> 30 s		no

Applicable tests include:

ASTM F1173 Fiberglass pipe and fittings (offshore/marine)

UL 94 and 746C Tests for Flammability of Plastic Materials for Parts in Devices and Applications

UL 723

IEEE-45 - recommended practice for electrical installation on shipboard

IEEE-383 - standard for type test of class IE electrical cables, field splices and connections for nuclear power generation stations.

ASTM-D-1360 - fire retardancy of paints (cabinet method)

ASTM-E-84 - test for surface burning characteristics of building materials

ASTM-E-119 - fire test of building construction materials

ASTM-E-162 - surface flammability of materials using a radiant heat energy source

ASTM F 84

FAA 14-25.853, .855,.856,.867 - aeronautics and space (fire protection)

Paper substrates (saturants) (Michelman): ASTM E-162, ASTM E-662, NFPA 701, TAPPI 461

Corrugated materials w/FR coatings (Michelman): ASTM E-162/662, FMR heat release, NFPA 30, ASTM E-84, NFPA 703, UL723

NFPA 703: Standard for Fire Retardant Impregnated Wood and Fire Retardant Coatings for Building Materials

NFPA 255, Fire Endurance Tests of Building Construction Materials

Military specifications DOD-En 24607A and DOD-R-21417A (SH)

Coadditives found particularly useful for use with the instant compounds in flame retardant compositions are as follows:

UV absorbers:

2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole, (TINUVIN[®] 234, Ciba Specialty Chemicals Corp.);

2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, (TINUVIN[®] P, Ciba Specialty Chemicals Corp.);

5-chloro-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole, (TINUVIN[®] 327, Ciba Specialty Chemicals Corp.);

2-(2-hydroxy-3,5-di-tert-amylphenyl)-2H-benzotriazole, (TINUVIN[®] 328, Ciba Specialty Chemicals Corp.);

2-(2-hydroxy-3- α -cumyl-5-tert-octylphenyl)-2H-benzotriazole, (TINUVIN[®] 928, Ciba Specialty Chemicals Corp.);

2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, (TINUVIN[®] 120, Ciba Specialty Chemicals Corp.);

2-hydroxy-4-n-octyloxybenzophenone, (CHIMASSORB[®] 81, Ciba Specialty Chemicals Corp.);

2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-octyloxyphenyl)-s-triazine, (CYASORB[®] 1164, Cytec).

The following examples are meant for illustrative purposes only and are not to be construed to limit the scope of this invention in any manner whatsoever. Where given, room temperature depicts a temperature in the range 20-25°C. Percentages are by weight of the coating substrate unless otherwise indicated.

Test Methods

NFPA 701 Standard Methods of Fire Tests for Flame-Resistant Textiles and Films, 1989 and 1996 editions;

UL 94 Test for Flammability of Plastic Materials for Parts in Devices and Appliances, 5th Edition, October 29, 1996;

Limiting Oxygen Index (LOI), ASTM D-2863;

Cone Calorimetry, ASTM E-1 or ASTM E 1354;

ASTM D 2633-82, burn test.

Example 1 Coatings over TPO

Molded test specimens are prepared by injection molding thermoplastic olefin (TPO) pellets containing pigments, a phosphite, a phenolic antioxidant or hydroxylamine, a metal stearate, ultraviolet light absorbers or a hindered amine stabilizer or a mixture of UV absorber and hindered amine stabilizer.

Pigmented TPO pellets are prepared from pure pigment or pigment concentrate, coadditives and commercially available TPO by mixing the components in a Superior/MPM 1" single screw extruder with a general all-purpose screw (24:1 L/D) at 400°F (200°C), cooled in a water bath and pelletized. The resulting pellets are molded into 60 mil (0.006 inch), 2"x2" plaques at about 375°F (190°C) on a BOY 30M Injection Molding Machine.

Pigmented TPO formulations composed of polypropylene blended with a rubber modifier where the rubber modifier is an in-situ reacted copolymer or blended product containing copolymers of propylene and ethylene with or without a ternary component such as ethylidene norbornene are stabilized with a base stabilization system consisting of an

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N,N-dialkylhydroxylamine or a hindered phenolic antioxidant with or without an organophosphorus compound.

All additive and pigment concentrations in the final formulation are expressed as weight percent based on the resin.

Formulations contain thermoplastic olefin pellets and one or more of the following components:

0.0 to 2.0% pigment,
0.0 to 50.0% talc,
0.0 to 0.1% phosphite,
0.0 to 1.25% phenolic antioxidant,
0.0 to 0.1% hydroxylamine
0.05 to 0.10 calcium stearate,
0.0 to 1.25% UV absorber and
0.0 to 1.25% hindered amine stabilizer.

The components are dry-blended in a tumble dryer prior to extrusion and molding.

Polymer substrate is commercially available polyolefin blend POLYTROPE® TPP 518-01 supplied by A. Schulman Inc. Akron, Ohio)

The light stable formulations are painted with one-pack paint systems and tested for TPO/paint interactions and flame retardancy. Before painting, the test specimens are first washed in accordance with GM998-4801 and dried for 15 minutes at 200°F (94°C). Adhesion promoter is applied to the dry film thickness of 0.2-0.4 mils. The samples are dried for five minutes before a 1K basecoat is applied to a film thickness of 1.2-1.4 mils. The painted panels are dried for three minutes, a clearcoat is then applied to a dry film thickness of 1.2-1.5 mils followed by ten minutes flash drying and a 30 minute oven bake at 250°F (121°C).

One or more of the coating formulations comprise an additive selected from present compounds (a)-(o) and a conventional organohalogen, organophosphorus, isocyanurate or

melamine based flame retardant.

Further coating formulations comprise an additive selected from present compounds (i)-(v) and optionally a conventional organohalogen, organophosphorus, isocyanurate or melamine based flame retardant.

Paint adhesion is measured by Aggressive Adhesion Testing (proprietary test procedure conducted at Technical Finishing, Inc.) and Taber Scuff. Painted panels which retain greater than 80% of the paint finish are considered acceptable. After Aggressive Adhesion Testing, samples with less than 5% paint loss are deemed acceptable.

The present painted articles exhibit excellent paint adhesion and flame retardancy. The additives (a)-(o) or (i)-(v) combined with convention flame retardants may be in any or all coating layers.

Example 2 Waterborne Wood Varnish

Waterborne coatings comprise a significant and increasing proportion of the coating in use for a wide variety of applications including automotive basecoats, industrial coatings and trade sale coatings. These coatings may be pigmented or transparent.

The test stabilizers (a)-(o) and (i)-(v) and a conventional organohalogen, organophosphorus, isocyanurate or melamine based flame retardant are incorporated into a waterborne dispersion by predissolution in a cosolvent blend. The waterborne dispersion is a commercially available acrylic/urethane hybrid resin. The cosolvent blend is a 1:1 mixture of TEXANOL[®] (2,2,4-trimethyl-1,3-pentanediol, Texaco) and ARCOSOLVE[®] TPM (tripropylene glycol methyl ether, AtlanticRichfield).

Each of the test stabilizers (a)-(o) and (i)-(v), 0.45 grams, and an appropriate amount of conventional flame retardant is predissolved in 10 g of the cosolvent blend which is then incorporated into the following composition:

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	<u>ppw</u>
FLEXTHANE® 630 (Air Products)	100.0
Foamaster VF	0.1
Water	10.0
TEXANOL/ARCOSOLVE/hindered amine	10.5
UV absorber (TINUVIN® 1130, Ciba)	1.2
BYK 346	0.5
MICHEMLUBE® 162	2.0

Each coating is brush applied onto 6" x 6" sections of cedar and pine boards. The weight of the coating applied is regulated by weighing the coating and brush before and after application and ensuring that the same weight of coating is applied to each section.

The coated board sections are allowed to dry at ambient temperature for two weeks, then evaluated for flame retardancy. The boards exhibit excellent flame retardancy.

Example 3 Optical Fiber Coatings

A radiation curable optical fiber coating is formulated as below:

	<u>weight percent</u>
urethane acrylate oligomer	37
bisphenol A epoxy diacrylate	28
tetraethyleneglycol diacrylate	21
triethyleneglycol diacrylate	4
trimethylolpropane triacrylate	6
benzophenone	1.5
2,2-dimethoxy-2-phenylacetophenone	0.7
benzil	0.5
diethylamine	0.6
phenothiazine	0.01
2-hydroxy-4-n-octoxybenzophenone	0.01
silicon	0.2

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N-[(2-vinylbenzylamino)-ethyl]-3-aminopropyltrimethoxysilane (40% in MeOH)	0.2
--	-----

The coating formulations additionally contain a present additive selected from (a)-(o) and a conventional flame retardant. Other photoinitiators are suitable, for example phosphine oxide photoinitiators. The cured coatings exhibit excellent flame retardancy.

Example 4 Optical Fiber Coatings

A radiation curable optical fiber coating is formulated as below:

	<u>weight percent</u>
urethane acrylate oligomer	20
ethoxylated bisphenol A diacrylate	20
propoxylated trimethylol propane triacrylate	32
di-trimethylolpropane tetraacrylate	25

The formulation may additionally contain an anti-blocker or a silane additive or a phenolic antioxidant.

The formulation contains one or more photoinitiators, for example one or more photoinitiators selected from bis(2,4,6-trimethylbenzoyl)phenyl phosphine oxide (Irgacure[®] 819), bis(2,6-dimethoxybenzoyl)isooctyl phosphine oxide, [[4-(ethyl-methyl-amino)-phenyl]-(2,4,6-trimethyl-benzoyl)-phosphinoyl]-(2,4,6-trimethyl-phenyl)-methanone, [(4-dimethylamino-phenyl)-(2,4,6-trimethyl-benzoyl)-phosphinoyl]-(2,4,6-trimethyl-phenyl)-methanone, 2,4,6-trimethylbenzoyldiphenyl phosphine oxide, [benzyl-(4-methylsulfanyl-phenyl)-phosphinoyl]-(2,4,6-trimethyl-phenyl)-methanone and 1-hydroxycyclohexyl phenyl ketone (Irgacure[®] 184).

The coating formulations additionally contain a present additive selected from (i)-(v) and an optional conventional flame retardant. The cured coatings exhibit excellent flame retardancy.

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Good results are also achieved when combining an additive (a)-(o) or (i)-(v) with one of the conventional flame retardants listed above in an application system as follows:

Urethane Clearcoat over Steel
Coil Coating
Tung Oil Phenolic Varnish
Aromatic Urethane Varnish
Abrasion-Resistant Coating Compositions
Polyester Urethane Coating over Polycarbonate
Glycidyl Methacrylate-based Powder Clearcoat
Oil Modified Urethane Alkyd for Wood Application
Preformed Film for Lamination to Plastic Parts
Coextrusion over PVC
Coextrusion over Polycarbonate
Coextrusion over ABS
Multilayer Polymer Structures
Photo-cured White Pigmented Coating
Photo-cured Clear Coating
Photo-cured White Powder Coating
Photo-cured White Gel Coat
Intumescent Coating
Coating for Grease Filled Cable Construction
Intumescent Mastic Fire Resistant Coatings
Coating over Fiberglass
Textile Composite

What is Claimed is:

1. A flame retardant coating composition which comprises

(A) a coating and

(B) an effective flame retarding amount of a mixture of

(i) at least one compound selected from the group consisting of the

(a) sterically hindered nitroxyl stabilizers,

(b) sterically hindered hydroxylamine stabilizers and

(c) sterically hindered alkoxyamine stabilizers and

(ii) at least one conventional flame retardant selected from the group
consisting of

(d) organohalogen flame retardants,

(e) organophosphorus flame retardants

(f) isocyanurate flame retardants and

(g) melamine based flame retardants.

2. A flame retardant coating composition which comprises

(A) a resin binder and

(B) an effective flame retarding amount of

(i) at least one ethylenically unsaturated, polymerizable monomer, which
monomer contains a sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety, and

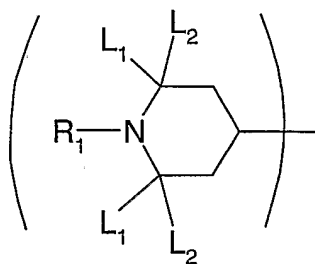
optionally

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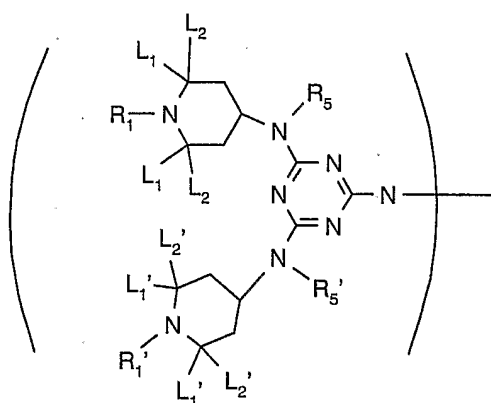
(ii) at least one conventional flame retardant selected from the group consisting of

- (a) organohalogen flame retardants,
- (b) organophosphorus flame retardants,
- (c) isocyanurate flame retardants and
- (d) melamine based flame retardants.

3. A composition according to claim 2 in which the sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety is independently of the formula



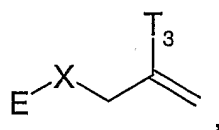
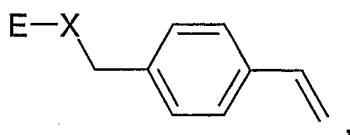
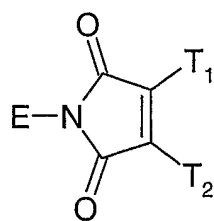
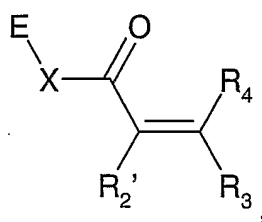
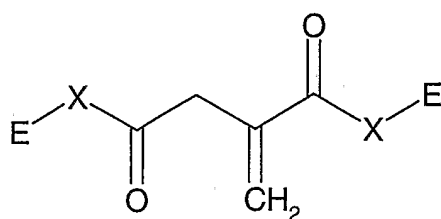
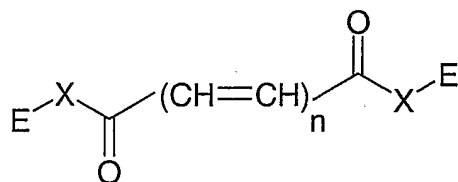
or



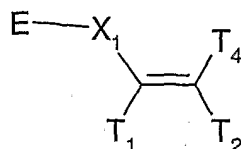
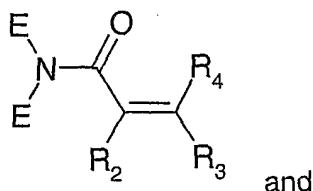
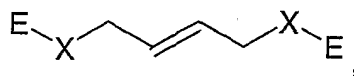
where

L_1 , L_1' , L_2 and L_2' are independently alkyl of 1 to 4 carbon atoms, or L_1 and L_2 or L_1' and L_2' together are pentamethylene, and

where said monomer is selected from the group consisting of formulae



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where

E is independently a sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety,

R₁ is oxyl, hydroxyl, straight or branched chain alkoxy of 1 to 36 carbon atoms, straight or branched chain alkenyloxy of 2 to 18 carbon atoms, straight or branched chain alkynyloxy of 2 to 18 carbon atoms, aralkoxy of 7 to 15 carbon atoms, cycloalkoxy of 5 to 12 carbon atoms, cycloalkenyloxy of 5 to 12 carbon atoms, a radical of a saturated or unsaturated bicyclic or tricyclic hydrocarbyloxy of 7 to 12 carbon atoms, or aryloxy of 6 to 10 carbon atoms or said aryloxy substituted by alkyl,

or R₁ is is -O-T-(OH)_b, R₁ preferably being oxyl, hydroxyl, methoxy, propoxy, cyclohexyloxy octyloxy, 2-hydroxy-2-methylpropoxy or 1-hydroxycyclohexyloxy,

R₁' is independently defined as for R₁,

T is a straight or branched chain alkylene of 1 to 18 carbon atoms, cycloalkylene of 5 to 18 carbon atoms, cycloalkenylene of 5 to 18 carbon atoms, a straight or branched chain

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alkylene of 1 to 4 carbon atoms substituted by phenyl or by phenyl substituted by one or two alkyl groups of 1 to 4 carbon atoms;

b is 1, 2 or 3 with the proviso that b cannot exceed the number of carbon atoms in T, and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T,

X is a direct bond, -O(polyoxyalkyleneO)- of 2 to 12 carbon atoms, -O-, -NH- or -NG-, where G is alkyl of 1 to 8 carbon atoms,

X₁ is a direct bond or -O-,

n is 1 or 2,

T₁, T₂ and T₄ are independently hydrogen, halogen, alkyl of 1 to 18 carbon atoms or aryl of 6 to 10 carbon atoms,

T₃ is hydrogen or methyl, and

R₂ is hydrogen or alkyl of 1 to 12 carbon atoms,

R₂' is hydrogen, alkyl of 1 to 12 carbon atoms or cyano,

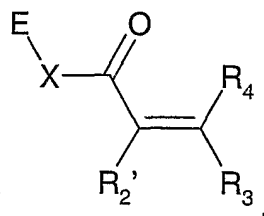
R₃ and R₄ independently are hydrogen, alkyl of 1 to 12 carbon atoms, -COOH, or -COOG₁ where G₁ is straight or branched chain alkyl of 1 to 12 carbon atoms,

R₅ is straight or branched chain alkyl of 1 to 8 carbon atoms and

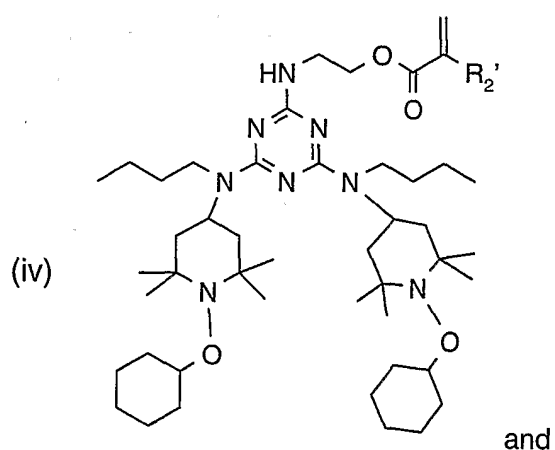
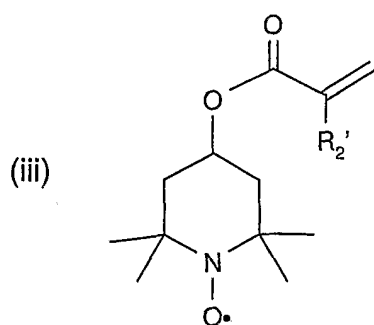
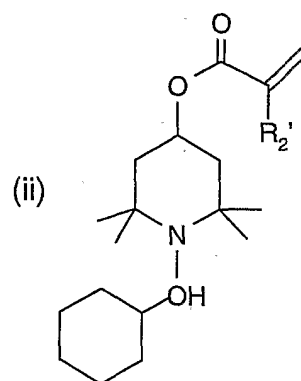
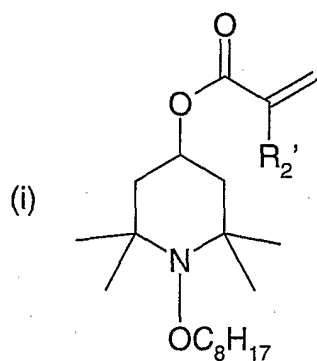
R₅' is independently defined as for R₅.

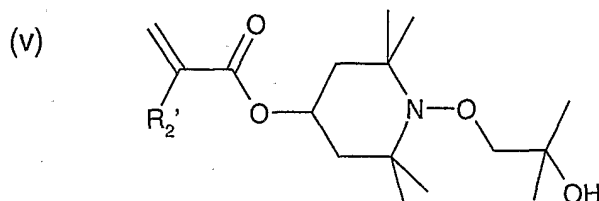
4. A composition according to claim 3 in which the monomer is of the formula

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where R_2' is hydrogen or methyl and R_3 and R_4 are hydrogen, or in which the ethylenically unsaturated, polymerizable monomer, which monomer contains a sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety, is selected from the group consisting of





5. A composition according to claims 1 or 2 containing no antimony compounds or antimony compounds in an amount less than about 1% by weight based on the weight of the component (A); and containing no filler or a filler in an amount less than about 3% by weight based on the weight of the component (A).

6. A composition according to claims 1 or 2 in which component (A) is a resin binder selected from alkyd resins; chlorinated alkyd resins; polyurethane resins; thermoplastic acrylic resins; acrylic alkyls; acrylic resins; latex emulsions; acrylic alkyd or polyester resins; acrylic alkyd or polyester resins modified with silicon, isocyanates, ketimines or oxazolidines; phenol-formaldehyde resins; resorcinol-formaldehyde resins; epoxy resins; epoxide resins crosslinked with carboxylic acids, anhydrides, polyamines or mercaptans; and acrylic or polyester resin systems modified with reactive groups in the backbone thereof and crosslinked with epoxide; especially the epoxy resins.

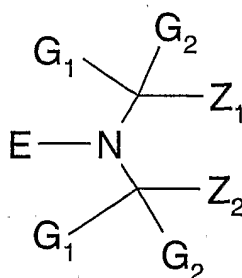
7. A composition according to claim 1 in which the coating is a thermoplastic layer, especially a polypropylene layer.

8. A composition according to claims 1 or 2 which is waterborne or is solvent borne, a powder coating composition or a gel coat formulation, a mastic, an adhesive, a binder, a caulk, a putty, a mortar or a sealant formulation, a ambient cured, radiation cured, oven cured or catalyst cured composition, and which is clear or is pigmented.

9. A composition according to claims 1 or 2 further comprising a component selected from foaming agents, blowing agents, charring agents, binding agents, thixotropic agents, spumific agents and carbonific materials, pigments, dyes, plasticisers, phenolic antioxidants, thixotropic agents, levelling assistants, basic costabilizers, nitrene stabilizers, amine oxide stabilizers, benzofuranone stabilizers, UV absorbers, sterically hindered amines,

metal passivators, metal oxides, organophosphorus compounds, hydroxylamines, and mixtures thereof.

10. A composition according to claim 1 in which the compounds of component (i) are of the formula



where

G_1 and G_2 are independently alkyl of 1 to 8 carbon atoms or are together pentamethylene,

Z_1 and Z_2 are each methyl, or Z_1 and Z_2 together form a linking moiety which may additionally be substituted by an ester, ether, amide, amino, carboxy or urethane group, and

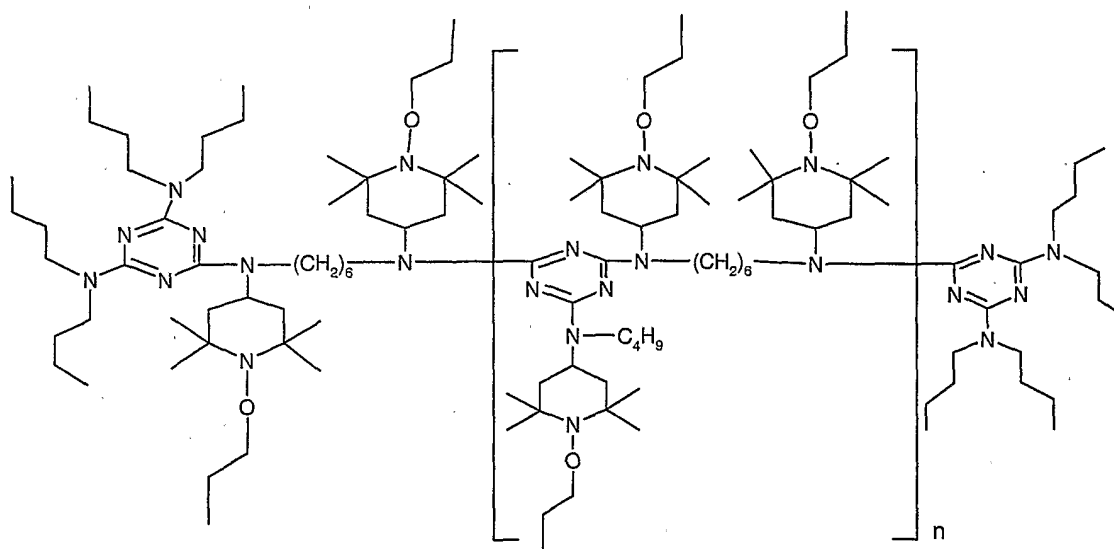
E is oxyl, hydroxyl, alkoxy, cycloalkoxy, aralkoxy, aryloxy, $-\text{O}-\text{CO}-\text{OZ}_3$, $-\text{O}-\text{Si}(\text{Z}_4)_3$, $-\text{O}-\text{PO}(\text{OZ}_5)_2$ or $-\text{O}-\text{CH}_2-\text{OZ}_6$ where Z_3 , Z_4 , Z_5 and Z_6 are selected from the group consisting of hydrogen, an aliphatic, araliphatic and aromatic moiety; or E is $-\text{O}-\text{T}-(\text{OH})_b$,

T is a straight or branched chain alkylene of 1 to 18 carbon atoms, cycloalkylene of 5 to 18 carbon atoms, cycloalkenylene of 5 to 18 carbon atoms, a straight or branched chain alkylene of 1 to 4 carbon atoms substituted by phenyl or by phenyl substituted by one or two alkyl groups of 1 to 4 carbon atoms; and

b is 1, 2 or 3 with the proviso that b cannot exceed the number of carbon atoms in T, and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T.

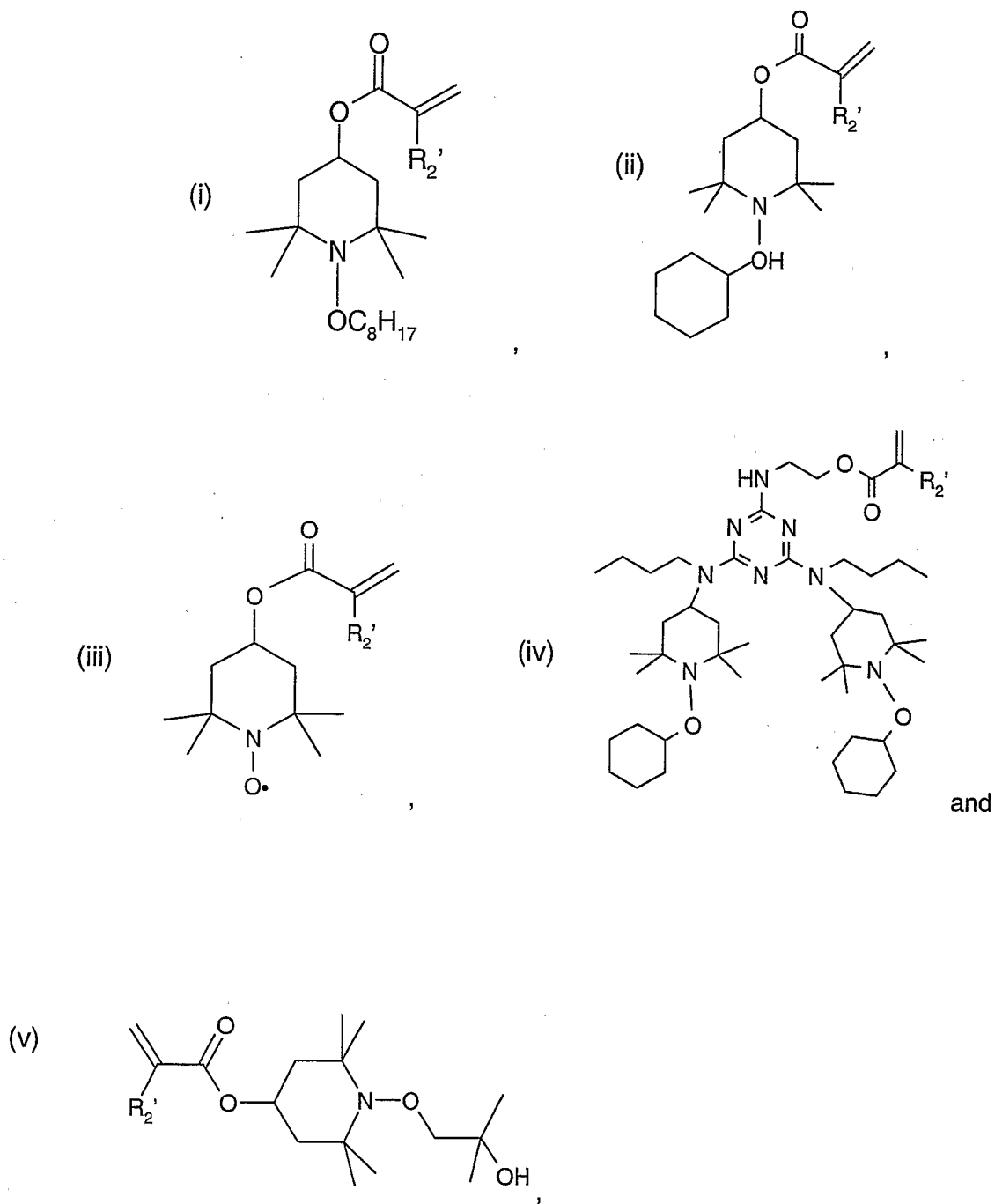
11. A composition according to claim 1 in which the compound of component (i) is selected from the group consisting of

- (a) the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine;
- (b) 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine;
- (c) bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (d) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxyethylamino)-s-triazine;
- (e) bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
- (h) 2,4-bis[(1-cyclohexyloxy-2,2,6,6-piperidin-4-yl)butylamino]-6-chloro-s-triazine;
- (i) 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine;
- (j) 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine;
- (k) 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine;
- (l) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
- (m) bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
- (n) 2,4-bis[N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino]-6-(2-hydroxyethylamino)-s-triazine; and
- (o) the compound of formula



in which n is from 1 to 15, and the compounds

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as well as mixtures thereof.

12. A composition according to claims **1** or **2** in which the flame retardants of component (ii) are selected from the group consisting of

chloroalkyl phosphate esters,
tris(2-chloroethyl)phosphate,

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polybrominated diphenyl oxide,
decabromodiphenyl oxide,
tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate,
tris(2,3-dibromopropyl)phosphate,
tris(2,3-dichloropropyl)phosphate,
chlorendic acid,
tetrachlorophthalic acid,
tetrabromophthalic acid,
bis-(N,N'-hydroxyethyl)tetrachlorophenylene diamine,
poly- β -chloroethyl triphosponate mixture,
bis(2,3-dibromopropyl ether) of bisphenol A,
brominated epoxy resin,
ethylene-bis(tetrabromophthalimide),
bis(hexachlorocyclopentadieno)cyclooctane,
chlorinated paraffins,
octabromodiphenyl ether,
hexachlorocyclopentadiene derivatives,
1,2-bis(tribromophenoxy)ethane,
tetrabromo-bisphenol A,
ethylene bis-(dibromo-norbornanedicarboximide),
bis-(hexachlorocyclopentadieno) cyclooctane,
PTFE
tris-(2,3-dibromopropyl)-isocyanurate, and
ethylene-bis-tetrabromophthalimide,
tetraphenyl resorcinol diphosphite,
triphenyl phosphate,
trioctyl phosphate,
tricresyl phosphate,
tetrakis(hydroxymethyl)phosphonium sulfide,
diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate,
hydroxyalkyl esters of phosphorus acids,
ammonium polyphosphate,
resorcinol diphosphate oligomer,
phosphazene flame retardants,

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ethylenediamine diphosphate,
polyisocyanurate,
esters of isocyanuric acid,
isocyanurates,
hydroxyalkyl isocyanurates,
melamine cyanurate,
melamine borate,
melamine phosphates,
melamine polyphosphates and
melamine pyrophosphates.

13. A composition according to claims **1 or 2** in which component (i) is present from about 0.1 to about 10% by weight based on component (A), and the flame retardant of component (ii) are present from about 0.5 to about 45% by weight based on the weight of the resin binder (A).

14. A flame retardant coated article comprising

a substrate coated with a flame retardant coating composition comprising

(A) a coating and

(B) an effective flame retarding amount of a mixture of

(i) at least one compound selected from the group consisting of the

- (a) sterically hindered nitroxyl stabilizers,
- (b) sterically hindered hydroxylamine stabilizers and
- (c) sterically hindered alkoxyamine stabilizers and

(ii) at least one conventional flame retardant selected from the group consisting of

- (d) organohalogen flame retardants,

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- (e) organophosphorus flame retardants,
- (f) isocyanurate flame retardants and
- (g) melamine based flame retardants.

15. A flame retardant coated article comprising

a substrate coated with a flame retardant coating composition comprising

(A) a resin binder and

(B) an effective flame retarding amount of

(i) at least one ethylenically unsaturated, polymerizable monomer, which monomer contains a sterically hindered nitroxyl, hydroxylamine or alkoxyamine moiety, and

optionally

(ii) at least one conventional flame retardant selected from the group consisting of

- (a) organohalogen flame retardants,
- (b) organophosphorus flame retardants,
- (c) isocyanurate flame retardants and
- (d) melamine based flame retardants.

16. A coated article according to claims 14 or 15 in which the substrate is selected from the group consisting of iron, steel, stainless steel, aluminum and other non-ferrous metals, wood, plywood, paper, cardboard, chip board, particle board, plastics, thermoplastics, epoxies, neoprene, rubber, composites, fiberglass reinforced composites, polyesters, polymeric foam, masonry, fabric or textiles, wire and cable constructions and circuit boards.

17. A coated article according to claims 14 or 15 in which the substrate is selected from the group consisting of polyvinyl chloride, polycarbonate, polyolefin, thermoplastic

polyolefin, ABS or polyester, or fabrics or textiles which are woven, knitted or nonwoven and based on polyethylene, polypropylene, polyethylene terephthalate, polyamide, cellulose or cotton.

18. A coated article according to claims 14 or 15 which is an automotive thermoplastic olefin structure or a coextruded plastic article or a coated optical fiber.

19. A coated article according to claims 14 or 15 which the coating is an extruded plastic.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/03492

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/00 C08K5/3435

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

BEILSTEIN Data, CHEM ABS Data, EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 389 419 A (CIBA GEIGY AG) 26 September 1990 (1990-09-26) claims 25-31; examples 10A, 21A, 21B, 36, 36A, 36B, 36C page 8, line 53 - page 10, line 41 page 13, line 24 - line 28 page 13, line 44 - page 14, line 3 page 15, line 3 - line 6 page 15, line 17 - line 27 ---	1-19
X	US 5 096 950 A (GALBO JAMES P ET AL) 17 March 1992 (1992-03-17) claims 1-22, 25 column 15, line 60 - column 16, line 26 column 19, line 31 - line 39 column 20, line 33 - column 21, line 8 --- -/--	1, 5-13

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

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- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search

16 July 2003

Date of mailing of the international search report

29/07/2003

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Authorized officer

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 03/03492

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 99 00450 A (CIBA GEIGY AG ;DYAS DARRELL DAVID JR (US); PUGLISI JOSEPH STEVEN () 7 January 1999 (1999-01-07) cited in the application abstract; claims 1-6,9; examples 28,29 page 23 -page 29 -----	1,5-14, 16-19
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