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(54) Title: FLAME RETARDANT POLYLACTIC ACID

(57) Abstract: Polylactic acid is made flame retardant by the incorporation of a synergistic mixture of (i) at least one sterically hindered amine stabilizer and (ii) at least one conventional flame retardant selected from the group consisting of the organohalogen, phosphorus containing, isocyanurate and melamine based flame retardants. The compositions of the invention combine good flame retardant properties with light stability and good mechanical properties.

FLAME RETARDANT POLYLACTIC ACID

The instant invention pertains to a novel method of flame retarding polylactic acid by adding thereto a synergistic mixture of at least one sterically hindered amine stabilizer and at least one conventional flame retardant. The instant invention also pertains to polylactic acid fibers, films, molded articles and foamed articles that are stabilized against light, heat and oxygen and made flame retardant with the incorporation therein of at least one sterically hindered amine stabilizer and at least one conventional flame retardant.

Background of the Invention

10

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.

15 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 traditional flame retardants.

20

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

25 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.

30 U.S. Pat. No. 6,262,161 discloses random interpolymers, for example polymers of ethylene and/or one or more α -olefin monomers with one or more vinyl aromatic monomers, with improved ignition resistance that comprises a filler and at least one other component which may be a hindered amine stabilizer.

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

10 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.

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

15 U.S. Pat. No. 6,472,456 and copending U.S. application No. 09/714,717, filed Nov. 16, 2000, disclose the use of certain N-alkoxy hindered amines as flame retardants.

20 EP 1038912 discloses specific hydrocarbyloxy hindered amine compounds as flame retardants.

Research Disclosure, Sept. 2000, No. 437087, June 2000, No. 434095 and Dec. 2000, No. 440128 also disclose the efficacy of certain hydrocarbyloxy hindered amine compounds as flame retardants.

25 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 interferes in the gas phase with free radical organic "fuel" 30 from the polymer substrate. Synergists are proposed to react with HX to form additional 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 a radical scavenger forming antimony halides. Thus, it can inhibit the propagation of the fire.

Although antimony compounds are efficient in terms of cost performance, it recently raised a lot of 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

5 trace amounts of arsenic compounds which are suspected carcinogens. Because of these ecological concerns, there is a motion 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 the cost performance is concerned.

10 Another reason to add flame retardant additives is to prevent dripping during the application of the fire. Dripping during combustion is the process of the separation of parts of the polymer from the matrix in the shape of droplets. Most often, the droplets are flaming and are imposing tremendous danger for fire spread. It is a common measure to add fillers such as talc in large amounts to the polymer, with some negative consequences on the

15 mechanical properties. 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 and magnesium silicate.

20 It has been found that polylactic acid polymers with good flame retardant properties are prepared when a sterically hindered amine stabilizer is added thereto together with a conventional organohalogen flame retardant, phosphorus containing flame retardant, isocyanurate flame retardant or melamine based flame retardant. With this combination, flame-retardant fillers or conventional fillers may be largely reduced or replaced. As the

25 instant hindered amine compounds are active as stabilizers, the polymer compositions of the invention are efficiently protected from the deleterious effects of light, oxygen and/or heat.

Detailed Disclosure

The instant invention pertains to a flame retardant polylactic acid polymer composition which comprises

5

a polylactic acid polymer substrate and a synergistic mixture of

(i) at least one sterically hindered amine stabilizer and

10

(ii) at least one conventional flame retardant selected from the group consisting of the organohalogen, phosphorus containing, isocyanurate and melamine based flame retardants.

15

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 3%, for instance less than 1%, for example less than 0.1% by weight of the polylactic acid polymer component; for example, the present compositions are essentially free of flame-retardant fillers.

20

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

25

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 3%, for instance less than 1%, for example less than 0.1% by weight of the polylactic acid polymer component; for example, the present compositions are essentially free of conventional fillers.

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

The present compositions meet flame retardant specifications while containing only 5 minor amounts of antimony compounds such as Sb₂O₃, e.g. less than 1%, for instance less than 0.1% by weight of the polylactic acid component; for example, the present compositions are essentially free of antimony.

10 Polylactic acid

Polylactic acids are polymers and copolymers as disclosed in U.S. Pat. Nos. 5,447,962, 5,484,881, 6,114,495 and 6,214,967, the relevant disclosures of which are hereby incorporated by reference.

15

Polylactic acid or a copolymer of lactic acid and hydroxycarboxylic acid for use in the invention is prepared by using lactic acid or lactide, namely a cyclic dimers of lactic acid, and hydroxycarboxylic acid as raw materials.

20

Exemplary hydroxycarboxylic acids include glycolic acid, hydroxybutyric acid, hydroxyvaleric acid, hydroxypentanoic acid, hydroxycaproic acid and hydroxyheptanoic acid. Specially, glycolic acid, 3-hydroxylactic acid, 4-hydroxylactic acid, 3-hydroxyvaleric acid or 6-hydroxy caproic acid is used preferably. In certain cases, other monomers can be suitably used as a mixture.

25

The lactic acid polymer may be prepared directly from lactic acid by dehydrating polycondensation or may be prepared by ring-opening polymerization of lactide.

30

When a low molecular weight polymer is permitted, the polymer is obtained by

dehydrating condensation of lactic acid. When a high molecular weight polymer is required, the polymer is preferably obtained by ring-opening polymerization of lactide.

Lactides which can be used for the ring-opening polymerization are L-lactide, D-lactide, meso-lactide and a mixture of these lactides. A mixture of D- or L-lactide with a

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lactide having opposite optical activity is preferred. Mixing ratios, D- or L-lactide/optical antipode are between for example 95/5 to 50/50.

By polymerizing the pure optical isomers or different blends, polymers may be 5 obtained which have different stereochemical structures, affecting their resilience and crystallinity and also their mechanical and thermal properties.

The polymerization degree of lactic acid-base polymer is for example in the range of from 150 to 20,000.

10 Polymerization can be carried out in the presence or absence of a solvent. In view of solvent recovery problem, bulk polymerization without solvent is preferred in industry.

15 A process for preparing lactic acid-based polymer by ring-opening polymerization of lactide and glycolide will be exemplified hereinafter.

The ring-opening polymerization is carried out in the presence of a catalyst. Catalysts which can be used are generally chloride or carboxylate of zinc or tin and include, for example, stannous octoate, tin tetrachloride, zinc chloride, titanium tetrachloride, iron 20 chloride, boron trifluoride ether complex, aluminium chloride, antimony trifluoride, lead oxide and other polyvalent metal containing compounds. No particular restriction is imposed upon the polyvalent metals. Tin compounds and zinc compounds are preferably used. However, in the case of using the foam for biocompatible materials and food products, these metals must be selected in view of toxicity.

25 The amount of the catalyst used is for example in the range of from 0.001 to 0.1% by weight for lactide or for the total weight of lactide and glycolide.

Known chain extenders can be used for the polymerization. Preferred chain 30 extenders are higher alcohols such as lauryl alcohol and hydroxy acids such as lactic acid and glycolic acid. The polymerization rate increases in the presence of a chain extender and the polymer can be obtained within a short time. The molecular weight of the polymer can also be controlled by varying the amount of the chain extender. However, too much of the chain extender tends to decrease the molecular weight of polymer formed. Hence, the

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amount of the chain extender is preferably 0.1% by weight or less for lactide or for the total weight of lactide and glycolide.

5 Polymerization or copolymerization can be carried out in the presence or absence of a solvent. Bulk polymerization in a molten state of lactide or glycolide is preferably carried out in order to obtain high molecular weight polymer.

10 In the case of molten polymerization, the polymerization temperature may be generally above the melting point (around 90°C) of the monomer, lactide or lactide and glycolide. In the case of solution polymerization which uses solvents such as chloroform, polymerization can be carried out at temperatures below the melting point of lactide or lactide and glycolide. In any case, polymerization temperatures above 250°C are unfavorable because decomposition of the formed polymer may develop.

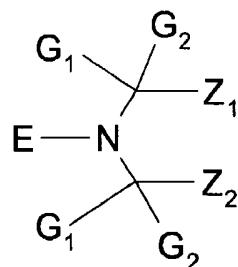
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Sterically Hindered Amine Stabilizers of Component (i)

The present hindered amines are for example monomeric compounds or are oligomeric or polymeric compounds.

20

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



25

where

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

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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

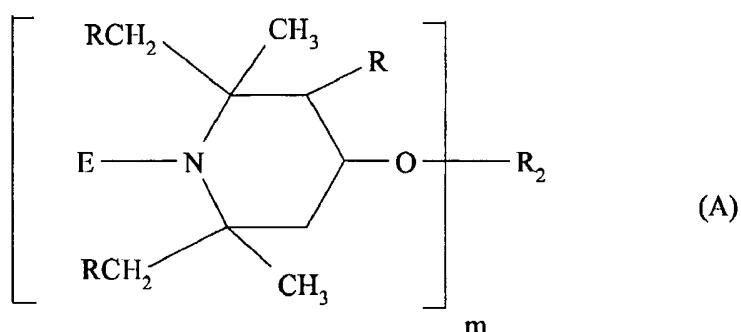
E is oxyl, hydroxyl, alkoxy, cycloalkoxy, aralkoxy, aryloxy, -O-CO-OZ₃, -O-Si(Z₄)₃, -O-
 5 PO(OZ₅)₂ or -O-CH₂-OZ₆ where Z₃, Z₄, Z₅ and Z₆ are selected from the group consisting of hydrogen, an aliphatic, araliphatic and aromatic moiety; or E is -O-T-(OH)_b,

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
 10 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;

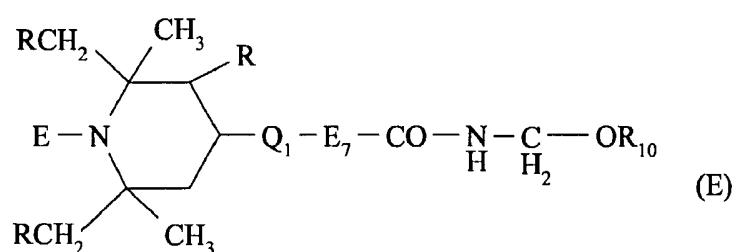
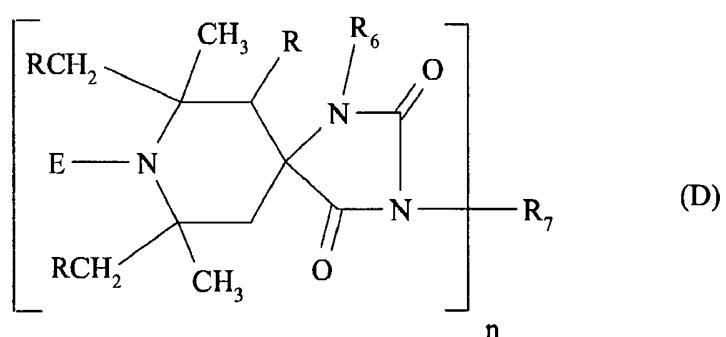
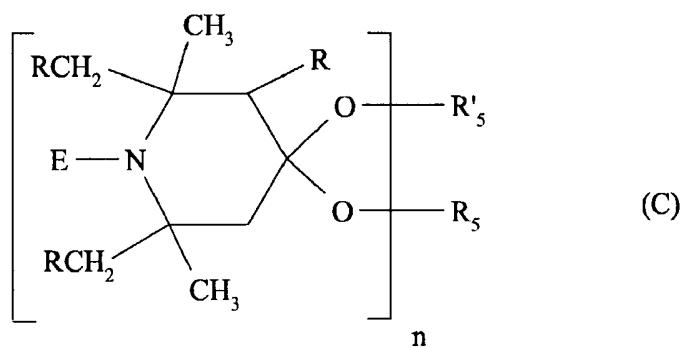
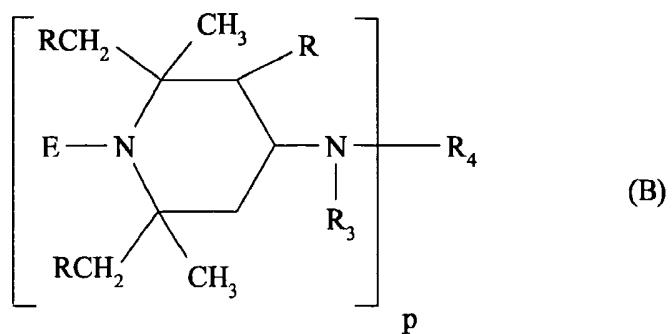
b is 1, 2 or 3 with the proviso that b cannot exceed the number of carbon atoms in T, and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T.

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

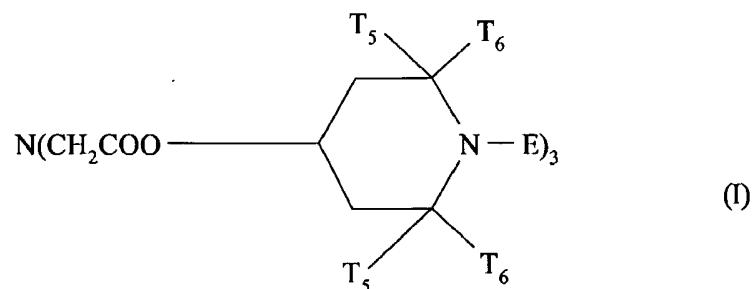
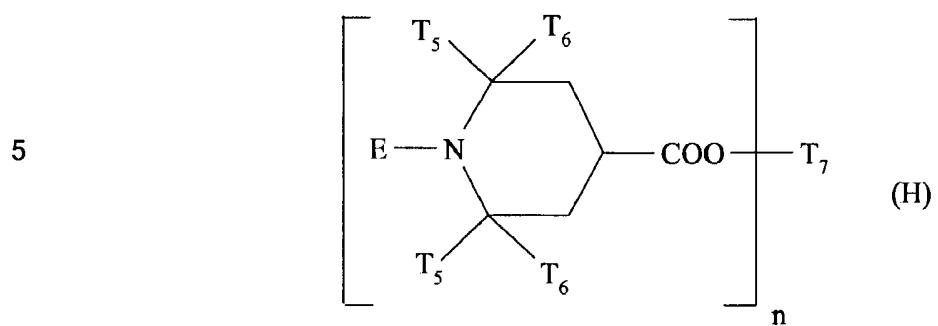
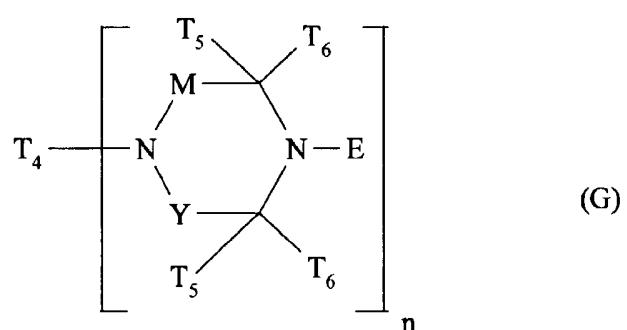
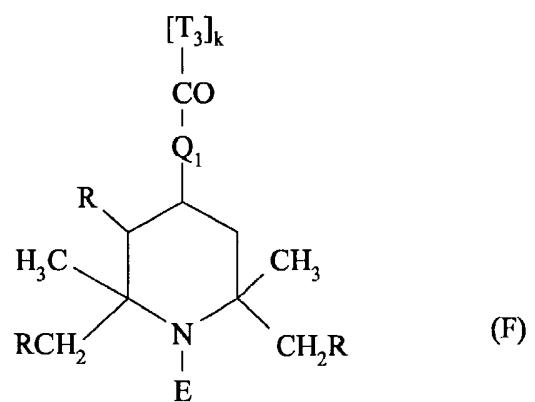
The present sterically hindered amine stabilizers of component (i) are for example of
 20 the formula A-R



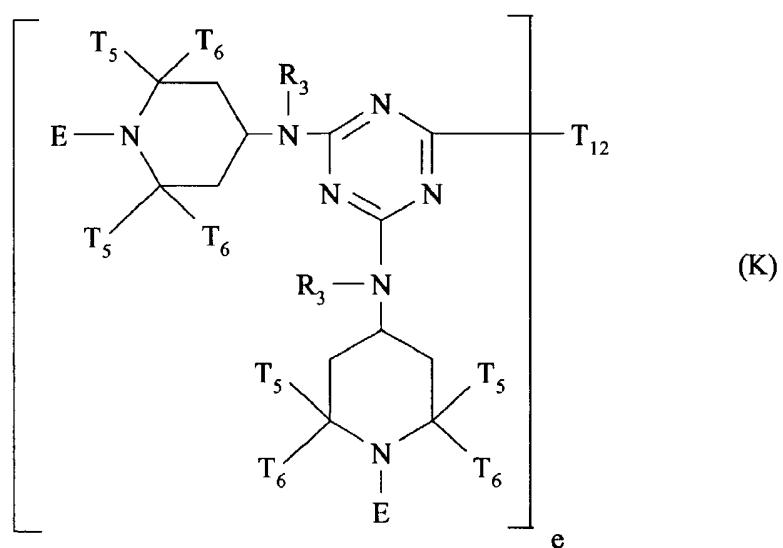
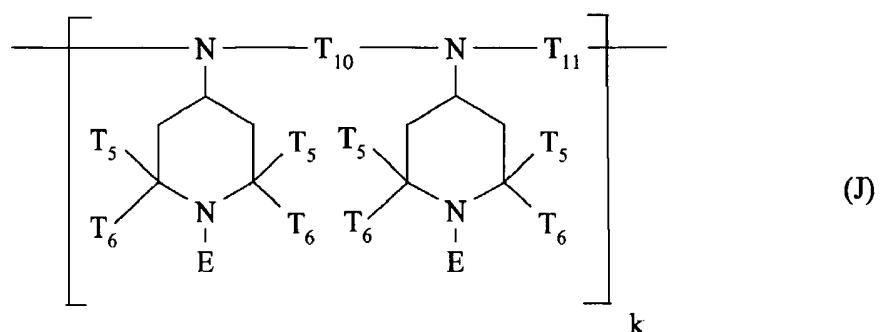
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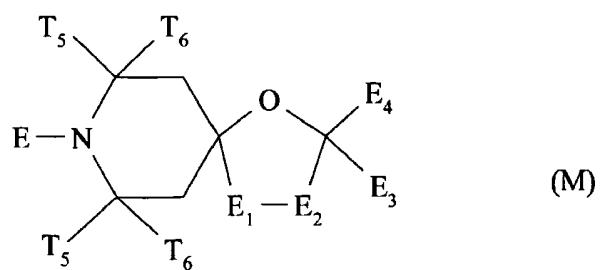
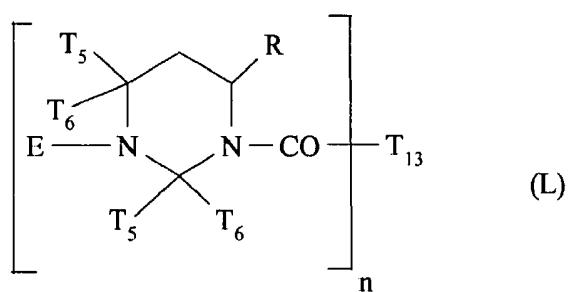
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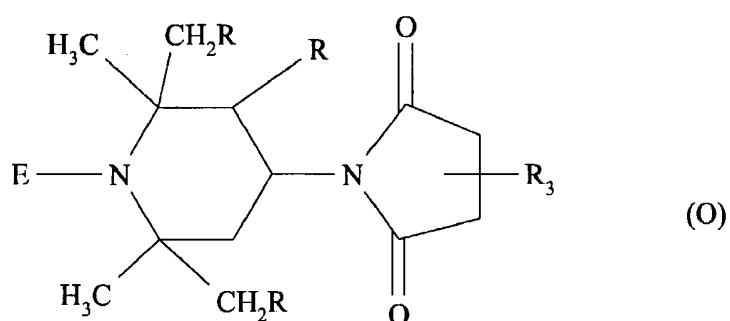
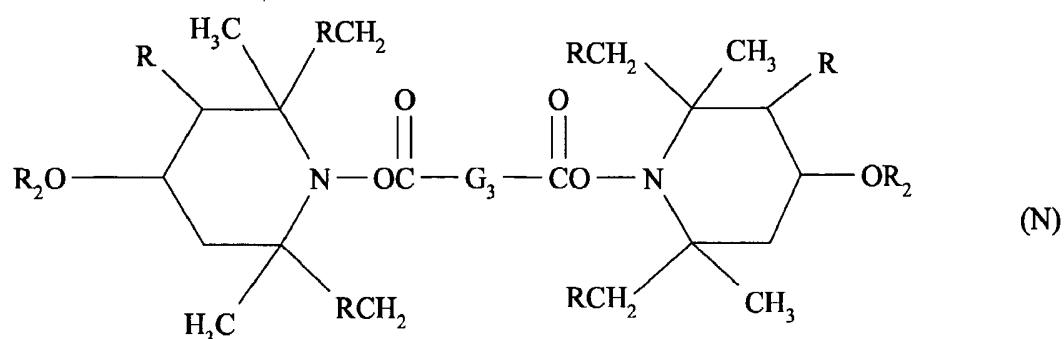
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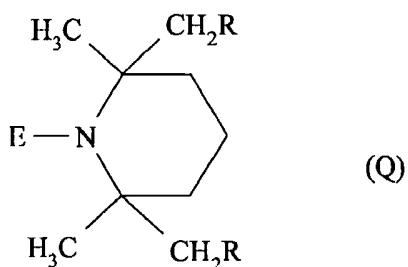
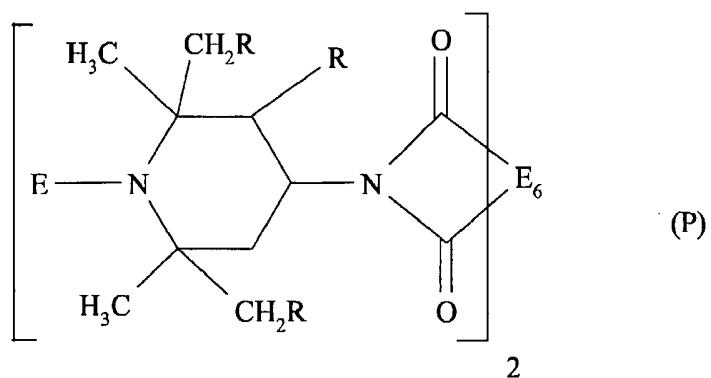
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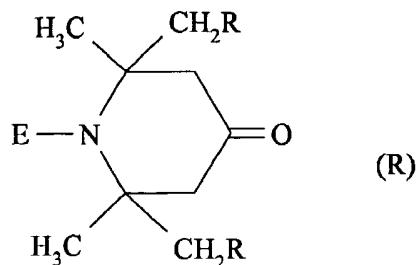
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wherein

5 E is oxy, 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,

10 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;

15 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;

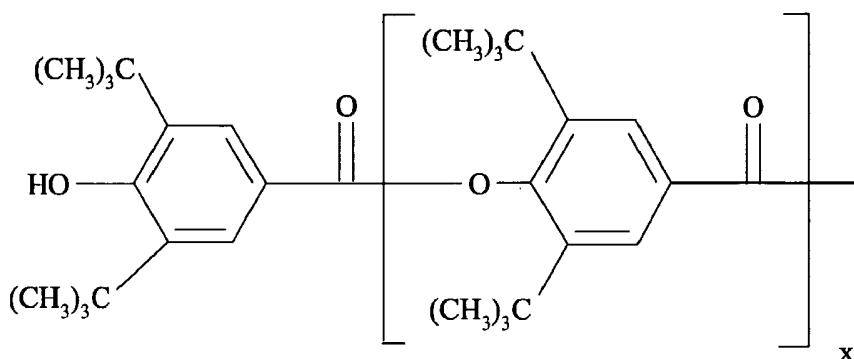
R is hydrogen or methyl,

m is 1 to 4,

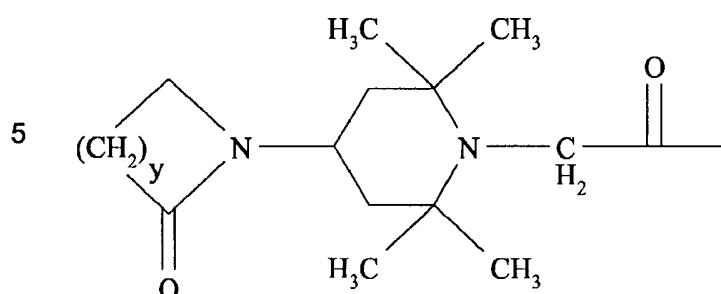
20 when m is 1,

25 R₂ is hydrogen, C₁-C₁₈alkyl or said alkyl optionally interrupted by one or more oxygen atoms, C₂-C₁₂alkenyl, C₆-C₁₀aryl, C₇-C₁₈aralkyl, 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

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wherein x is 0 or 1,



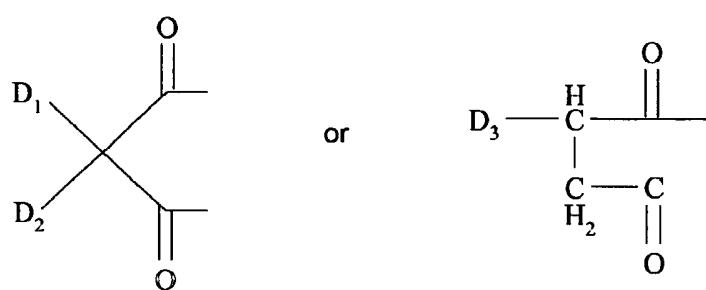
wherein y is 2-4;

when m is 2,

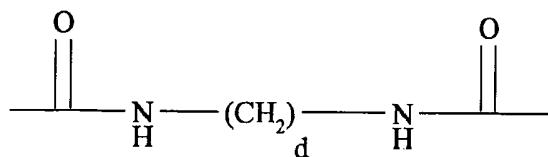
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R_2 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, xylylene, a divalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid or of a dicarbamic acid, for example an acyl radical of an aliphatic dicarboxylic acid having 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;

15



- 15 -



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;

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

10

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-pantanetetracarboxylic acid;

15

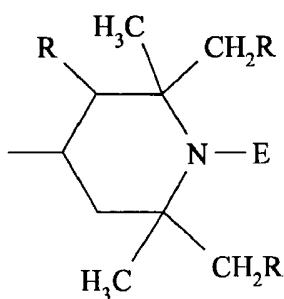
R₃ is hydrogen, C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₉aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl;

20

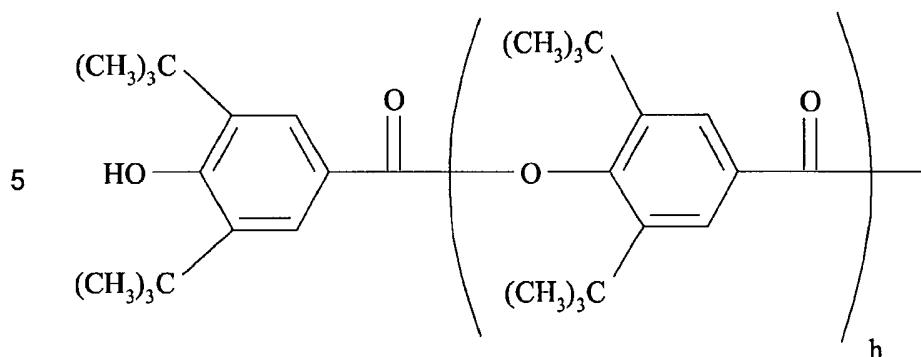
when p is 1,

25 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,

R₃ and R₄ 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,

10

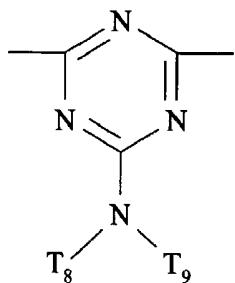
when p is 2,

R₄ is a direct bond or is C₁-C₁₂alkylene, C₆-C₁₂arylene, xylylene, a -CH₂CH(OH)-CH₂ group or a group -CH₂-CH(OH)-CH₂-O-X-O-CH₂-CH(OH)-CH₂- wherein X is C₂-C₁₀alkylene, 15 C₆-C₁₅arylene or C₆-C₁₂cycloalkylene; or, provided that R₃ is not alkanoyl, alkenoyl or benzoyl, R₄ 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

R₄ is

20

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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;

5 when p is 3,

10 R_4 is 2,4,6-triazinyl,
 n is 1 or 2,

15 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;

20 when n is 2,
 R_5 and R'_5 together are $(-CH_2)_2C(CH_2)_2$;

25 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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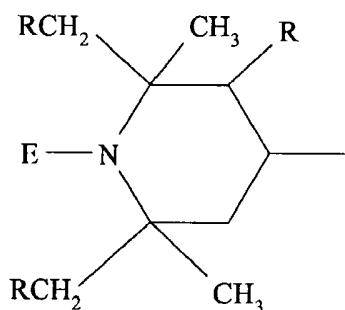
when n is 2,

5 R_7 is C_2 - C_{12} alkylene, C_6 - C_{12} arylene, a group $-CH_2CH(OH)-CH_2-O-X-O-CH_2-CH(OH)-CH_2-$ wherein X is C_2 - C_{10} alkylene, C_6 - C_{15} arylene or C_6 - C_{12} cycloalkylene, or a group $-CH_2CH(OZ')CH_2-(OCH_2-CH(OZ')CH_2)_2-$ wherein Z' is hydrogen, C_1 - C_{18} alkyl, allyl, benzyl, C_2 - C_{12} alkanoyl or benzoyl;

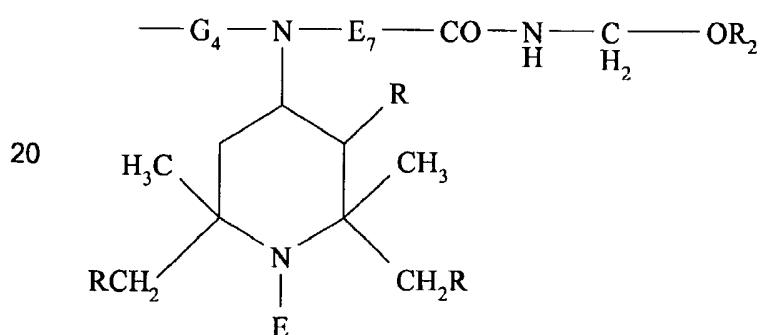
10 Q_1 is $-N(R_8)-$ or $-O-$; E_7 is C_1 - C_3 alkylene, the group $-CH_2-CH(R_9)-O-$ wherein R_9 is hydrogen, methyl or phenyl, the group $-(CH_2)_3-NH-$ or a direct bond;

15 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 $-CH_2-CH(R_9)-OH$ wherein R_9 has the meaning defined above; a group of the formula

15



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 $-E_7-CO-NH-CH_2-OR_{10}$;

- 19 -

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 5 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,

10

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,

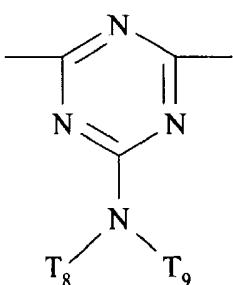
M and Y are independently methylene or carbonyl, and T_4 is ethylene where n is 2;

15

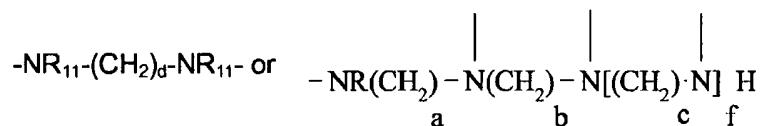
T_7 is the same as R_7 , and T_7 is for example octamethylene where n is 2,

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

20



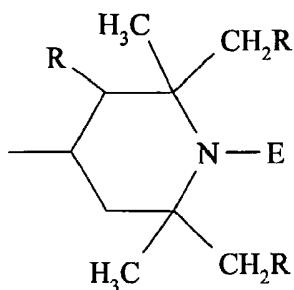
T_{12} is piperazinyl,



25

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

- 20 -



5 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

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

T₁₃ is the same as R₂ with the proviso that T₁₃ cannot be hydrogen when n is 1;

15

E₁ and E₂, being different, each are -CO- or -N(E₅)- where E₅ is hydrogen, C₁-C₁₂ alkyl or C₄-C₂₂ alkoxy carbonyl alkyl, for instance E₁ is -CO- and E₂ is -N(E₅)-,

20

E₃ 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,

25 E₄ is hydrogen, alkyl of 1 to 30 carbon atoms, phenyl, naphthyl or phenylalkyl of 7 to 12 carbon atoms, or

30

E₃ and E₄ 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,

35

E₆ is an aliphatic or aromatic tetravalent radical,

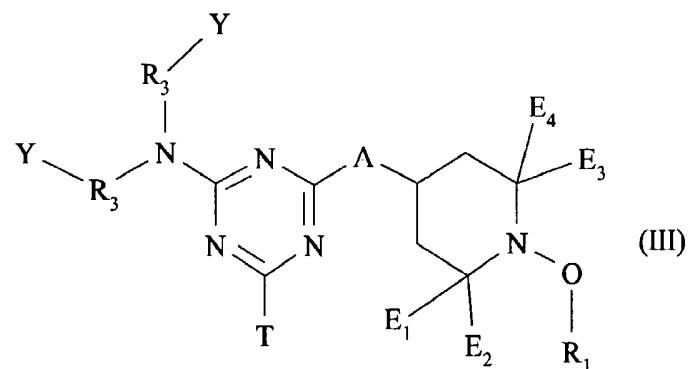
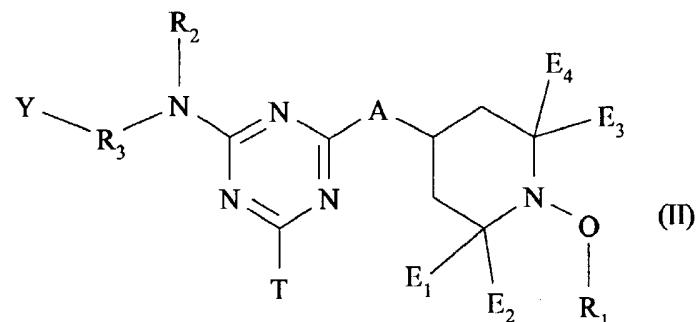
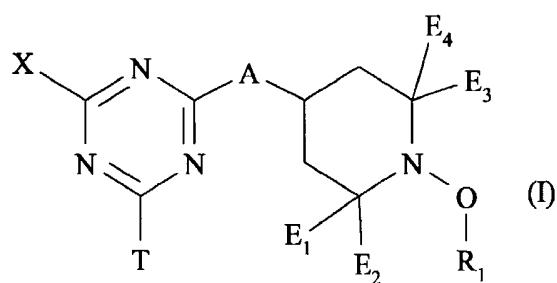
R₂ of formula (N) is a previously defined when m is 1;

40 G₁ a direct bond, C₁-C₁₂ alkylene, phenylene or -NH-G'-NH wherein G' is C₁-C₁₂ alkylene; or

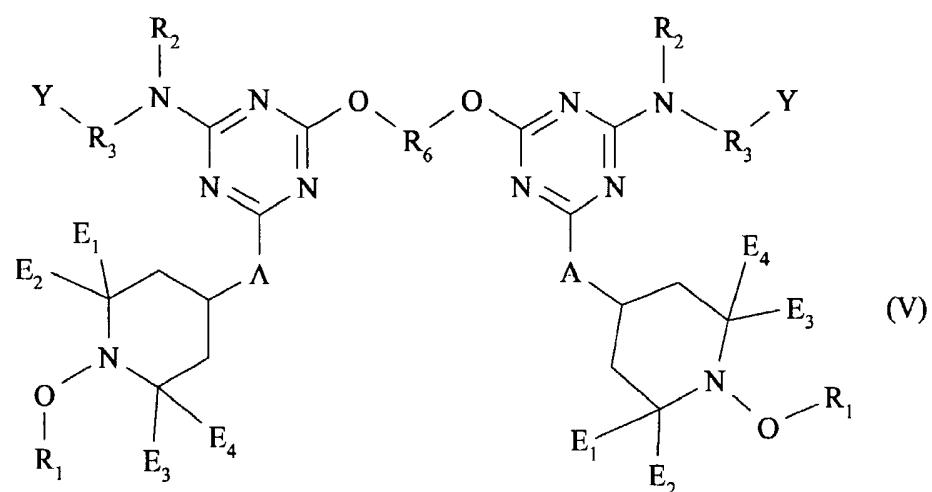
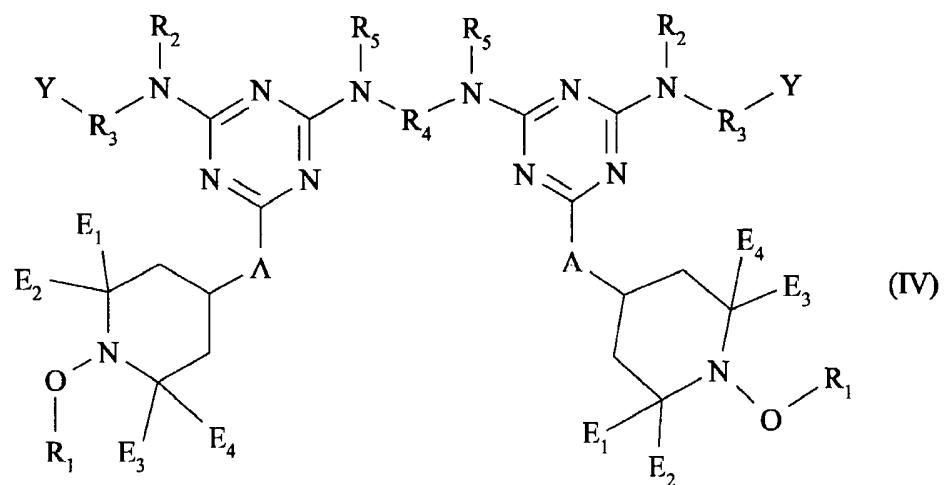
- 21 -

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

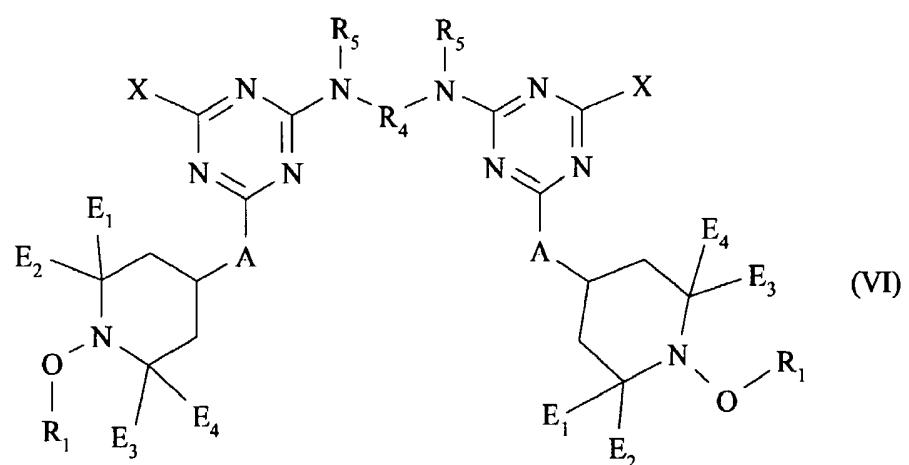
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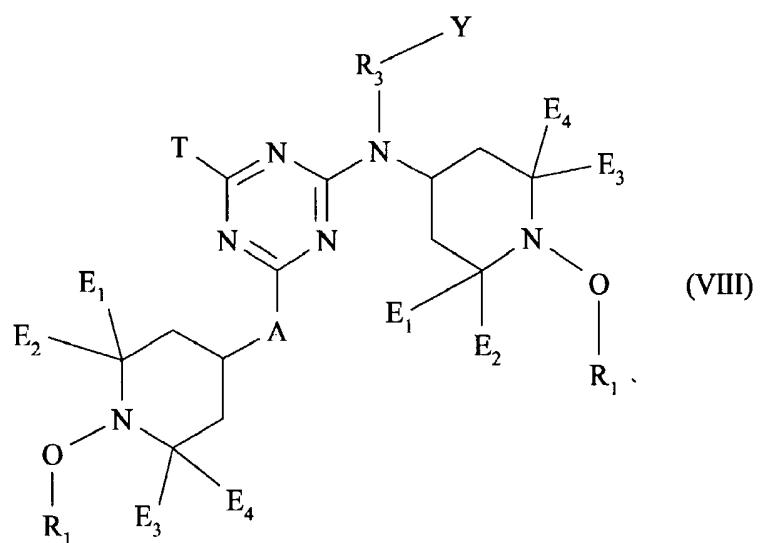
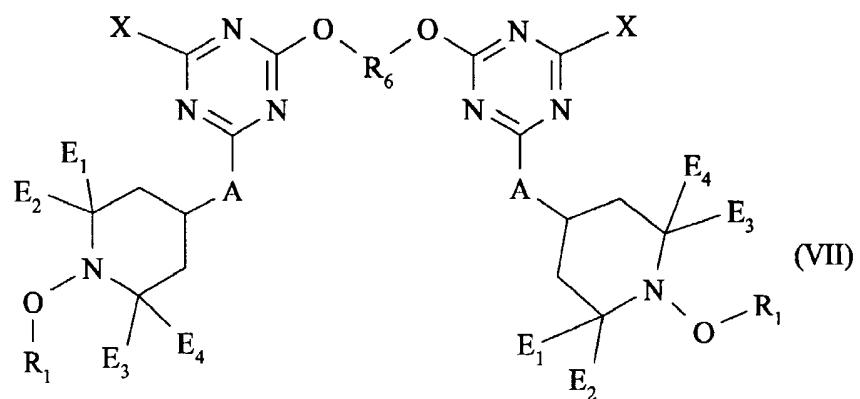
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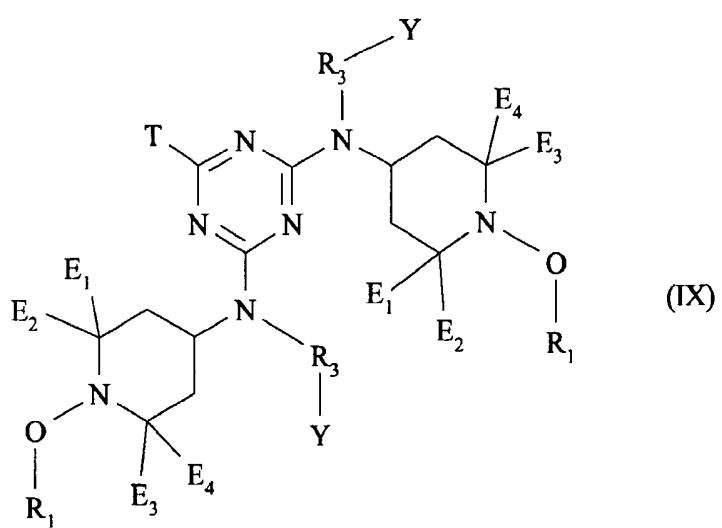
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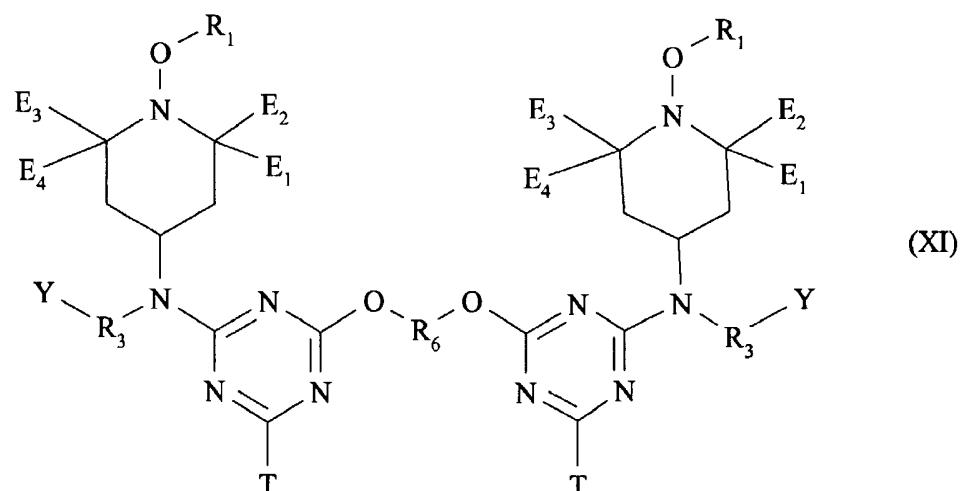
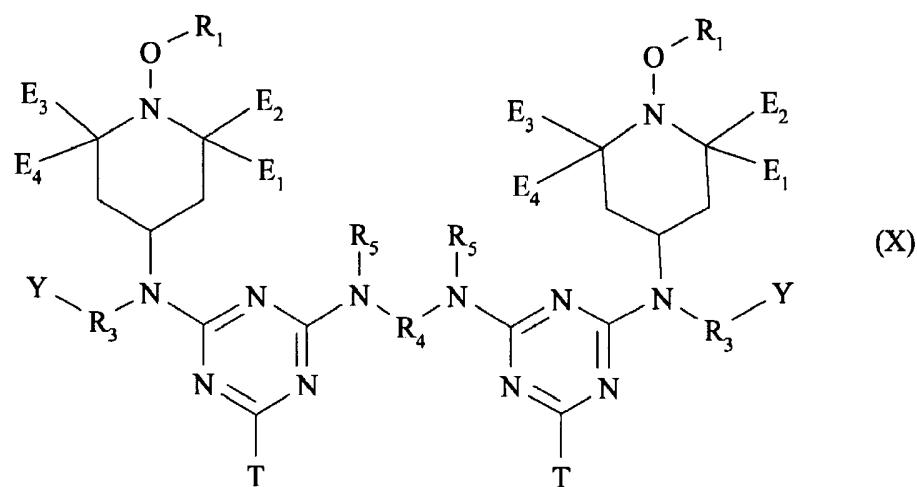
- 23 -



5



- 24 -



5 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,

10

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,

15

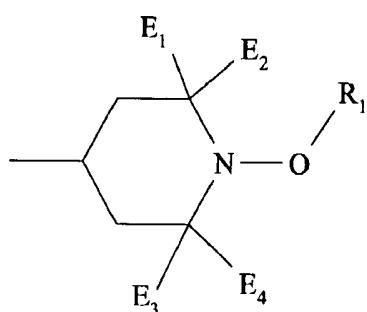
- 25 -

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 $-CO-$, $-CO-R_4-$, $-CONR_2-$ or $-CO-NR_2-R_4-$,

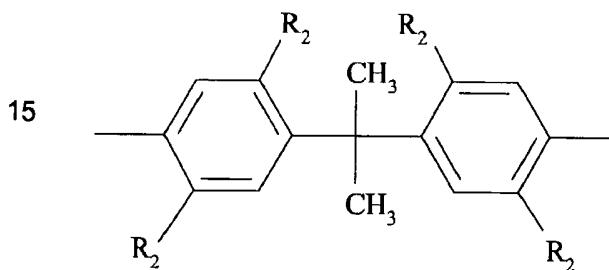
5 R_4 is alkylene of 1 to 8 carbon atoms,

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



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

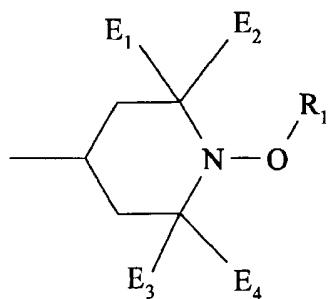
R_6 is alkylene of 2 to 8 carbon atoms or R_6 is



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

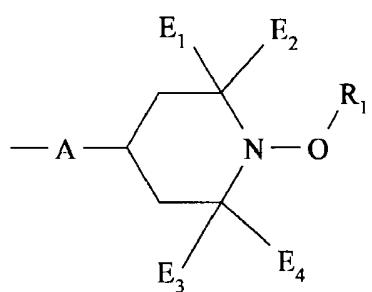
20 A is $-O-$ or $-NR_7-$ where R_7 is hydrogen, a straight or branched chain alkyl of 1 to 12 carbon atoms, or R_7 is

- 26 -



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(R₂)₂ with the stipulation that R₂ is not hydrogen, or T is

5



X is -NH₂, -NCO, -OH, -O-glycidyl, or -NHNH₂, and

10 Y is -OH, -NH₂, -NHR₂ where R₂ is not hydrogen; or Y is -NCO, -COOH, oxiranyl, -O-glycidyl, or -Si(OR₂)₃; or the combination R₃-Y- is -CH₂CH(OH)R₂ where R₂ is alkyl or said alkyl interrupted by one to four oxygen atoms, or R₃-Y- is -CH₂OR₂;

or

15

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'-ethylenediaminodipropylamine; N,N',N'''-tris{2,4-bis[(1-hydrocarbyloxy-2,2,6,6-tetramethylpiperidin-4-yl)alkylamino]-s-triazin-6-yl}-3,3'-ethylenediaminodipropylamine, and bridged derivatives as described by formulas I,

20 II, IIA and III



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T-E₁-T₁ (II)

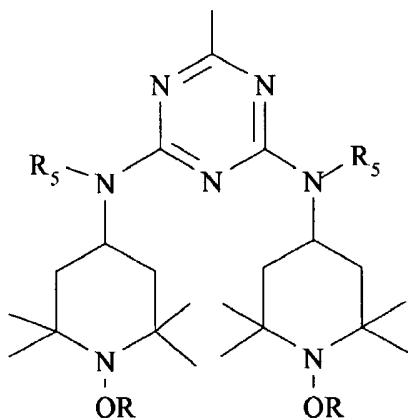
T-E₁ (IIA)

5 G-E₁-G₁-E₁-G₂ (III)

where in the tetraamine of formula I

10 R₁ and R₂ are the s-triazine moiety E; and one of R₃ and R₄ is the s-triazine moiety E
with the other of R₃ or R₄ being hydrogen,

E is



15

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

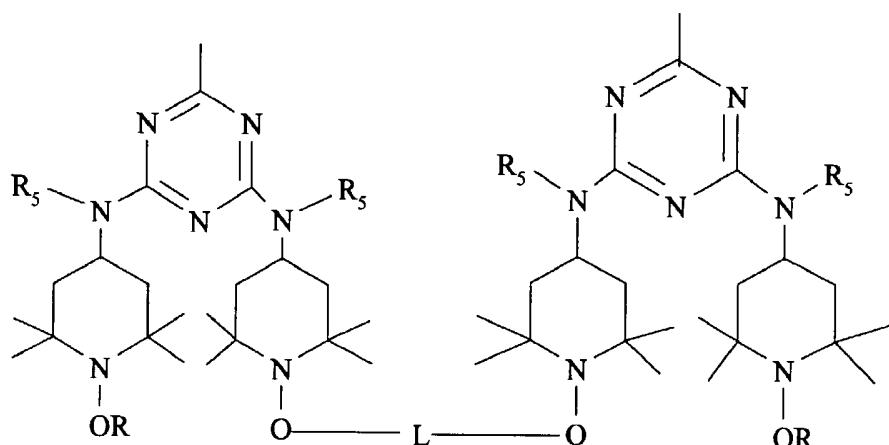
R₅ is alkyl of 1 to 12 carbon atoms, for example n-butyl,

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

T and T₁ are each a tetraamine substituted by R₁-R₄ as is defined for formula I, where

(1) one of the s-triazine moieties E in each tetraamine is replaced by the group E,
25 which forms a bridge between two tetraamines T and T₁,

E_1 is



5

or

10 (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,

15

L is propanediyl, cyclohexanediyI or octanediyI;

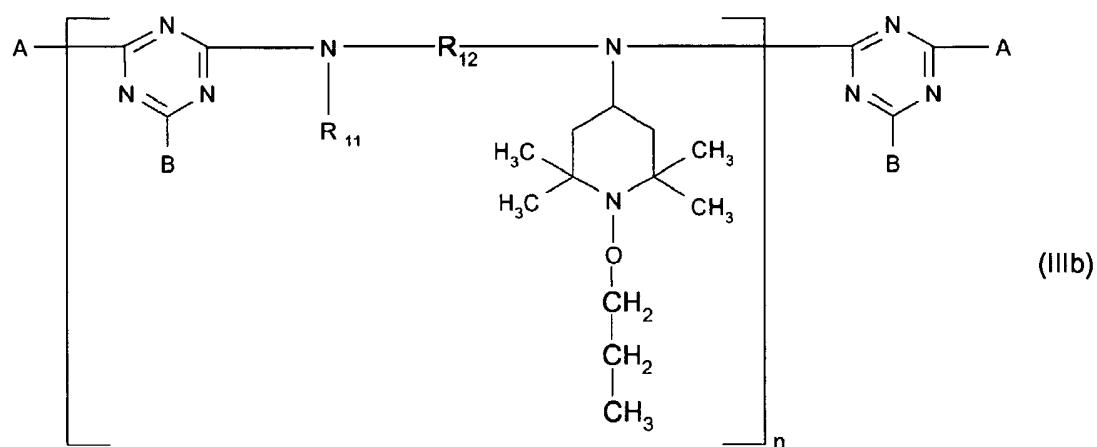
where in the compound of formula III

20 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 ;

- 29 -

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

5 or the hindered amine is a compound of the formula IIIb

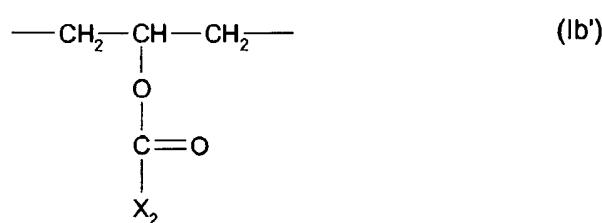


in which the index n ranges from 1 to 15;

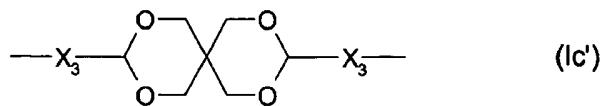
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R_{12} is C_2-C_{12} alkylene, C_4-C_{12} alkenylene, C_5-C_7 cycloalkylene, C_5-C_7 cycloalkylene-di(C_1-C_4 alkylene), C_1-C_4 alkylenedi(C_5-C_7 cycloalkylene), phenylenedi(C_1-C_4 alkylene) or C_4-C_{12} alkylene interrupted by 1,4-piperazinediyl, -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;

15 or R_{12} is a group of the formula (Ib') or (Ic');



- 30 -

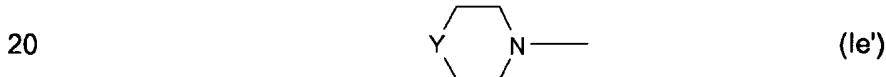


with m being 2 or 3,

5 X_2 being C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl; phenyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl or C_1 - C_4 alkoxy; C_7 - C_9 phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3 C_1 - C_4 alkyl; and

10 the radicals X_3 being independently of one another C_2 - C_{12} alkylene;

15 R_{13} , R_{14} and R_{15} , which are identical or different, are hydrogen, C_1 - C_{18} alkyl, C_5 - C_{12} cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl; C_3 - C_{18} alkenyl, phenyl which is unsubstituted or substituted by 1, 2 or 3 C_1 - C_4 alkyl or C_1 - C_4 alkoxy; C_7 - C_9 phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3 C_1 - C_4 alkyl; tetrahydrofurfuryl or C_2 - C_4 alkyl which is substituted in the 2, 3 or 4 position by -OH, C_1 - C_8 alkoxy, di(C_1 - C_4 alkyl)amino or a group of the formula (Ie');

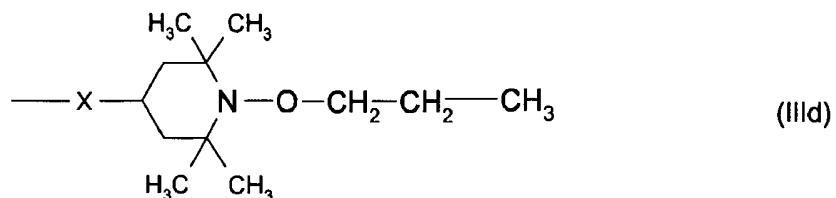


with Y being -O-, -CH₂-, -CH₂CH₂- or >N-CH₃,

or -N(R_{14})(R_{15}) is additionally a group of the formula (Ie');

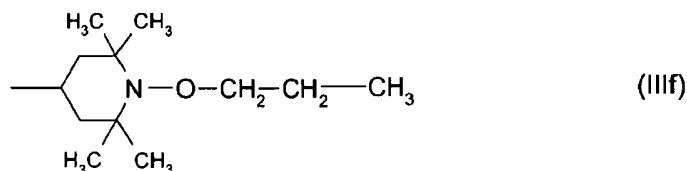
25 the radicals A are independently of one another -OR₁₃, -N(R_{14})(R_{15}) or a group of the formula (IIId);

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X is -O- or >N-R₁₆;

5 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 (IIIe),



10 or C₂-C₄alkyl which is substituted in the 2, 3 or 4 position by -OH, C₁-C₆alkoxy, di(C₁-C₄alkyl)amino or a group of the formula (Ie');

R₁₁ has one of the definitions given for R₁₆; and

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

Alkyl is straight or branched 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-20 tridecyl, n-tetradecyl, n-hexadecyl or n-octadecyl.

Cycloalkyl groups include cyclopentyl and cyclohexyl; typical cycloalkenyl groups include cyclohexenyl; while typical aralkyl groups include benzyl, alpha-methyl-benzyl, alpha,alpha-dimethylbenzyl or phenethyl, whereas typical aryl groups include for example 25 phenyl or naphthyl.

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If R_2 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.

5 If R_2 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.

10

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.

15

Hindered alkoxyamine stabilizers of component (i) 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.

20

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, 6,117,995, 6,271,377, 6,392,041, 6,376,584 and 6,472,456 and U.S. application Ser. Nos. 09/714,717, filed Nov. 16, 2000 and 60/312,517, filed Aug. 15, 2001. The relevant disclosures of these patents and applications are hereby incorporated by reference.

25

U.S. Pat. Nos. 6,271,377, 6,392,041 and 6,376,584, 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 (i). Hindered hydroxyalkoxyamine stabilizers are also known as N-hydroxyalkoxy hindered amines, or NORol HALS.

30

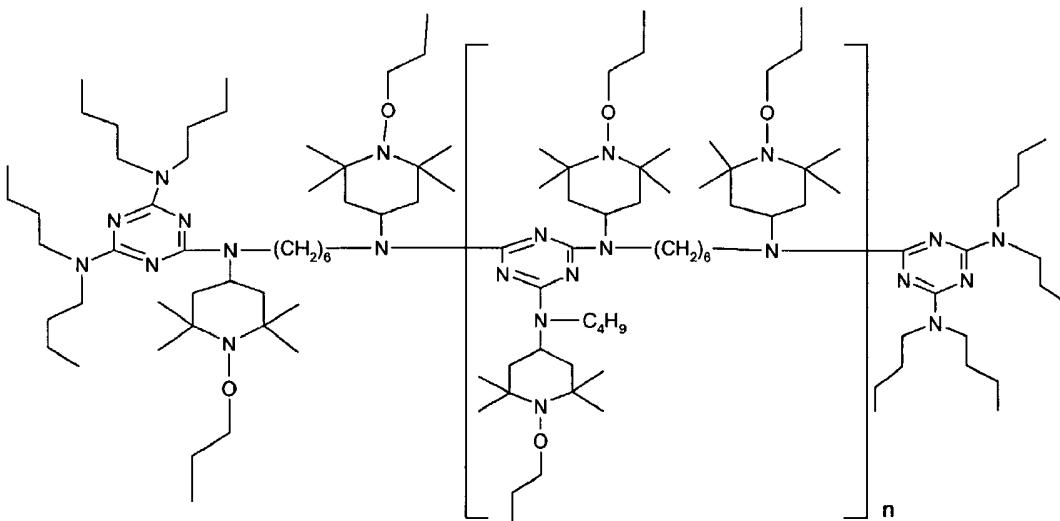
Suitable hindered amines of component (i) include for example:

NOR1 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine;

- 33 -

NOR2 bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
 NOR3 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxyethylamino-s-triazine;
 NOR3 bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
 5 NOR4 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-chloro-s-triazine;
 NOR5 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine;
 NOR6 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine;
 NOR7 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethyl-
 10 piperidine;
 NOR8 bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
 NOR9 bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
 NOR10 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-
 N-butylamino}-6-(2-hydroxyethylamino)-s-triazine;
 15 NOR11 the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine) [CAS Reg. No. 191680-81-6]; and

NOR12 the compound of formula



20

in which n is from 1 to 15.

Compound NOR12 is disclosed in example 2 of U.S. Patent No. 6,117,995.

The hindered amine stabilizers of component (i) are advantageously contained in the composition of the invention in an amount from 0.05% to 20% by weight based on the polylactic acid polymer substrate; for example from 0.1% to 10% by weight; for example from 0.2% to 8% by weight; for instance from 0.5% to 3% by weight. For example, the 5 stabilizers of component (i) are present from 0.05% to 15%, from 0.05% to 10%, from 0.05% to 8%, from 0.05% to 5% or from 0.05% to 3% by weight based on the weight of the polylactic acid substrate. For example, the stabilizers of component (i) are present from 0.1% to 20%, from 0.2 to 20%, from 0.5 to 20% or from 1% to 20% by weight based on the weight of the polylactic acid substrate.

10

Conventional Flame Retardants of Component (ii)

Oganohalogen flame retardants are for example:

15 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,
20 chlorendic acid,
tetrachlorophthalic acid,
tetrabromophthalic acid,
bis-(N,N'-hydroxyethyl)tetrachlorophenylene diamine,
poly-β-chloroethyl triphosponate mixture
25 tetrabromobisphenol A bis(2,3-dibromopropyl ether) (PE68),
brominated epoxy resin,
ethylene-bis(tetrabromophthalimide) (SAYTEX® BT-93),
bis(hexachlorocyclopentadieno)cyclooctane (DECLORANE PLUS®),
chlorinated paraffins,
30 octabromodiphenyl ether,
hexachlorocyclopentadiene derivatives,
1,2-bis(tribromophenoxy)ethane (FF680),
tetrabromo-bisphenol A (SAYTEX® RB100),
ethylene bis-(dibromo-norbornanedicarboximide) (SAYTEX® BN-451),
35 bis-(hexachlorocyclopentadieno) cyclooctane,

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

5 The phosphorus containing flame retardants are for example:

Tetraphenyl resorcinol diphosphite (FYROLFLEX® RDP, Akzo Nobel),
tetrakis(hydroxymethyl)phosphonium sulfide,
diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate,
10 hydroxyalkyl esters of phosphorus acids,
ammonium polyphosphate (APP) or (HOSTAFLAM® AP750),
resorcinol diphosphate oligomer (RDP),
phosphazene flame retardants,
ethylenediamine diphosphate (EDAP),
15 phosphonates and their metal salts and
phosphinates and their metal salts.

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-proyl)isocyanurate or triglycidyl isocyanurate.

The melamine based flame retardants are for example:

25 melamine cyanurate,
melamine borate,
melamine phosphates,
melamine polyphosphates,
melamine pyrophosphates,
30 melamine ammonium polyphosphate and
melamine ammonium pyrophosphate.

Boric acid may be included as a flame retardant.

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

5 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.

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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.

15

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.

20 Component (ii) is advantageously contained in the composition of the invention in an amount from 0.5% to 45% by weight of the polylactic acid polymeric substrate; for instance 3% to 40%; for example 5% to 35% by weight of the polylactic acid component. For example, component (ii) is employed from 0.5% to 10% by weight, from 1% to 10%, from 3% to 10% or from 5% to 10% by weight, based on the weight of the polylactic acid polymer

25 substrate. For example, component (ii) is employed from 0.5% to 8%, from 0.5% to 6%, from 0.5% to 5%, or from 0.5% to 3% by weight, based on the weight of the polylactic acid polymer substrate.

The ratio (parts by weight) of component (i) to component (ii) is for example between

30 1:5 to 1:200, for instance from 1:50 to 1:100, or 1:10 to 1:25. For example the ratio of component (i) to component (ii) is from 1:10 to 1:200, from 1:25 to 1:200, from 1:50 to 1:200 or from 1:100 to 1:200. For example, the weight ratio of component (i) to component (ii) is from 1:5 to 1:100, from 1:5 to 1:50, from 1:5 to 1:25, or from 1:5 to 1:10.

The amount of component (ii) used also depends on the effectiveness of the specific compound(s) and the specific application type.

The compositions of this invention may further comprise acid scavengers.

5

Acid scavengers are for example hydrotalcites and amorphous basic aluminum magnesium carbonates, such as those described in U.S. Pat. Nos. 4,427,816, 5,106,898 and 5,234,981, the relevant disclosures of which are hereby incorporated by reference.

Hydrotalcite is also known as hycite or DHT4A.

10

Hydrotalcites are natural or synthetic. The natural hydrotalcite is held to possess a structure $Mg_6Al_2(OH)_{16}CO_3 \cdot 4 H_2O$.

15 H₂O.

A typical empirical formula of a synthetic hydrotalcite is $Al_2Mg_{4.35}OH_{11.36}CO_{3(1.67)} \cdot x$

H₂O.

Examples of the synthetic product include: $Mg_{0.7}Al_{0.3}(OH)_2(CO_3)_{0.15} \cdot 0.54 H_2O$,
 $Mg_{4.5}Al_2(OH)_{13}CO_3 \cdot 3.5 H_2O$ and $Mg_{4.2}Al(OH)_{12.4}CO_3$.

20

The acid scavengers are present in the polylactic acid polymeric compositions for example at a level of 0.1% to 1.0% by weight, based on the weight of the polylactic acid component. For instance, the present acid scavengers are present from 0.2% to 0.8% or from 0.4% to 0.6% by weight, based on the weight of the polylactic acid component. For example, the present acid scavengers are present from 0.1% to 0.8%, from 0.1% to 0.6%,
25 from 0.1% to 0.4% or from 0.1% to 0.2% by weight based on the weight of the polylactic acid component. For instance, the present acid scavengers are present from 0.2% to 1.0%, from 0.4% to 1.0%, from 0.6% to 1.0% or from 0.8% to 1.0% by weight based on the weight of the polylactic acid component.

30

The acid scavengers aid the present compositions in color, odor and stability.

The present polymer compositions can contain further additives. These additional additives are mainly from the group of heat stabilizers and /or light stabilizers. The thermal

stabilization embraces both processing and use (long-term stability). Said additives are known to the skilled person and most of them are commercially available.

Suitable additional additives are for example:

5

1. Antioxidants

10 1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-di-methylphenol, 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-methoxyphenol, 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.

15

20 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.

25

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.

30 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'-ethyldenebis(4,6-di-tert-butylphenol), 2,2'-ethyldenebis(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-methyl-phenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)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'-dihydroxydi-benzyl 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, isoctyl-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, di-dodecylmercaptoethyl-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.

5 1.11. Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate,
10 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.

15 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-nonenediol, 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-phospho-2,6,7-trioxabicyclo[2.2.2]octane.
20

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-nonenediol, 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-phospho-2,6,7-trioxabicyclo[2.2.2]octane.
25

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-nonenediol, 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-phospho-2,6,7-trioxabicyclo[2.2.2]octane.
30

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, 5 triethylene glycol, pentaerythritol, tris(hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospho-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 (Naugard[®]XL-1 supplied by Uniroyal).

15 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, 20 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-nanoylaminophenol, 4-dodecanoylaminophenol, 4-octadecanoylaminophenol, bis(4-methoxyphenyl)amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4'-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, 25 30 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-octyl-diphenylamines, a mixture of mono- and dialkylated nonyldiphenylamines, a mixture of mono- and dialkylated dodecyldiphenylamines, a mixture of mono- and dialkylated isopro-

pyl/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

10 2.1. 2-(2'-Hydroxyphenyl)benzotriazoles, for example known commercial hydroxyphenyl-2H-benzotriazoles and benzotriazoles as disclosed in, United States Patent Nos. 3,004,896; 3,055,896; 3,072,585; 3,074,910; 3,189,615; 3,218,332; 3,230,194; 4,127,586; 4,226,763; 4,275,004; 4,278,589; 4,315,848; 4,347,180; 4,383,863; 4,675,352; 4,681,905; 4,853,471; 5,268,450; 5,278,314; 5,280,124; 5,319,091; 5,410,071; 15 5,436,349; 5,516,914; 5,554,760; 5,563,242; 5,574,166; 5,607,987; 5,977,219 and 6,166,218 such as 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3,5-di-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-t-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-t-octylphenyl)-2H-benzotriazole, 5-chloro-2-(3,5-di-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 5-chloro-2-(3-t-butyl-2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-sec-20 butyl-5-t-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-4-octyloxyphenyl)-2H-benzotriazole, 2-(3,5-di-t-amyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3,5-bis- α -cumyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-(ω -hydroxy-octa-(ethyleneoxy)carbonyl-ethyl)-, phenyl)-2H-benzotriazole, 2-(3-dodecyl-2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-octyloxycarbonyl)ethylphenyl)-25 2H-benzotriazole, dodecylated 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-octyloxycarbonylethyl)phenyl)-5-chloro-2H-benzotriazole, 2-(3-tert-butyl-5-(2-(2-ethylhexyloxy)-carbonylethyl)-2-hydroxyphenyl)-5-chloro-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-methoxycarbonylethyl)phenyl)-5-chloro-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-methoxycarbonylethyl)phenyl)-2H-benzotriazole, 2-(3-t-butyl-5-(2-30 ethylhexyloxy)carbonylethyl)-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-isooctyloxycarbonylethyl)phenyl)-2H-benzotriazole, 2,2'-methylene-bis(4-t-octyl-(6-2H-benzotriazol-2-yl)phenol), 2-(2-hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-t-octyl-5- α -cumylphenyl)-2H-benzotriazole, 5-fluoro-2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole, 5-chloro-2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole, 5-

chloro-2-(2-hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 2-(3-t-butyl-2-hydroxy-5-(2-isoctyloxycarbonylethyl)phenyl)-5-chloro-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-t-octylphenyl)-2H-benzotriazole,

5 methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-t-butyl-4-hydroxyhydrocinnamate, 5-butylsulfonyl-2-(2-hydroxy-3- α -cumyl-5-t-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3- α -cumyl-5-t-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di- α -cumylphenyl)-2H-benzotriazole, 5-butylsulfonyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole and 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-t-butylphenyl)-2H-benzotriazole.

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

15 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.

20 2.4. Acrylates, for example ethyl α -cyano- β , β -diphenylacrylate, isoctyl 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.

25 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 dibutylthiocarbamate, 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)-

5 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-di-chloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitritoltriacetate, tetrakis(2,2,6,6-tetra-methyl-4-piperidyl)-1,2,3,4-butane-tetracarboxylate, 1,1'-(1,2-ethanediyl)-bis(3,3,5,5-tetra-methylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearylxy-2,2,6,6-tetramethyl-10 piperidine, 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)hexamethylenedi-amine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-15 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-tetra-methyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyr-roldin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidine-2,5-dione, a mix-20 ture of 4-hexadecyloxy- and 4-stearylxy-2,2,6,6-tetramethylpiperidine, a condensation pro-duct 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-25 (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-cyclounde-cyl-1-oxa-3,8-diaza-4-oxospiro [4.5]decane und epichlorohydrin, 1,1-bis(1,2,2,6,6-pentame-thyl-4-piperidyl)hexamethylenediamine, diester of 4-methoxy-methylene-malonic acid 30 with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine, poly[methylpropyl-3-oxy-4-(2,2,6,6-tetra-methyl-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 5 oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example known commercial tris-aryl-o-hydroxyphenyl-s-triazines and triazines as disclosed in, WO 96/28431 and United States Patent Nos. 3,843,371; 4,619,956; 4,740,542; 5,096,489; 5,106,891; 5,298,067; 10 5,300,414; 5,354,794; 5,461,151; 5,476,937; 5,489,503; 5,543,518; 5,556,973; 5,597,854; 5,681,955; 5,726,309; 5,736,597; 5,942,626; 5,959,008; 5,998,116; 6,013,704; 6,060,543; 6,187,919; 6,242,598 and 6,255,483, for example 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-octyloxyphenyl)-s-triazine, Cyasorb® 1164, Cytec Corp, 4,6-bis-(2,4-dimethylphenyl)-2-(2,4-dihydroxyphenyl)-s-triazine, 2,4-bis(2,4-dihydroxyphenyl)-6-15 (4-chlorophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(2,4-dimethylphenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxyethoxy)phenyl]-6-(4-bromophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-acetoxyethoxy)phenyl]-6-(4-chlorophenyl)-s-triazine, 2,4-bis(2,4-dihydroxyphenyl)-6-(2,4-dimethylphenyl)-s-triazine, 2,4-bis(4-biphenyl)-6-(2-20 hydroxy-4-octyloxycarbonylethylideneoxyphenyl)-s-triazine, 2-phenyl-4-[2-hydroxy-4-(3-sec-butyloxy-2-hydroxypropyloxy)phenyl]-6-[2-hydroxy-4-(3-sec-amyoxy-2-hydroxypropyloxy)-phenyl]-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-benzyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4-bis(2-hydroxy-4-n-butyloxyphenyl)-6-(2,4-di-n-butyloxy-phenyl)-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-nonyloxy*-2-hydroxy-25 propyloxy)-5- α -cumylphenyl]-s-triazine (* denotes a mixture of octyloxy, nonyloxy and decyloxy groups), methylenebis-{2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-butyloxy-2-hydroxypropoxy)phenyl]-s-triazine}, methylene bridged dimer mixture bridged in the 3:5', 5:5' and 3:3' positions in a 5:4:1 ratio, 2,4,6-tris(2-hydroxy-4-isooctyloxycarbonylisopropylideneoxyphenyl)-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-(2-hydroxy-4-hexyloxy-5- α -cumylphenyl)-s-triazine, 2-(2,4,6-trimethylphenyl)-4,6-bis[2-hydroxy-4-(3-butyloxy-2-hydroxypropyloxy)phenyl]-s-triazine, 2,4,6-tris[2-hydroxy-4-(3-sec-butyloxy-2-hydroxypropyloxy)-phenyl]-s-triazine, mixture of 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-dodecyloxy-2-hydroxypropoxy)-phenyl)-s-triazine and 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-tridecyloxy-2-hydroxypropoxy)-phenyl)-s-triazine, Tinuvin® 400, Ciba Specialty Chemicals

Corp., 4,6-bis-(2,4-dimethylphenyl)-2-(2-hydroxy-4-(3-(2-ethylhexyloxy)-2-hydroxypropoxy)-phenyl)-s-triazine and 4,6-diphenyl-2-(4-hexyloxy-2-hydroxyphenyl)-s-triazine.

3. Metal deactivators, for example N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine,

5 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.

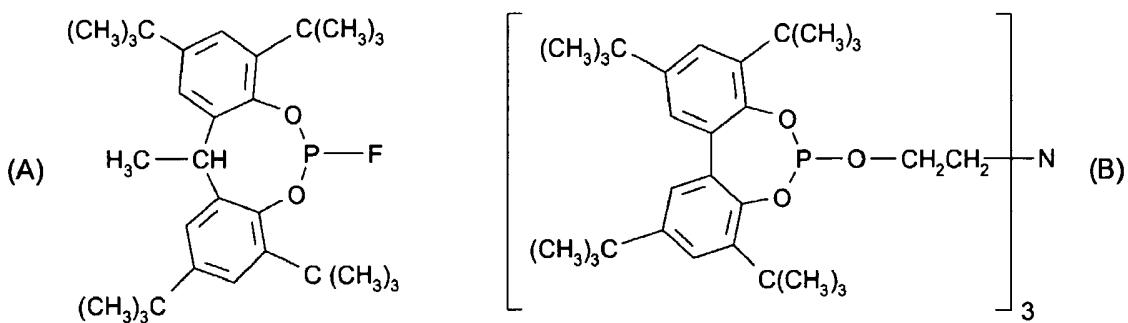
10 4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphites, phenyl dialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol 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, tristearyl 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, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-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, 2,2',2"-nitrilo[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.

15

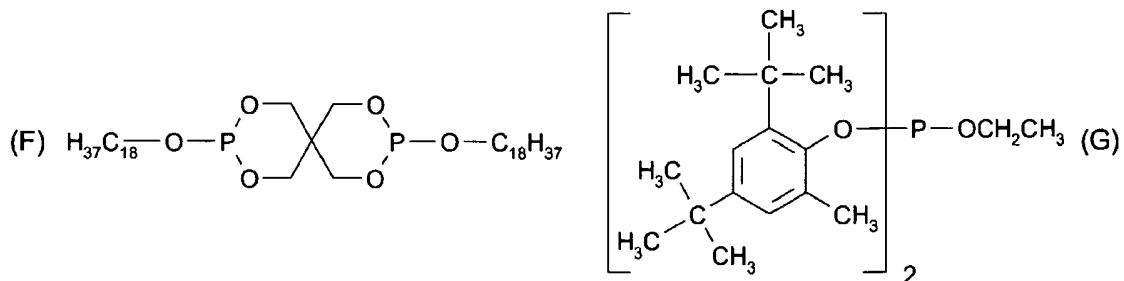
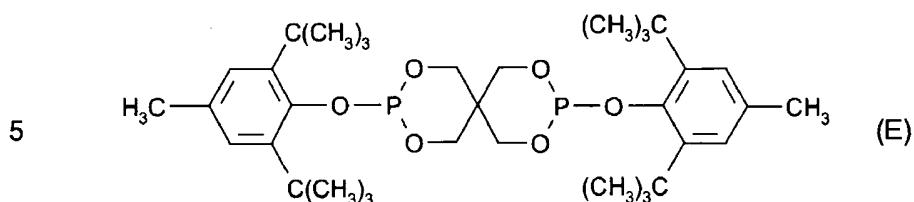
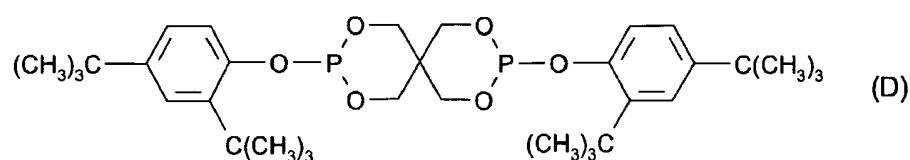
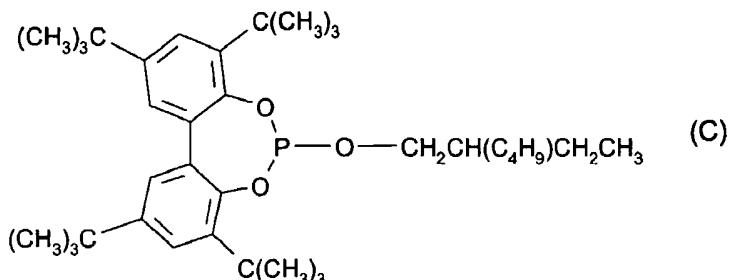
20

Especially preferred are the following phosphites:

25 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-
10 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.

15 6. Nitrones, for example N-benzyl-alpha-phenyl-nitron, N-ethyl-alpha-methyl-nitron, N-octyl-alpha-heptyl-nitron, N-lauryl-alpha-undecyl-nitron, N-tetradecyl-alpha-tridecyl-nitron, N-

hexadecyl-alpha-pentadecyl-nitrone, N-octadecyl-alpha-heptadecyl-nitrone, N-hexadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-pentadecyl-nitrone, N-heptadecyl-alpha-heptadecyl-nitrone, N-octadecyl-alpha-hexadecyl-nitrone, nitrone derived from N,N-dialkylhydroxylamine derived from hydrogenated tallow amine.

5

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-mercapto-10 benzimidazole, zinc dibutyldithiocarbamate, dioctadecyl disulfide, pentaerythritol tetrakis(β -dodecylmercapto)propionate.

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

15

10. Basic co-stabilizers, 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.

25 11. Nucleating agents, for example inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, 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).

30 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.

Suitable lubricants are for example:

montan wax, fatty acid esters, PE waxes, amide waxes, polyol partial esters, partially saponified PE waxes, so-called complex ester chloroparaffins, glycerol esters, alkaline earth metal soaps or fatty ketones, such as described in DE4204887. Suitable lubricants are also described in "Taschenbuch der Kunststoffadditive", editors R. Gächter and H. Müller, Hanser Verlag, 3rd edition, 1990, pages 443-503. Other lubricant embodiments, in particular combinations of lubricants, are to be found in EP 0062813 and EP 0336289.

The instant composition 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, phosphite and phosphonite stabilizers, benzofuranone stabilizers, UV absorbers of the 2-(2'-hydroxyphenyl)benzotriazole and 2-(2-hydroxyphenyl)-1,3,5-triazine classes, and sterically hindered amines.

The compositions of this invention may be prepared by known methods, for example by mixing the cited additives and optional further additives with the polymer using appliances

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such as calenders, mixers, kneaders, extruders and the like. The additives can be added singly or in admixture with each other. It is also possible to use masterbatches. For masterbatches, the carrier polymer is not necessarily a polylactic acid polymer. In such operations, the carrier polymer can be used in the form of powder, granules, solutions, 5 suspensions or in the form of latices.

The flame retardant finished polymers of the invention may be brought into the desired form by known methods. Such methods are, for example, calendering, extruding, spray coating, spinning, compression melting, rotational casting, thermoforming or extrusion 10 blowing. The flame retardant finished polymer can also be processed into foamed articles.

The finished flame retardant polylactic acid polymer articles are for example fibers, films, molded articles and foamed articles.

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

20 Further, the instant invention pertains to a process for imparting light stability and flame retardancy to a polylactic acid polymer substrate, which process comprises adding to said polymer substrate a synergistic mixture of

25 (i) at least one sterically hindered amine stabilizer and
(ii) at least one conventional flame retardant selected from the group consisting of the organohalogen, phosphorus containing, isocyanurate and melamine based flame retardants.

30 A molded polylactic acid polymer article made flame retardant by the incorporation therein of a synergistic mixture of

(i) at least one sterically hindered amine stabilizer and

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(ii) at least one conventional flame retardant selected from the group consisting of the organohalogen, phosphorus containing, isocyanurate and melamine based flame retardants is another object of the invention.

5 Of interest are molded polylactic polymer articles, wherein the component (i) is selected from the group consisting of suitable hindered amines as mentioned above.

Also of interest are molded polylactic polymer articles, wherein the component (ii) is selected from the group consisting of conventional flame retardants as mentioned above.

10

It is also contemplated that 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.

15

The effective flame retarding amount of components (i) and (ii) 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

25 Coadditives found particularly useful for use with the instant combination of components (i) and (ii) in present flame retardant compositions are as follows:

UV absorbers:

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

5 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.);

10 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.);

15 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, (TINUVIN® 120, Ciba Specialty Chemicals Corp.);

20 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).

20

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 polymer substrate unless otherwise indicated.

25

Abbreviations:

v parts by volume

w parts by weight

$^1\text{Hnmr}$ nuclear magnetic resonance (NMR) of ^1H

30 m/z mass spectrometry (atomic units)

amu molecular weight in g/mol (= atomic units)

PLA polylactic acid

Test Methods

5 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;

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

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

ASTM D 2633-82, burn test.

15

Test compounds

20 Hindered amines of present component (i):
NOR1 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine;
NOR2 bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
NOR3 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxyethylamino-s-triazine;
NOR3 bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
NOR4 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-chloro-s-triazine;
NOR5 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine;
NOR6 1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine;
30 NOR7 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine;
NOR8 bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
NOR9 bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate;

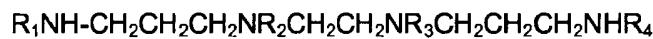
- 54 -

NOR10 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino}-6-(2-hydroxyethylamino)-s-triazine;

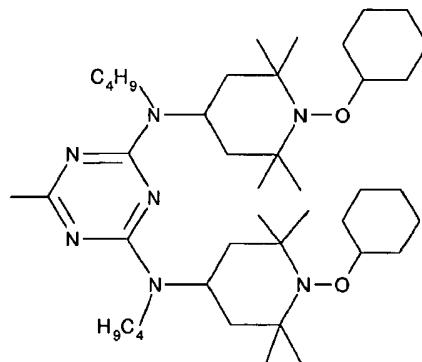
NOR11 the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine) [CAS Reg.

5 No. 191680-81-6];

NOR11 is represented as a mixture of compounds with main component of the formula



10 wherein 3 of R_1 , R_2 , R_3 and R_4 are residues of formula



and 1 of R_1 , R_2 , R_3 and R_4 is

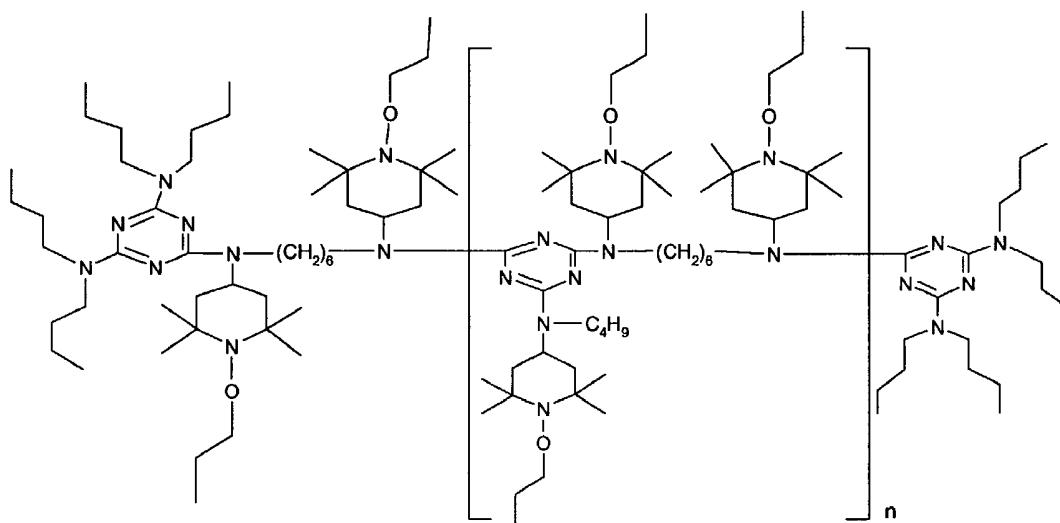
hydrogen

(NOR11 is a high molecular weight compound disclosed in example 3 of U.S. Pat. No. 5,844,026); and

15

NOR12 the compound of formula

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in which n is from 1 to 15.

Conventional flame retardants of component (ii):

5

DBDPO is decabromodiphenyl oxide,

- FR1 tris[3-bromo-2,2-bis(bromomethyl)propyl] phosphate, (PB 370®, FMC Corp.),
- FR2 ammonium polyphosphate (APP),
- 10 FR3 tetrabromobisphenol A bis(2,3-dibromopropyl ether) (PE68),
- FR4 ammonium polyphosphate/synergist blend, HOSTAFLAM® AP750,
- FR5 decabromodiphenyl oxide (DBDPO; obtained from Dead Sea Bromine),
- FR6 ethylene bis-(tetrabromophthalimide), (SAYTEX® BT-93),
- FR7 melamine phosphate, MELAPUR® P 46,
- 15 FR8 ammonium polyphosphate, EXOLIT® AP752,
- FR9 tris-(2,3-dibromopropyl)-isocyanurate,
- FR10 hexabromocyclododecane,
- FR11 melamine cyanurate, MELAPUR® MC,
- FR12 melamine borate,
- 20 FR13 melamine polyphosphate MELAPUR® 200 and
- FR14 melamine pyrophosphate.

Compounds NOR2, NOR7, NOR11, NOR12 are commercial stabilizers

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available from Ciba Specialty Chemicals. MELAPUR products are available from Ciba Specialty Chemicals.

Example 1

5

Polylactic acid polymer resin is blended with test additives by using a Turbula mixer for 15-20 minutes. Total formulation size is 1000g. The mixtures are then extruded with a 27 mm Leistritz twin screw extruder at 160-190°C. The obtained resin is palletized with a cutter. The compounded pellets are then injection molded into 5" x 0.5" x 0.125" bars. Flame

10 retardancy is measured by the UL 94 test. Results are below. Additives are weight percent based on the total formulation. Two sets of tests are performed.

- 57 -

	NOR11	FR1	FR5	rating
5	---	---	---	fail
	0.25	---	---	fail
	0.5	---	---	V2
	1.0	---	---	fail
	---	5	---	fail
	---	10	---	V2
10	---	---	5	V2
	---	---	10	V2
	1.0	5	---	V0
	0.25	10	---	V0
	0.25	---	10	V0
15	NOR11	FR1	FR5	rating
	---	---	---	fail
	0.25	---	---	fail
	0.5	---	---	fail
	1.0	---	---	V2
	---	5	---	V2
	---	---	2.5	fail
	---	---	5.0	V2
	---	---	10	V2
	0.5	5	---	V0
25	0.5	---	10	V0

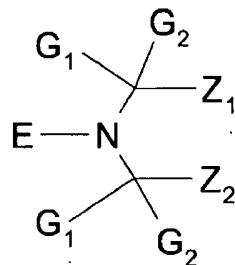
The flame retardant combination of a present hindered amine and a conventional flame retardant is synergistic in polylactic acid.

30 NOR11 may be replaced with one or more hindered amines selected from NOR1-NOR10 and NOR12. FR1 and FR5 may be replaced by one or more flame retardants selected from FR2-FR4 and FR6-FR14.

WHAT IS CLAIMED IS:

1. A flame retardant polylactic acid polymer composition which comprises
 - 5 a polylactic acid polymer substrate and a synergistic mixture of
 - (i) at least one sterically hindered amine stabilizer and
 - (ii) at least one conventional flame retardant selected from the group consisting of
 - 10 the organohalogen, phosphorus containing, isocyanurate and melamine based flame retardants.

2. A composition according to claim 1 in which the stabilizers of component (i) are of
 - 15 the formula



where

- 20 G_1 and G_2 are independently alkyl of 1 to 8 carbon atoms or are together pentamethylene,
- 25 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, $-O-CO-OZ_3$, $-O-Si(Z_4)_3$, $-O-PO(OZ_5)_2$ 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 $-O-T-(OH)_b$,

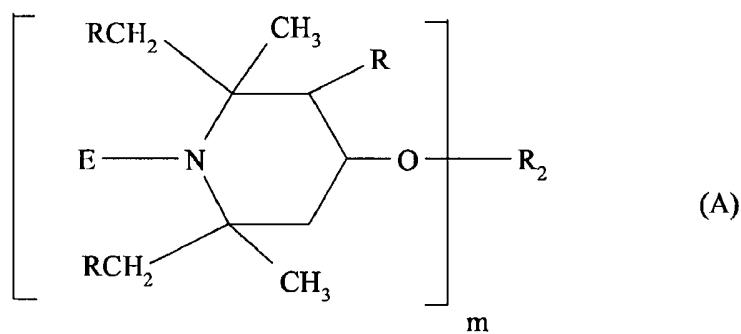
- 59 -

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

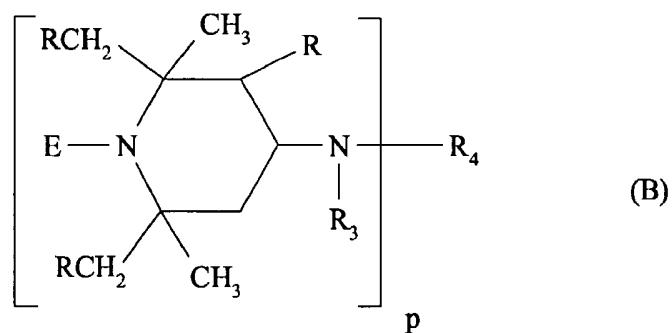
b is 1, 2 or 3 with the proviso that b cannot exceed the number of carbon atoms in T, and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T.

10

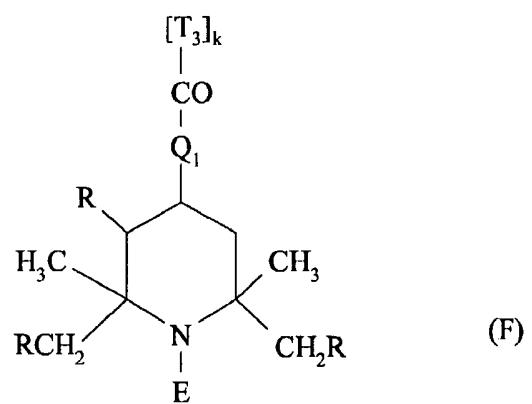
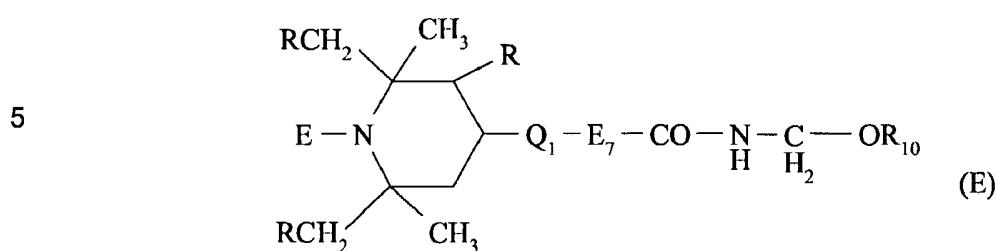
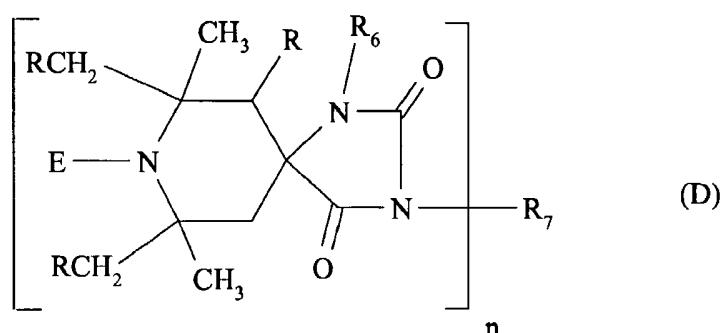
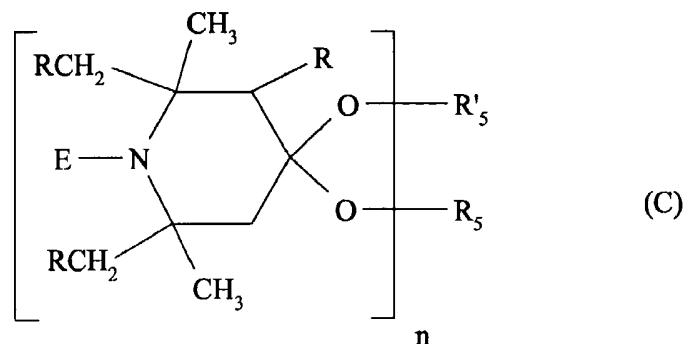
3. A composition according to claim 1 in which the stabilizers of component (i) are of the formula A-R



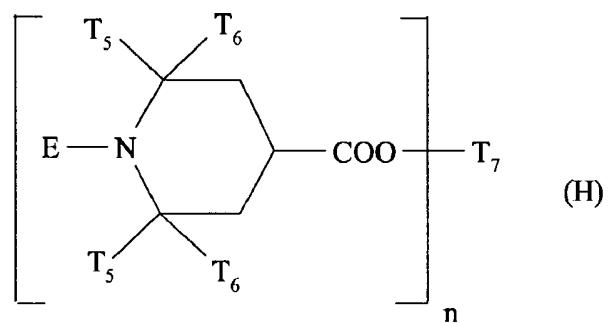
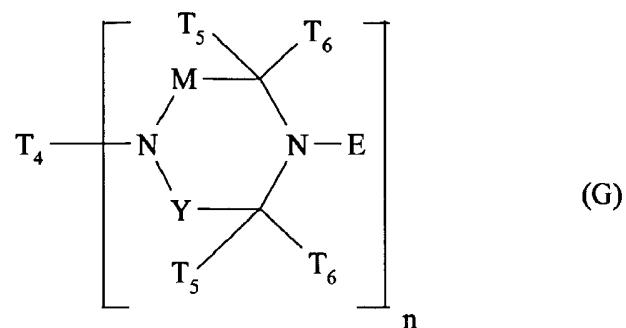
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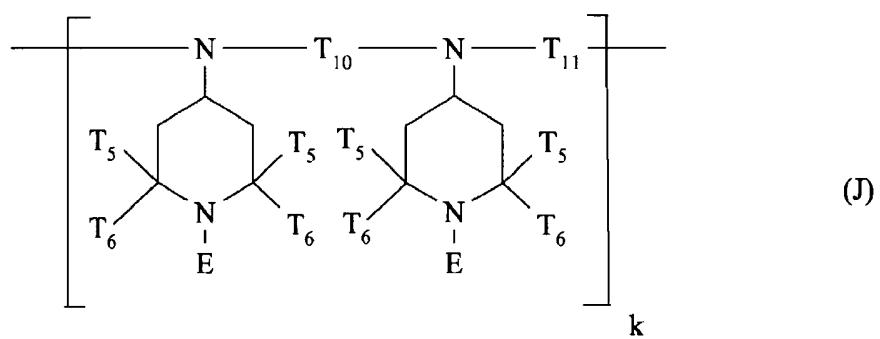
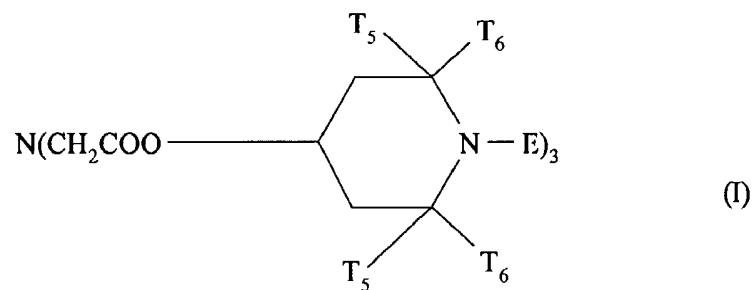
- 60 -



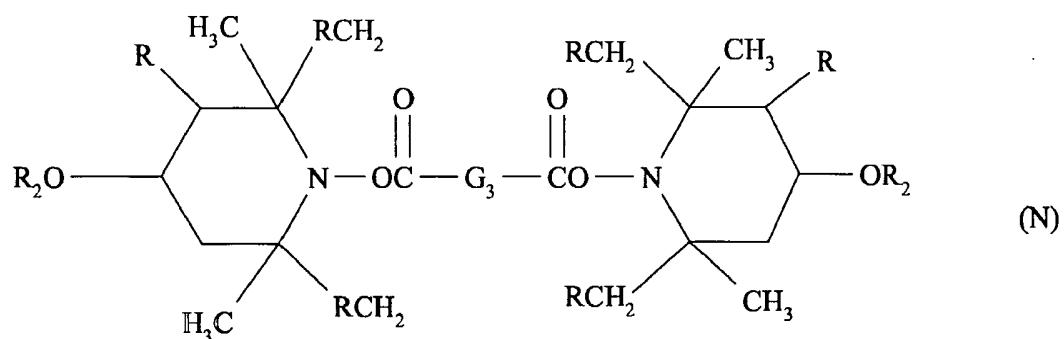
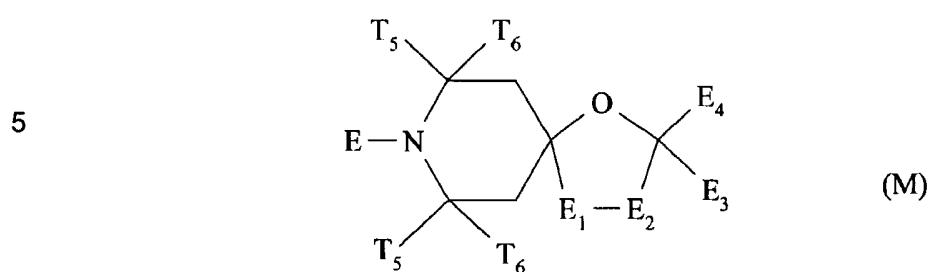
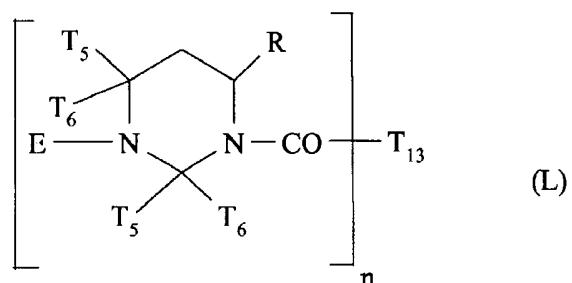
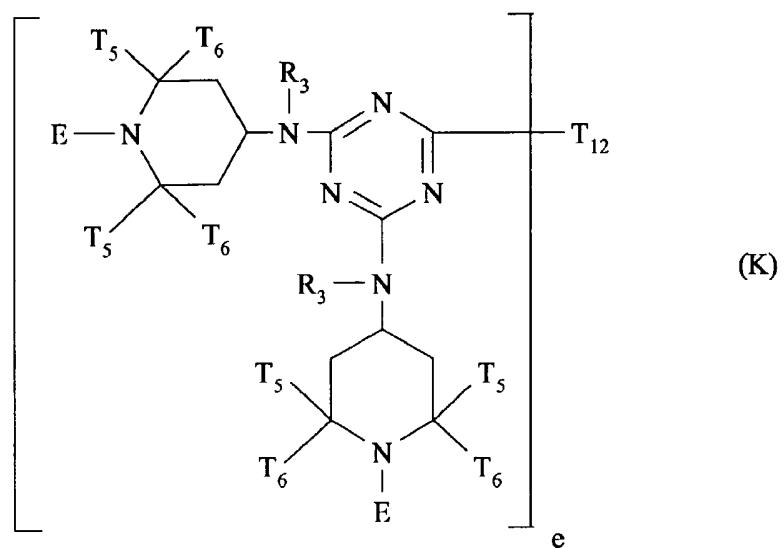
- 61 -



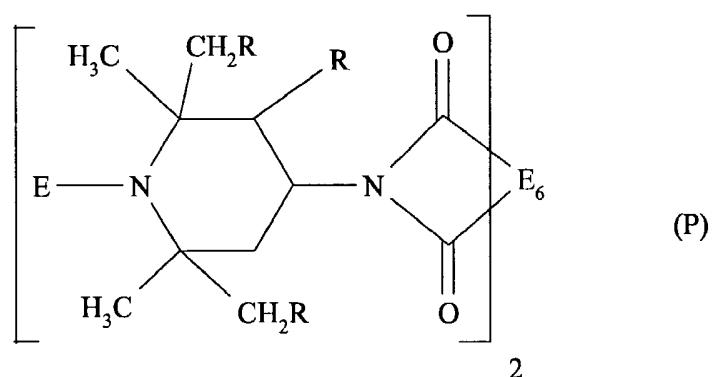
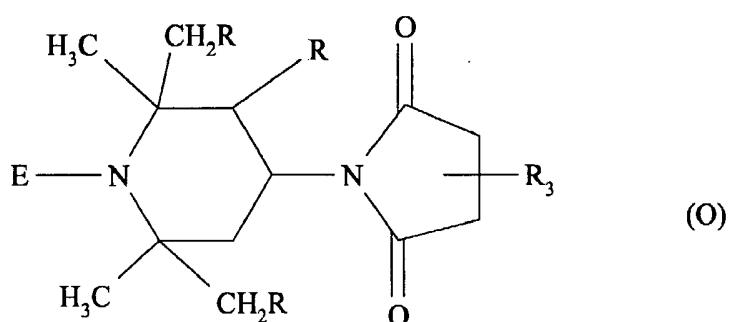
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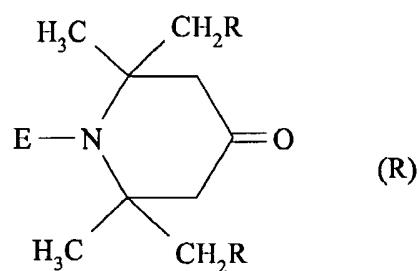
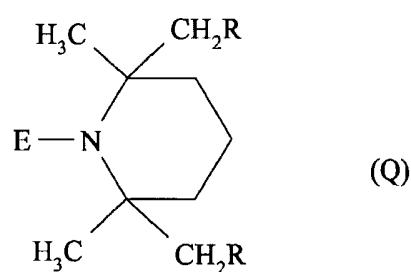
- 62 -



- 63 -



5



10 wherein

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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 5
 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,
 10 and when b is 2 or 3, each hydroxyl group is attached to a different carbon atoms of T;

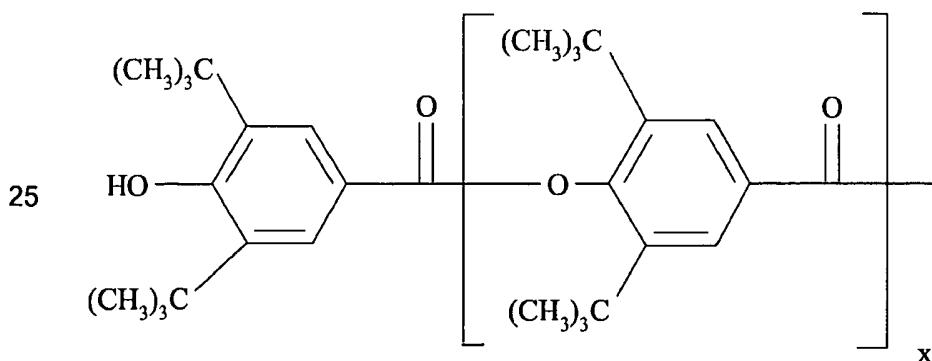
R is hydrogen or methyl,

m is 1 to 4,

15

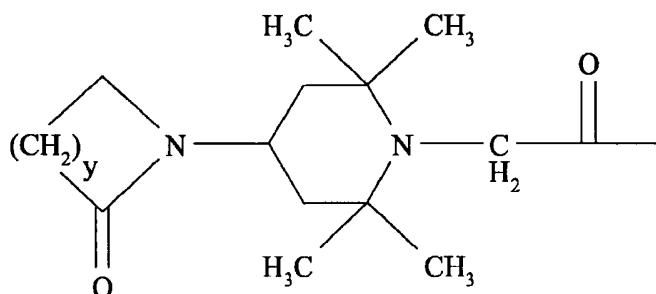
when m is 1,

R₂ is hydrogen, C₁-C₁₈alkyl or said alkyl optionally interrupted by one or more oxygen
 atoms, C₂-C₁₂alkenyl, C₆-C₁₀aryl, C₇-C₁₈aralkyl, glycidyl, a monovalent acyl radical of an
 20 aliphatic, cycloaliphatic or aromatic carboxylic acid, or a carbamic acid, 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,

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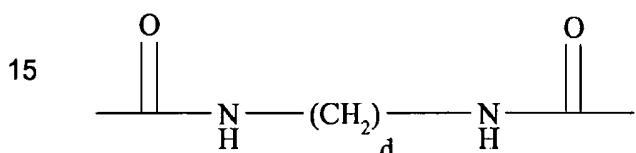
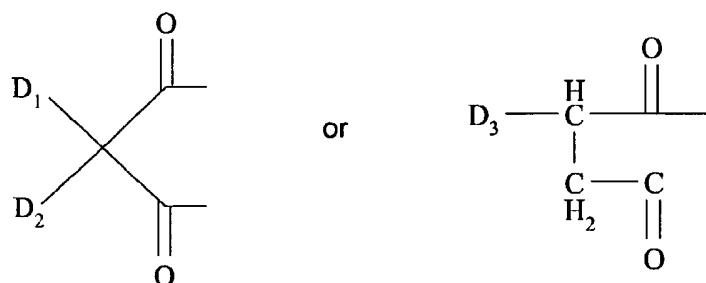


wherein y is 2-4;

5 when m is 2,

R_2 is C_1-C_{12} alkylene, C_4-C_{12} alkenylene, xylylene, a divalent acyl radical of an aliphatic, cycloaliphatic, araliphatic or aromatic dicarboxylic acid or of a dicarbamic acid, of an aliphatic dicarboxylic acid having 2-18 C atoms, of a cycloaliphatic or aromatic dicarboxylic acid

10 having 8-14 C atoms, or of an aliphatic, cycloaliphatic or aromatic dicarbamic acid having 8-14 C atoms;



wherein D_1 and D_2 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, D_3 is hydrogen, or an alkyl or alkenyl radical containing up to 18 carbon atoms, and d is 0-20;

- 66 -

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

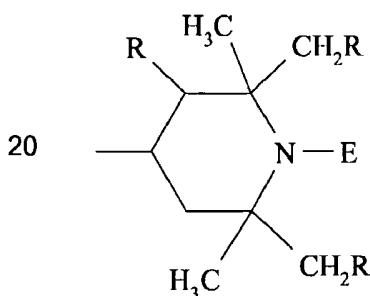
when m is 4, R₂ is a tetravalent acyl radical of a saturated or unsaturated aliphatic or aromatic tetracarboxylic acid including 1,2,3,4-butanetetracarboxylic acid, 1,2,3,4-but-2-ene-tetracarboxylic, and 1,2,3,5- and 1,2,4,5-pantanetetracarboxylic acid;

p is 1, 2 or 3,

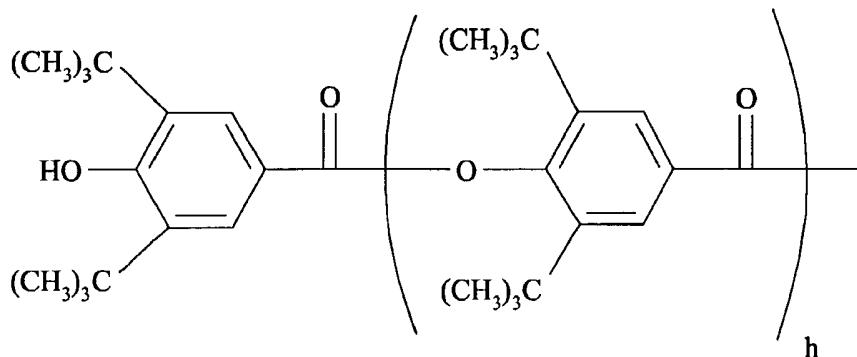
10 R₃ is hydrogen, C₁-C₁₂alkyl, C₅-C₇cycloalkyl, C₇-C₉aralkyl, C₂-C₁₈alkanoyl, C₃-C₅alkenoyl or benzoyl;

when p is 1,

15 R₄ is hydrogen, C₁-C₁₈alkyl, C₅-C₇cycloalkyl, C₂-C₆alkenyl, 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



or



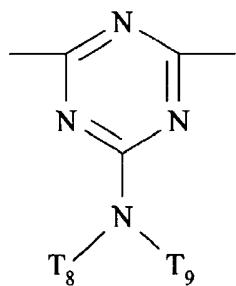
where h is 0 or 1,

5 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,

10 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

15 R_4 is



20 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;

when p is 3,

R₄ is 2,4,6-triazinyl,

n is 1 or 2,

5

when n is 1,

R₅ and R'₅ are independently C₁-C₁₂ alkyl, C₂-C₁₂ alkenyl, C₇-C₁₂ aralkyl, or R₅ is also hydrogen, or R₅ and R'₅ together are C₂-C₈alkylene or hydroxyalkylene or C₄-

10 C₂₂acyloxyalkylene;

when n is 2,

R₅ and R'₅ together are (-CH₂)₂C(CH₂-)₂;

15

R₆ is hydrogen, C₁-C₁₂alkyl, allyl, benzyl, glycidyl or C₂-C₆alkoxyalkyl;

when n is 1,

20

R₇ is hydrogen, C₁-C₁₂alkyl, C₃-C₅alkenyl, C₇-C₉aralkyl, C₅-C₇cycloalkyl, C₂-C₄hydroxyalkyl, C₂-C₆alkoxyalkyl, C₆-C₁₀aryl, glycidyl, a group of the formula -(CH₂)_t-COO-Q or of the formula -(CH₂)_t-O-CO-Q wherein t is 1 or 2, and Q is C₁-C₄alkyl or phenyl; or

when n is 2,

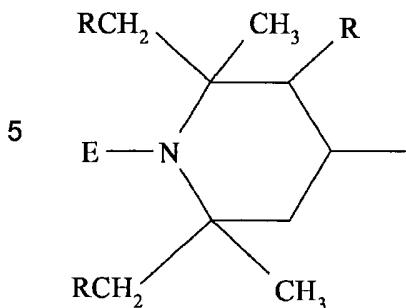
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R₇ is C₂-C₁₂alkylene, C₆-C₁₂arylene, a group -CH₂CH(OH)-CH₂-O-X-O-CH₂-CH(OH)-CH₂- wherein X is C₂-C₁₀alkylene, C₆-C₁₅arylene or C₆-C₁₂cycloalkylene, or a group -CH₂CH(OZ')CH₂-(OCH₂-CH(OZ')CH₂)₂- wherein Z' is hydrogen, C₁-C₁₈alkyl, allyl, benzyl, C₂-C₁₂alkanoyl or benzoyl;

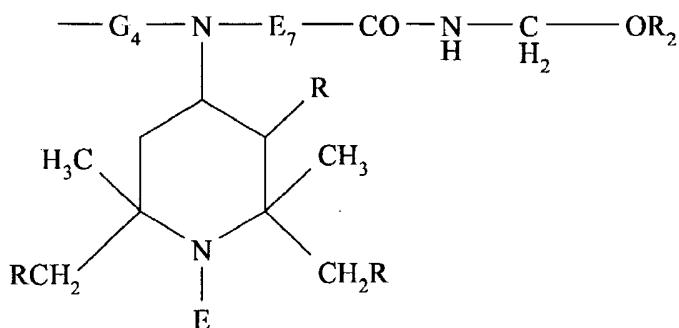
30

Q₁ is -N(R₈)- or -O-; E₇ is C₁-C₃ alkylene, the group -CH₂-CH(R₉)-O- wherein R₉ is hydrogen, methyl or phenyl, the group -(CH₂)₃-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 $-CH_2-CH(R_9)-OH$ wherein R_9 has the meaning defined above; a group of the formula



or a group of the formula



10

wherein G_4 is C_2-C_6 alkylene or C_6-C_{12} arylene; or R_8 is a group $-E_7-CO-NH-CH_2-OR_{10}$;

15 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; 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,

20

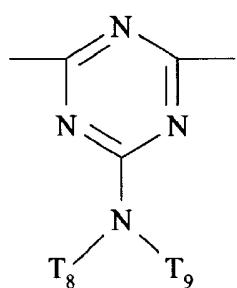
T_6 is methyl or ethyl, or T_5 and T_6 together are tetramethylene or pentamethylene,

- 70 -

M and Y are independently methylene or carbonyl, and T₄ is ethylene where n is 2;

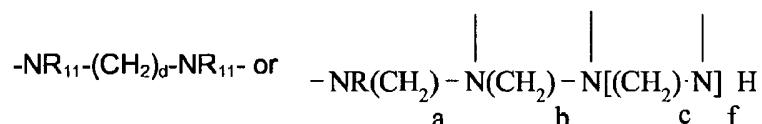
T₇ is the same as R₇,

5 T₁₀ and T₁₁ are independently alkylene of 2 to 12 carbon atoms, or T₁₁ is

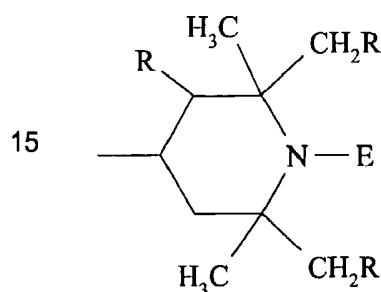


T₁₂ is piperazinyl,

10



where R₁₁ is the same as R₃ or is also



a, b and c are independently 2 or 3, and d is 0 or 1; and

e is 2, 3 or 4;

20

T₁₃ is the same as R₂ with the proviso that T₁₃ cannot be hydrogen when n is 1;

- 71 -

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,

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,

10 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,

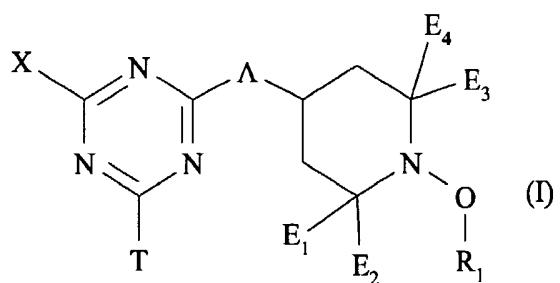
15 E_6 is an aliphatic or aromatic tetravalent radical,

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

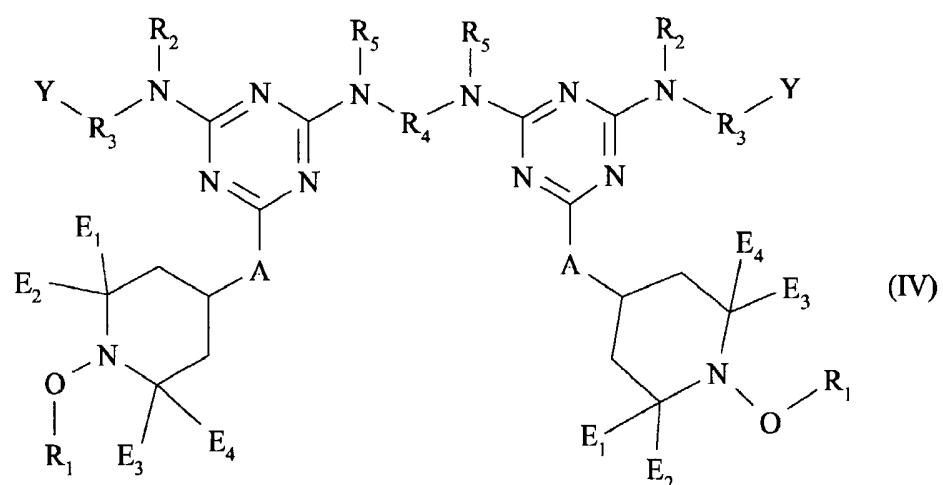
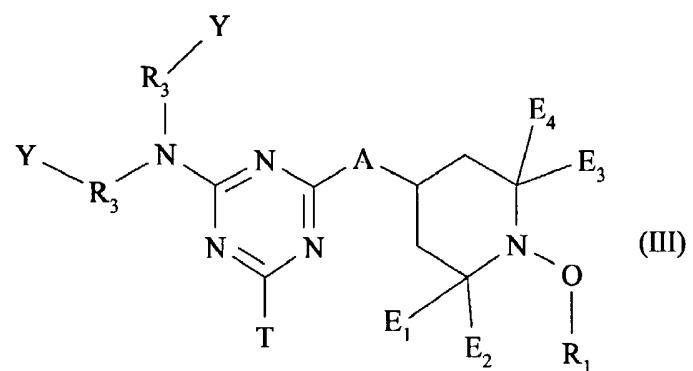
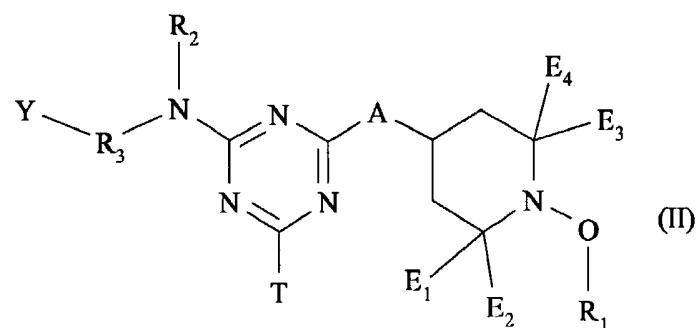
20 G_1 a direct bond, C_1-C_{12} alkylene, phenylene or $-NH-G'-NH$ wherein G' is C_1-C_{12} alkylene; or

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

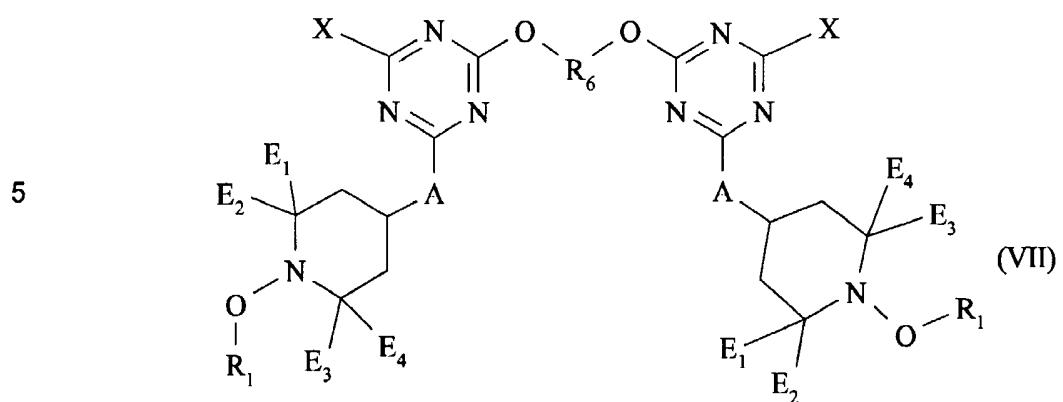
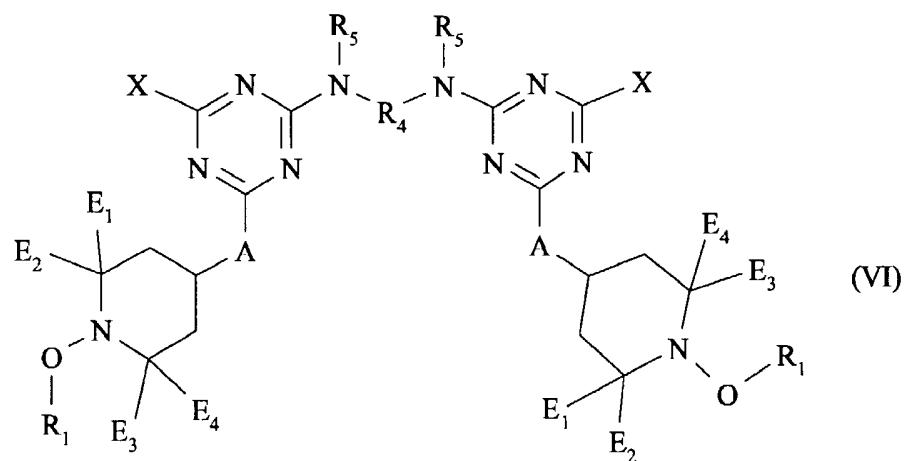
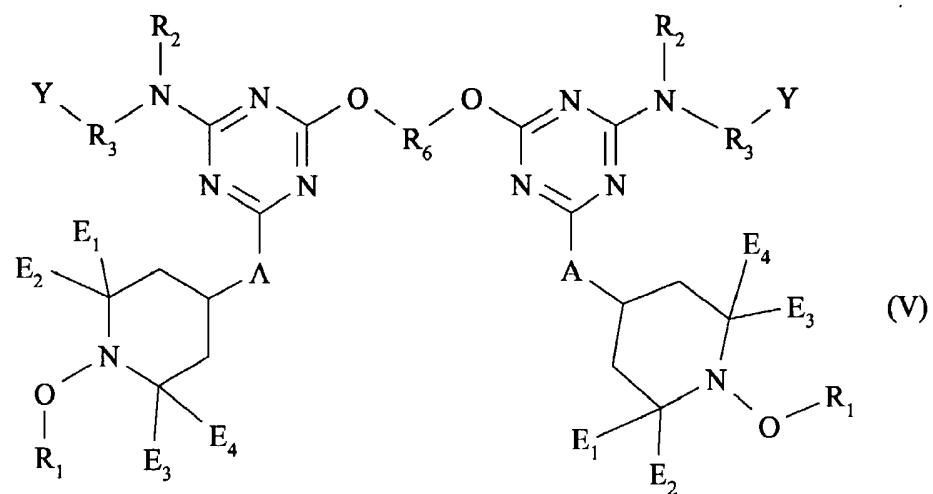
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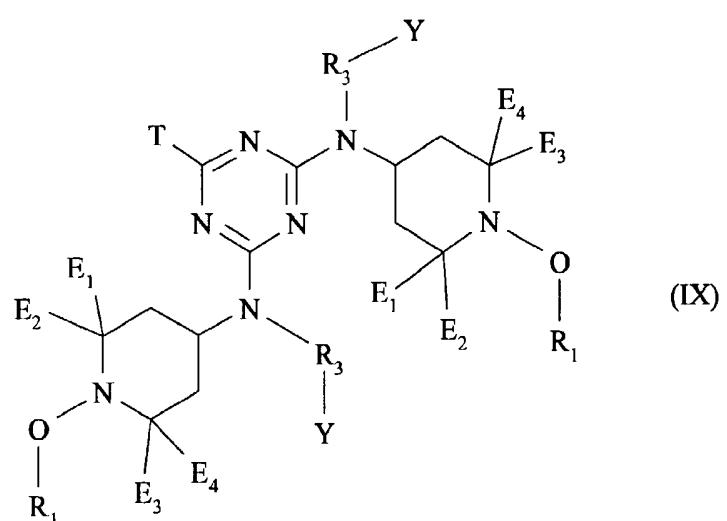
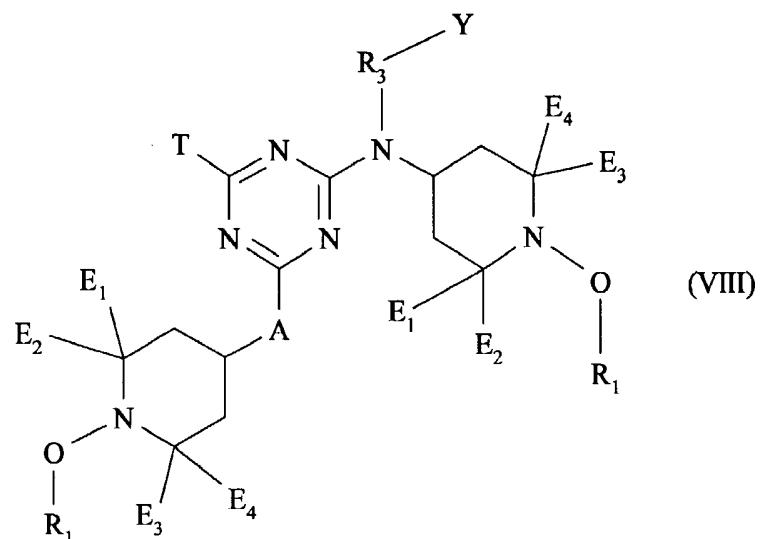
- 72 -



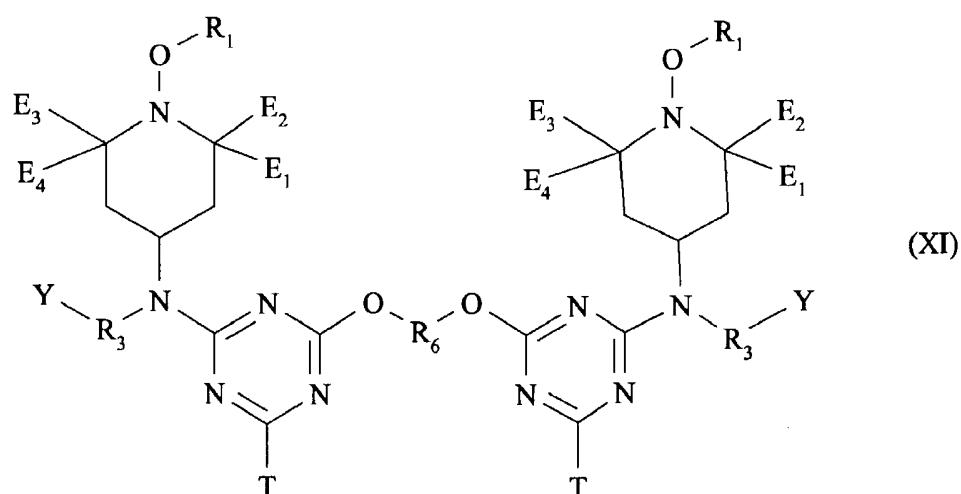
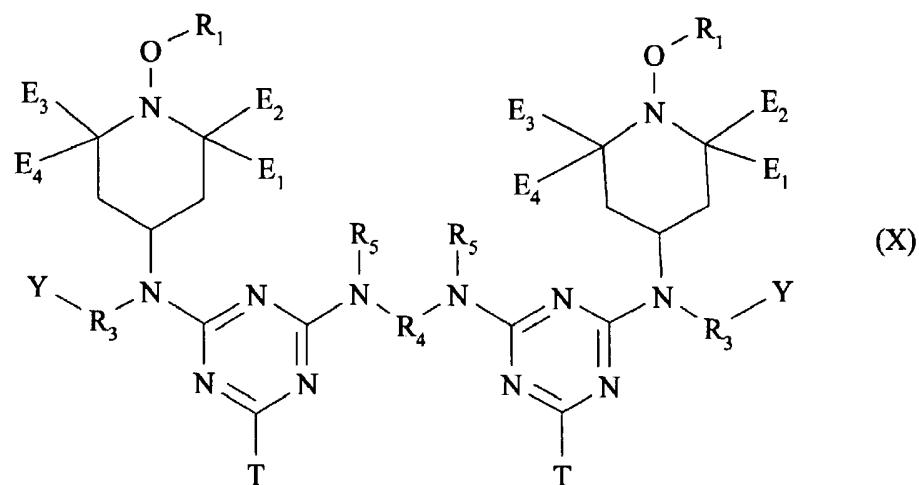
- 73 -



- 74 -



- 75 -



5 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,

10

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.

15

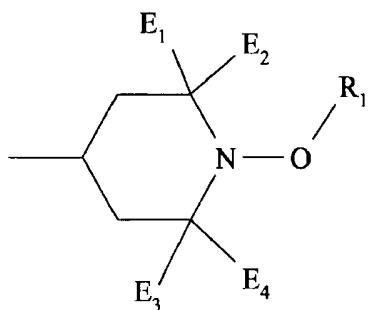
- 76 -

R₂ is hydrogen or a linear or branched chain alkyl of 1 to 12 carbon atoms,

R₃ is alkylene of 1 to 8 carbon atoms, or R₃ is -CO-, -CO-R₄-, -CONR₂- or -CO-NR₂-R₄-,

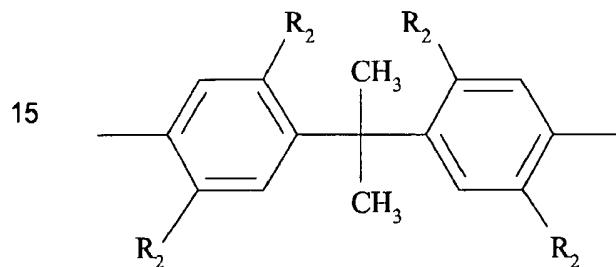
5 R₄ is alkylene of 1 to 8 carbon atoms,

R₅ is hydrogen, a linear or branched chain alkyl of 1 to 12 carbon atoms, or



10 or when R₄ is ethylene, two R₅ methyl substituents can be linked by a direct bond so that the triazine bridging group -N(R₅)-R₄-N(R₅)- is a piperazin-1,4-diyli moiety,

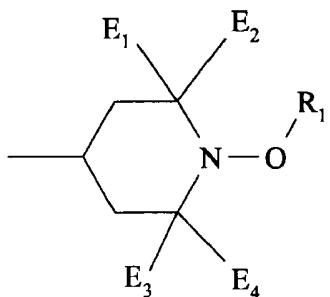
R₆ is alkylene of 2 to 8 carbon atoms or R₆ is



with the proviso that Y is not -OH when R₆ is the structure depicted above,

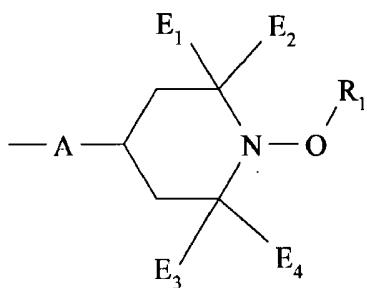
A is -O- or -NR₇- where R₇ is hydrogen, a straight or branched chain alkyl of 1 to 12 carbon atoms, or R₇ is

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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(R₂)₂ with the stipulation that R₂ is not hydrogen, or T is

5



X is -NH₂, -NCO, -OH, -O-glycidyl, or -NHNH₂, and

10 Y is -OH, -NH₂, -NHR₂ where R₂ is not hydrogen; or Y is -NCO, -COOH, oxiranyl, -O-glycidyl, or -Si(OR₂)₃; or the combination R₃-Y- is -CH₂CH(OH)R₂ where R₂ is alkyl or said alkyl interrupted by one to four oxygen atoms, or R₃-Y- is -CH₂OR₂;

or

15

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'-ethylenediaminodipropylamine; N,N',N'''-tris{2,4-bis[(1-hydrocarbyloxy-2,2,6,6-tetramethylpiperidin-4-yl)alkylamino]-s-triazin-6-yl}-3,3'-ethylenediaminodipropylamine, and bridged derivatives as described by formulas I,

20 II, IIA and III



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T-E₁-T₁ (II)

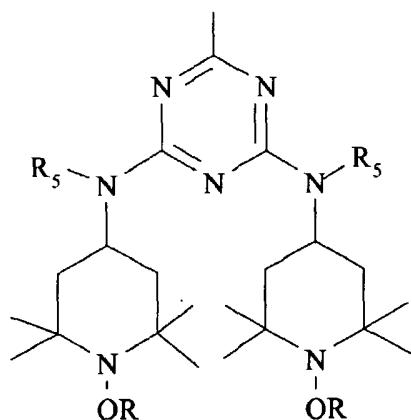
T-E₁ (IIA)

5 G-E₁-G₁-E₁-G₂ (III)

where in the tetraamine of formula I

10 R₁ and R₂ are the s-triazine moiety E; and one of R₃ and R₄ is the s-triazine moiety E with the other of R₃ or R₄ being hydrogen,

E is



15

R is methyl, propyl, cyclohexyl or octyl,

R₅ is alkyl of 1 to 12 carbon atoms,

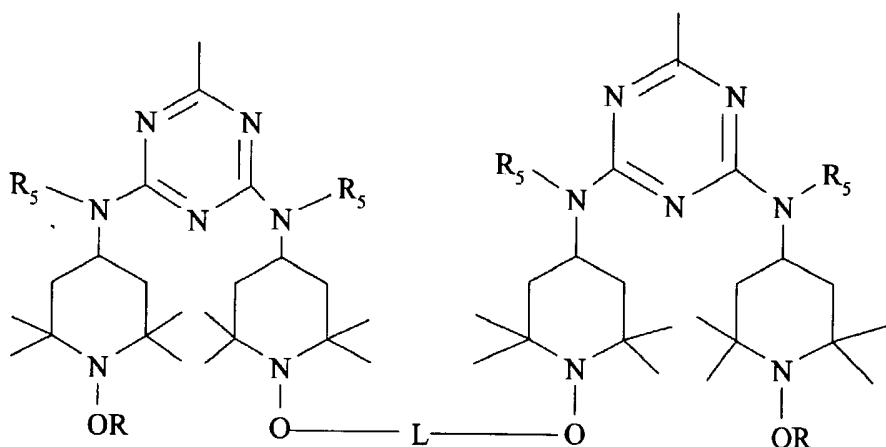
20 where in the compound of formula II or IIA when R is propyl, cyclohexyl or octyl,

T and T₁ are each a tetraamine substituted by R₁-R₄ as is defined for formula I, where

(1) one of the s-triazine moieties E in each tetraamine is replaced by the group E₁,
25 which forms a bridge between two tetraamines T and T₁,

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E_1 is



5

or

10 (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,

15

L is propanediyl, cyclohexanediyI or octanediyI;

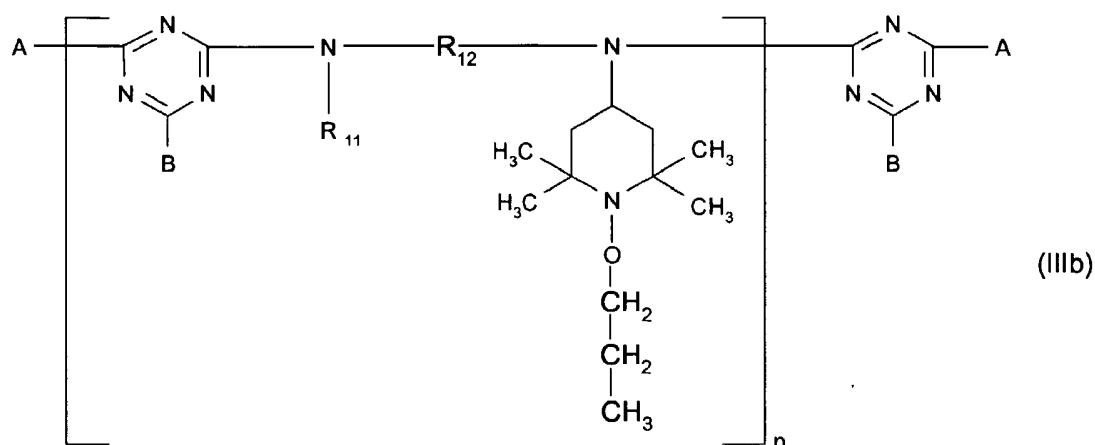
where in the compound of formula III

20 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 ;

- 80 -

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

5 or the hindered amine is a compound of the formula IIIb

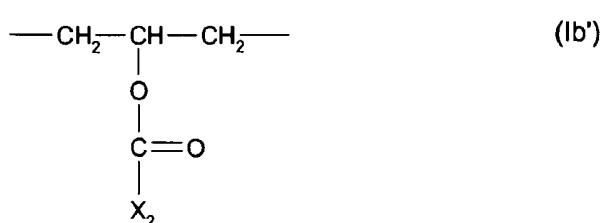


in which the index n ranges from 1 to 15;

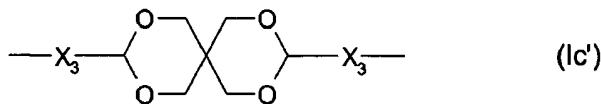
10

R₁₂ is C₂-C₁₂alkylene, C₄-C₁₂alkenylene, C₅-C₇cycloalkylene, C₅-C₇cycloalkylene-di(C₁-C₄alkylene), C₁-C₄alkylenedi(C₅-C₇cycloalkylene), phenylenedi(C₁-C₄alkylene) or C₄-C₁₂alkylene interrupted by 1,4-piperazinediyl, -O- or >N-X₁ with X₁ being C₁-C₁₂acyl or (C₁-C₁₂alkoxy)carbonyl or having one of the definitions of R₁₄ given below except hydrogen;

15 or R₁₂ is a group of the formula (Ib') or (Ic');



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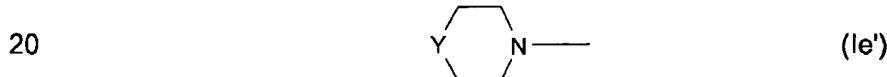


with m being 2 or 3,

5 X_2 being C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl which is unsubstituted or substituted by 1, 2 or 3
 C_1-C_4 alkyl; phenyl which is unsubstituted or substituted by 1, 2 or 3 C_1-C_4 alkyl or
 C_1-C_4 alkoxy; C_7-C_9 phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3
 C_1-C_4 alkyl; and

10 the radicals X_3 being independently of one another C_2-C_{12} alkylene;

15 R_{13} , R_{14} and R_{15} , which are identical or different, are hydrogen, C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl which is unsubstituted or substituted by 1, 2 or 3 C_1-C_4 alkyl; C_3-C_{18} alkenyl, phenyl which is unsubstituted or substituted by 1, 2 or 3 C_1-C_4 alkyl or C_1-C_4 alkoxy; C_7-C_9 phenylalkyl which is unsubstituted or substituted on the phenyl by 1, 2 or 3 C_1-C_4 alkyl; tetrahydrofurfuryl or
 C_2-C_4 alkyl which is substituted in the 2, 3 or 4 position by -OH, C_1-C_8 alkoxy, di(C_1-C_4 alkyl)amino or a group of the formula (Ie');

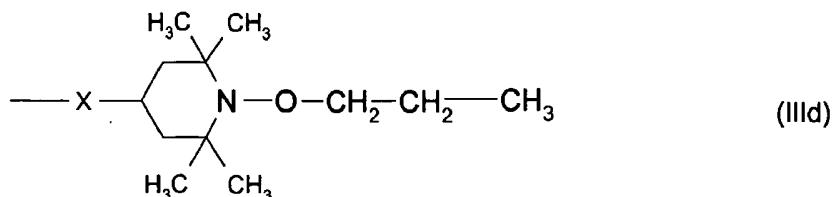


with Y being -O-, -CH₂-, -CH₂CH₂- or >N-CH₃,

or -N(R_{14})(R_{15}) is additionally a group of the formula (Ie');

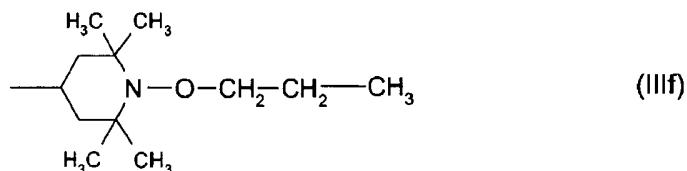
25 the radicals A are independently of one another -OR₁₃, -N(R_{14})(R_{15}) or a group of the formula (IIId);

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X is -O- or >N-R₁₆;

5 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 (IIIe),



10 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

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

4. A composition according to claim 1 wherein the hindered amine stabilizers of component (i) are selected from the group consisting of

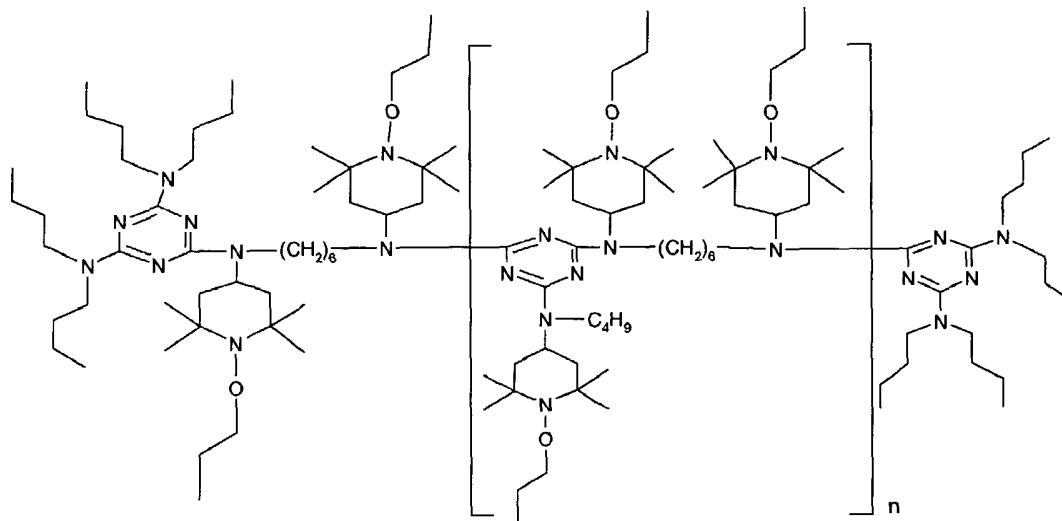
20 1-cyclohexyloxy-2,2,6,6-tetramethyl-4-octadecylaminopiperidine;
 bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-(2-hydroxyethylamino-s-triazine;

25 bis(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)butylamino]-6-chloro-s-triazine;
 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine;

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1-(2-hydroxy-2-methylpropoxy)-4-oxo-2,2,6,6-tetramethylpiperidine;
 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine;
 bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) sebacate;
 bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) adipate;
 5 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butylamino}-6-(2-hydroxyethylamino)-s-triazine;
 the reaction product of 2,4-bis[(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidin-4-yl)-butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine) and

10 the compound of formula



in which n is from 1 to 15.

15 5. A composition according to claim 1 in which the hindered amine stabilizers of component (i) are present from 0.05% to 20% by weight based on the weight of the polylactic acid polymer substrate.

20 6. A composition according to claim 1 in which the conventional flame retardants of component (ii) are selected from the group consisting of

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,
5 tetrachlorophthalic acid,
tetrabromophthalic acid,
bis-(N,N'-hydroxyethyl)tetrachlorophenylene diamine,
poly- β -chloroethyl triphosponate mixture,
tetrabromobisphenol A bis(2,3-dibromopropyl ether),
10 brominated epoxy resin,
ethylene-bis(tetrabromophthalimide),
bis(hexachlorocyclopentadieno)cyclooctane,
chlorinated paraffins,
octabromodiphenyl ether,
15 hexachlorocyclopentadiene derivatives,
1,2-bis(tribromophenoxy)ethane,
tetrabromo-bisphenol A,
ethylene bis-(dibromo-norbornanedicarboximide),
bis-(hexachlorocyclopentadieno) cyclooctane,
20 polytetrafluorethylene
tris-(2,3-dibromopropyl)-isocyanurate, and
ethylene-bis-tetrabromophthalimide,
tetraphenyl resorcinol diphosphite,
tetrakis(hydroxymethyl)phosphonium sulfide,
25 diethyl-N,N-bis(2-hydroxyethyl)-aminomethyl phosphonate,
hydroxyalkyl esters of phosphorus acids,
ammonium polyphosphate,
resorcinol diphosphate oligomer,
phosphazene flame retardants,
30 ethylenediamine diphosphate,
polyisocyanurate,
esters of isocyanuric acid,
isocyanurates,
hydroxyalkyl isocyanurates,

melamine cyanurate,
melamine borate,
melamine phosphates,
melamine polyphosphates,
5 melamine pyrophosphates,
melamine ammonium polyphosphate,
melamine ammonium pyrophosphate,
phosphonates and their metal salts and
phosphinates and their metal salts.

10

7. A composition according to claim 1 in which the conventional flame retardants of component (ii) are present in an amount from 0.5% to 45% by weight based on the weight of the polylactic acid polymeric substrate.

15

8. A composition according to claim 1 further comprising acid scavengers selected from the group consisting of hydrotalcites and amorphous basic aluminum magnesium carbonates.

20

9. A composition according to claim 8 in which the acid scavengers are present from 0.1% to 1.0% by weight based on the polylactic acid polymer substrate.

25

10. A composition according to claim 1 comprising a further component selected from the group consisting of pigments, dyes, plasticizers, antioxidants, thixotropic agents, levelling assistants, basic costabilizers, nitrone stabilizers, amine oxide stabilizers, benzofuranone stabilizers, UV absorbers, sterically hindered amines, metal passivators, 30 metal oxides, organophosphorus compounds, hydroxylamines, and mixtures thereof.

11. A composition according to claim 1 comprising a further component selected from the group consisting of phenolic antioxidants, calcium stearate, zinc stearate, phosphite and phosphonite stabilizers, benzofuranone stabilizers, UV absorbers of the 2-(2'-

hydroxyphenyl)benzotriazole and 2-(2-hydroxyphenyl)-1,3,5-triazine classes, and sterically hindered amines.

5 **12. Use a synergistic mixture of**

(i) at least one sterically hindered amine stabilizer and

(ii) at least one conventional flame retardant selected from the group consisting of
10 the organohalogen, phosphorus containing, isocyanurate and melamine based flame
retardants
for imparting light stability and flame retardancy to a polylactic acid polymer substrate.

15 **13. A process for imparting light stability and flame retardancy to a polylactic acid**
polymer substrate, which process comprises adding to said polymer substrate

(i) at least one sterically hindered amine stabilizer,

20 (ii) at least one conventional flame retardant selected from the group consisting
of the organohalogen, phosphorus containing, isocyanurate and melamine based
flame retardants.

25 **14. A molded polylactic acid polymer article comprising a polylactic acid polymer**
substrate and a synergistic mixture of

(i) at least one sterically hindered amine stabilizer and

30 (ii) at least one conventional flame retardant selected from the group consisting
of the organohalogen, phosphorus containing, isocyanurate and melamine based
flame retardants.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/051436

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08K5/00

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)

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1 304 352 A (MATSUSHITA ELECTRIC IND CO LTD) 23 April 2003 (2003-04-23) paragraphs '0044!, '0045!, '0051!; example 9 claims 1,9,11 -----	1-14
A	EP 0 677 561 A (MITSUI TOATSU CHEMICALS) 18 October 1995 (1995-10-18) examples 4,9 claims 1,2 -----	1-14
A	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 23, 10 February 2001 (2001-02-10) -& JP 2001 164463 A (NICCA CHEMICAL CO LTD; KANEBO LTD), 19 June 2001 (2001-06-19) abstract -----	1-14
	-/-	

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
11 October 2004	15/10/2004
Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Russell, G

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/051436

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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