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(54) **MACROMOLECULAR ANTIOXIDANTS BASED ON DUAL TYPE MOIETY PER MOLECULE: STRUCTURES METHODS OF MAKING AND USING THE SAME**

MAKROMOLEKULARE ANTIOXIDANZIEN AUF BASIS EINES DOPPELTYP-ANTEILS PRO MOLEKÜL: STRUKTUREN, VERFAHREN ZUR HERSTELLUNG UND VERWENDUNG DAVON

ANTIOXYDANTS MACROMOLÉCULAIRES BASÉS SUR DEUX TYPES DE FRACTIONS PAR MOLÉCULE : STRUCTURES, LEURS PROCÉDÉS DE FABRICATION ET D'UTILISATION

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Description

GOVERNMENT SUPPORT

[0001] This invention was made with government support under IIP-1138520 from the National Science Foundation. The government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0002] Antioxidants are employed to prevent oxidation in a wide range of materials, for example, plastics, elastomers, lubricants, bio- and petroleum- based products (lubricants, gasoline, aviation fuels, and engine oils), cooking oil, cosmetics, processed food products, and the like. While many small molecule antioxidants exist, there is a continuing need for new antioxidants that have improved properties and thermal stability to function at high operating temperatures in a wide range of applications.

SUMMARY OF THE INVENTION

[0003] The present invention is defined by the appended claims. It relates to compounds containing dual functionalities of aromatic amines and hindered phenols that can be useful as stabilizers for organic materials, lubricants and petroleum based products, plastics and elastomers, cosmetics, foods and cooking oils, and other materials. In particular, the present invention pertains to highly effective antioxidant macromolecules described herein. This invention also reports an improved, highly efficient and economical process for the synthesis of amine (nitrogen) and sterically hindered phenol containing dual functional macromolecules. The design of macromolecules in this invention can incorporate at least two antioxidant moieties having different reactivities. The present invention also discloses their superior antioxidant performance compared to presently used commercial antioxidants. This is demonstrated especially in biobased lubricants and oils. In general one unique feature and design of the antioxidants described herein is their improved compatibility and performance in many oils and fuels including bio-, petroleum- and synthetic oils and fuels such gasoline, diesel, and biodiesel compared with currently available antioxidants.

[0004] The antioxidants described herein which are prepared by the disclosed processes in general are superior antioxidants (compared to currently available antioxidants) against oxidative, thermal degradation of organic materials. These macromolecular antioxidants generally have comparatively higher antioxidant activities along with improved thermal stability and performance in a wide range of materials including but not limited to plastics; elastomers; thermo-plastic elastomers; lubricants; petroleum, bio- and synthetic oil based products (lubricants, gasoline, aviation fuels, and engine oils, biolubricants; metal working fluids, hydraulic fluids, drilling fluids, marine lubricants, environmentally acceptable lubricants (EALs), grease, and bio-and synthetic-oil based grease); cooking oil; cosmetics; processed food products.

[0005] The processes of the present invention have many advantages which can allow improved synthesis of these macromolecular antioxidants. For example, the disclosed processes can be economically carried out in the melt phase without the presence of catalysts. Moreover, the processes described herein generally reduce or eliminate purification steps for the final product compared to existing syntheses, which can lead to a superior performance/cost ratio for the product and reduced amounts of waste.

DETAILED DESCRIPTION OF THE INVENTION

[0006] A description of preferred embodiments of the invention follows.

[0007] As used herein, "dual functional" means any molecule with two functional groups which can optionally be the same or in certain embodiment are different, such as amine and hydroxy.

[0008] As used herein "adduct" means chemically linked.

[0009] Sterically hindered, as used herein means that the substituent group (e.g., bulky alkyl group) on a ring carbon atom adjacent (or *para*) to a ring carbon atom substituted with a phenolic hydroxy group (or thiol or amine group), is large enough to sterically hinder the phenolic hydroxy group (or thiol or amine groups). This steric hindrance, in certain embodiments results in more labile or weak bonding between the oxygen and the hydrogen (or sulfur or nitrogen and hydrogen) and in turn enhances the stability and antioxidant activity (proton donating activity) of the sterically hindered antioxidant.

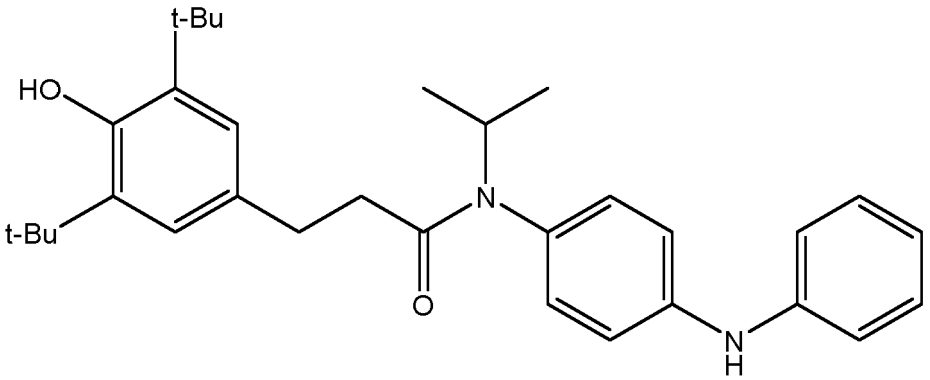
[0010] Repeat units of the antioxidants of the invention include substituted benzene molecules. Some of these benzene molecules are typically based on phenol or a phenol derivative, such that they have at least one hydroxyl or ether functional group. In certain embodiments, the benzene molecules have a hydroxyl group. The hydroxyl group can be a free hydroxyl group and can be protected or have a cleavable group attached to it (e.g., an ester group). Such cleavable groups can be released under certain conditions (e.g., changes in pH), with a desired shelf life or with a time-controlled

release (e.g., measured by the half-life), which allows one to control where and/or when an antioxidant can exert its antioxidant effect. The repeat units can also include analogous thiophenol and aniline derivatives, e.g., where the phenol -OH can be replaced by -SH, -NH-, and the like.

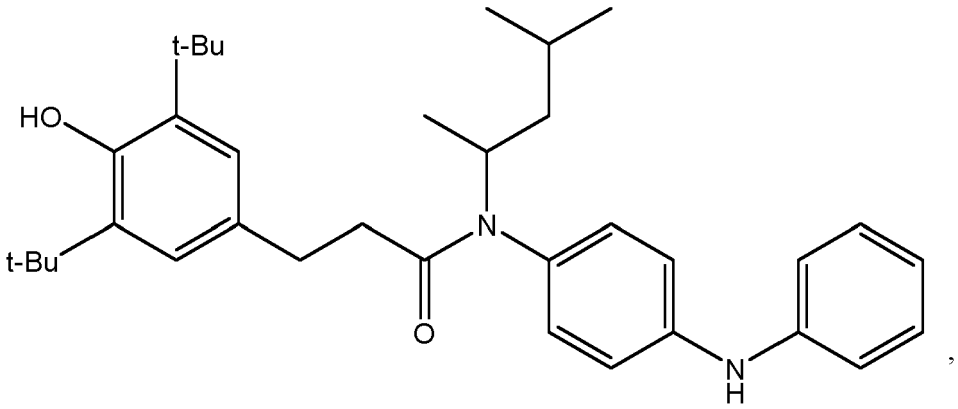
[0011] Substituted benzene repeat units of an antioxidant of the invention are also typically substituted with a bulky alkyl group or an n-alkoxycarbonyl group. In certain embodiments, the benzene monomers are substituted with a bulky alkyl group. In certain other embodiments, the bulky alkyl group is located *ortho* or *meta* to a hydroxyl group on the benzene ring, typically *ortho.* A "bulky alkyl group" is defined herein as an alkyl group that is branched *alpha-* or *beta-* to the benzene ring. In certain other embodiments, the alkyl group is branched alpha to the benzene ring. In certain other embodiments, the alkyl group is branched twice alpha to the benzene ring, such as in a *tert*-butyl group. Other examples of bulky alkyl groups include isopropyl, 2-butyl, 3-pentyl, 1, 1-dimethylpropyl, 1-ethyl-1-methylpropyl and 1, 1-diethylpropyl. In certain other embodiments, the bulky alkyl groups are unsubstituted, but they can be substituted with a functional group that does not interfere with the antioxidant activity of the molecule. Straight chained alkoxylcarbonyl groups include methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, n-butoxycarbonyl and n-pentoxycarbonyl. N-propoxycarbonyl is a preferred group. Similar to the bulky alkyl groups, n-alkoxycarbonyl groups are optionally substituted with a functional group that does not interfere with the antioxidant activity of the molecule.

[0012] The foregoing and other objects, features and advantages of the invention will be apparent from the following more particular description of preferred embodiments of the invention, as illustrated in the accompanying drawings in which like reference characters refer to the same parts throughout the different views. The drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the invention.

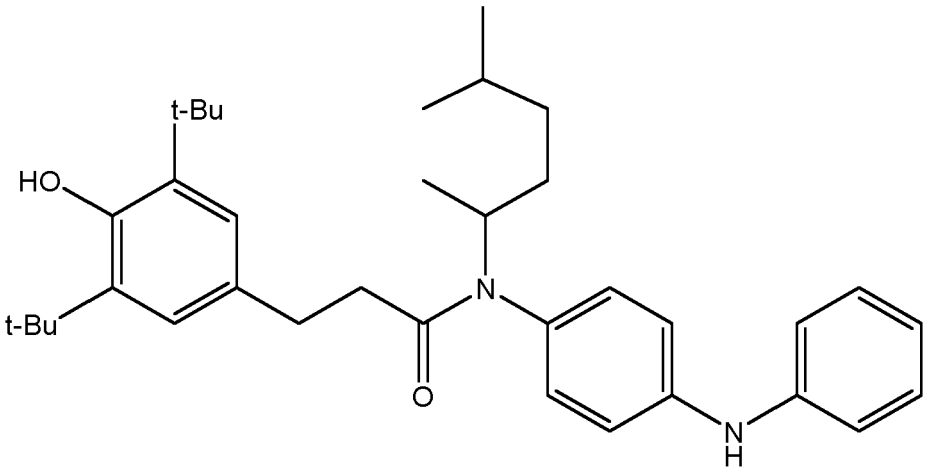
[0013] The invention is a composition that is a mixture of compounds with the following structures (i), (ii), (iii), (iv) and (v):



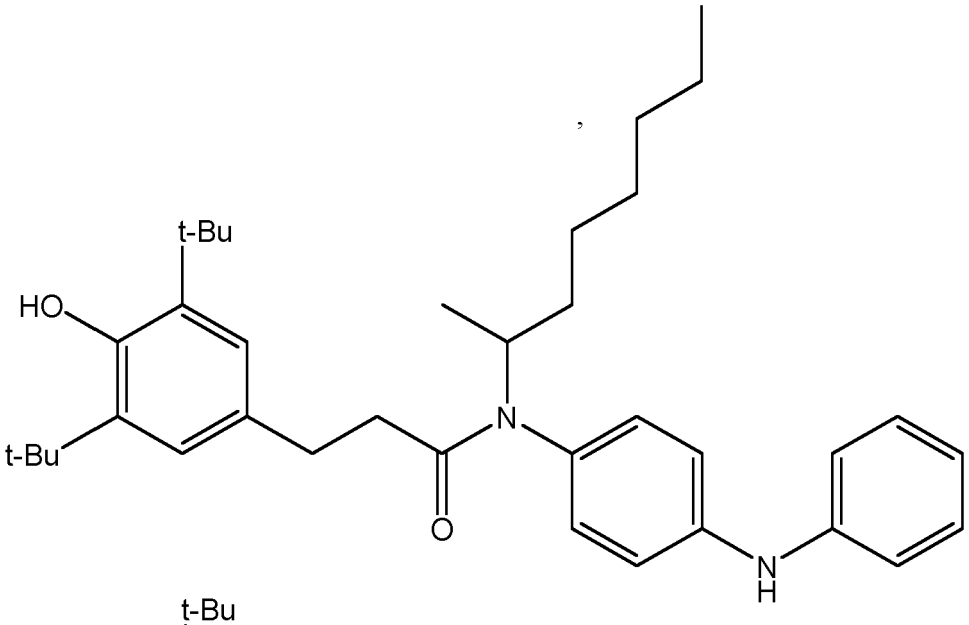
(i)



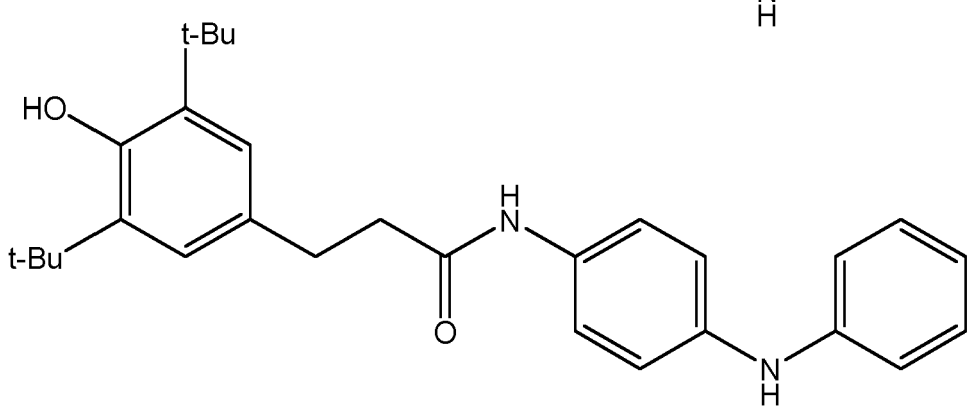
(ii),



(iii)



(iv)



(v)

[0014] In certain embodiments, the present invention is a composition that is a mixture of the compounds (i), (ii), (iii), (iv) in the following ratio: 1:1:1:1; 0:1:1:1; 1:0:1:1; 1:1:0:1 or 1:1:1:0.

[0015] In certain embodiments, the present invention is a composition that is a mixture of the compounds. The composition can include a mixture of two compounds, such as the mixture of the following compounds: (i):(ii), (i):(iii), (ii):(iii), (ii): (iv), (iii) : (iv), (v): (i), (v): (ii), (v):(iii), (v):(iv). As shown in Tables 1-9, each of these mixtures can be presented in a ratio of 10:90, 20:80, 30:70,40:60,50:50, 60:40, 70:30, 80:20, 90:10.

Table 1	
i	ii
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 2	
i	iii
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 3	
ii	iii
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 4	
ii	iv
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 5	
iii	iv
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 6	
v	i
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 7	
v	ii
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 8	
v	iii
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

Table 9	
v	IV
10	90
20	80
30	70
40	60
50	50
60	40
70	30
80	20
90	10

[0016] In certain embodiments of the present invention is a composition that is a mixture of three compounds, such as the mixture of the following compounds (i): (ii): (iii), (ii): (iii) :(iv), (iii): (iv): (i), (i):(ii):(iv). The ratio of these compounds in each of these mixtures is listed in Tables 10-28 below. Each of Tables 10-28 below describes the relative amounts of the different compounds. For example, Table 10 lists the relative amounts of compounds (i):(ii):(iii); the relative amounts

of compounds (ii):(iii):(iv); the relative amounts of compounds (iii):(iv)(i); and the relative amounts of compounds (i):(ii):(iv).

Table 10			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	10	80
	20	10	70
	30	10	60
	40	10	50
	50	10	40
	60	10	30
	70	10	20
	80	10	10
	90	10	0
	100	0	0

Table 11			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	20	70
	20	20	60
	30	20	50
	40	20	40
	50	20	30
	60	20	20
	70	20	10
	80	20	0
	90	0	10

Table 12			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv

(continued)

Table 12			
Ratio	10	30	60
	20	30	50
	30	30	40
	40	30	30
	50	30	20
	60	30	10
	70	30	0
	80	0	20
	90	0	10

Table 13			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	40	50
	20	40	40
	30	40	30
	40	40	20
	50	40	10
	60	40	0
	70	0	30
	80	0	20
	90	0	10

Table 14			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	50	40
	20	50	30
	30	50	20
	40	50	10
	50	50	0

Table 15			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	60	30
	20	60	20
	30	60	10
	40	60	0
	50	0	50

Table 16			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	70	20
	20	70	10
	30	70	0
	40	0	60

Table 17			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	80	10
	20	80	0
	30	0	70

Table 18			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	90	0
	20	0	80

Table 19			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	0	100	0

Table 20			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	80	10	10
	70	10	20
	60	10	30
	50	10	40
	40	10	50
	30	10	60
	20	10	70
	10	10	80
	0	10	90
	0	0	100

Table 21			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	70	20	10
	60	20	20
	50	20	30
	40	20	40
	30	20	50
	20	20	60
	10	20	70
	0	20	80
	10	0	90

Table 22			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	60	30	10
	50	30	20
	40	30	30
	30	30	40
	20	30	50
	10	30	60
	0	30	70
	20	0	80
	10	0	90

Table 23			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	50	40	10
	40	40	20
	30	40	30
	20	40	40
	10	40	50
	0	40	60
	30	0	70
	20	0	80
	10	0	90

Table 24			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv

(continued)

Table 24			
Ratio	40	50	10
	30	50	20
	20	50	30
	10	50	40
	0	50	50

Table 25			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	30	60	10
	20	60	20
	10	60	30
	0	60	40
	50	0	50

Table 26			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	20	70	10
	10	70	20
	0	70	30
	60	0	40

Table 27			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	80	10
	0	80	20
	70	0	30

Table 28			
Mixture	i	ii	iii
	ii	iii	iv
	iii	iv	i
	i	ii	iv
Ratio	10	90	10
	80	0	20

[0017] In certain embodiments, the present invention is a composition that is a mixture of compounds in the following ratio: (i):(ii) is 50:50.

[0018] In certain embodiments, the present invention is a composition that is a mixture of compounds in the following ratio: (i) :(iii) is 50:50.

[0019] In certain embodiments, the present invention is a composition that is a mixture of compounds in the following ratio: (i) :(iv) is 50:50.

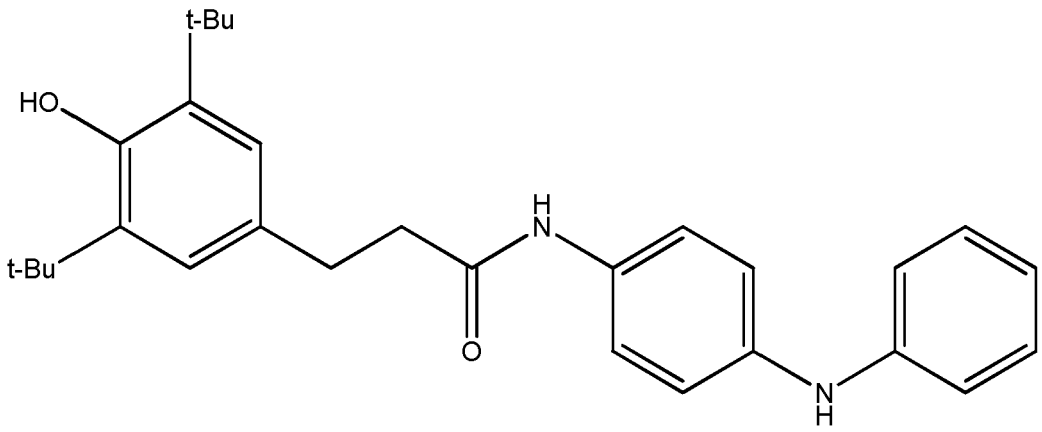
[0020] In certain embodiments, the present invention is a composition that is a mixture of compounds in the following ratio: (ii) :(iii) is 50:50.

[0021] In certain embodiments, the present invention is a composition that is a mixture of compounds in the following ratio: (ii) :(iv) is 50:50.

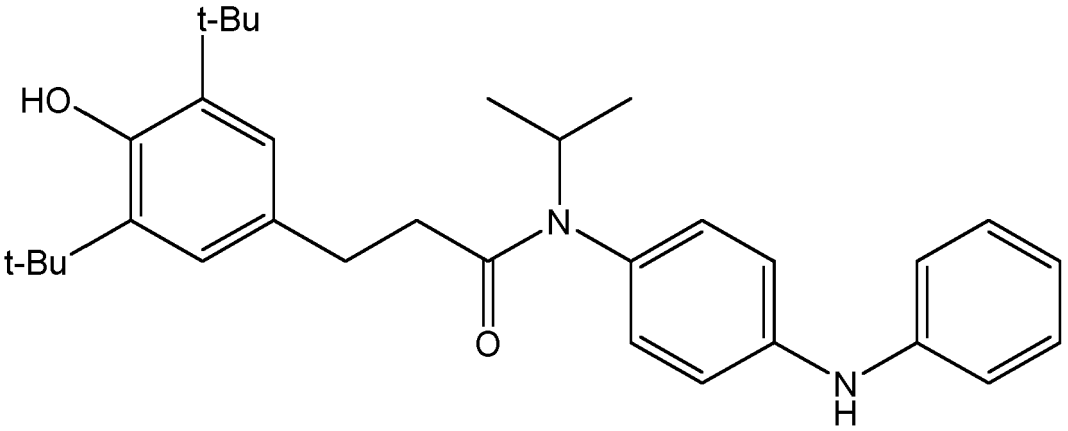
[0022] In certain embodiments, the present invention is a composition that is a mixture of compounds in the following ratio: (iii) :(iv) is 50:50.

[0023] In certain embodiments, the present invention is a composition that is a mixture of the following compounds : (v): (i), (v): (ii), (v):(iii), (v):(iv). Each of these mixtures can be present in a ratio of is 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10.

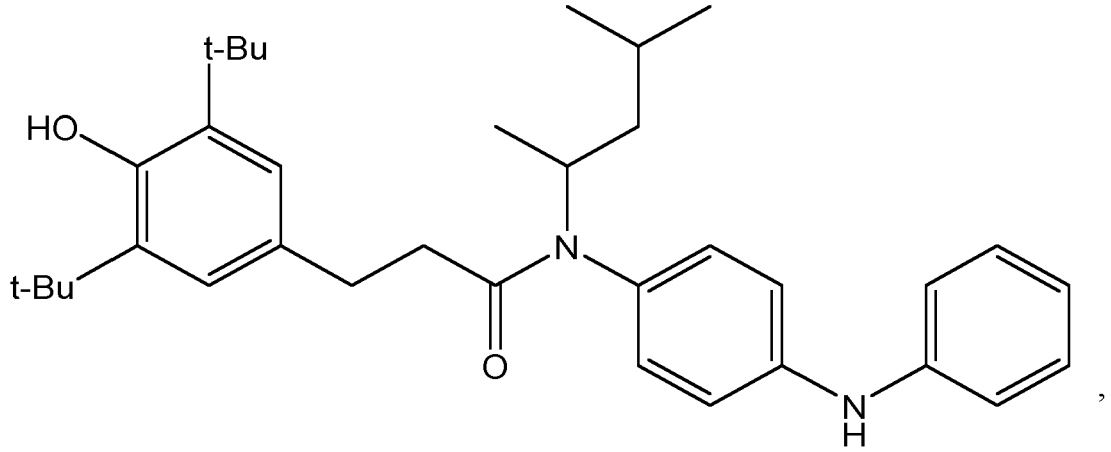
[0024] In yet other embodiments of the present invention the compound is represented by the following structural formula:



[0025] In one embodiments, the present invention is represented by the following structural formula:

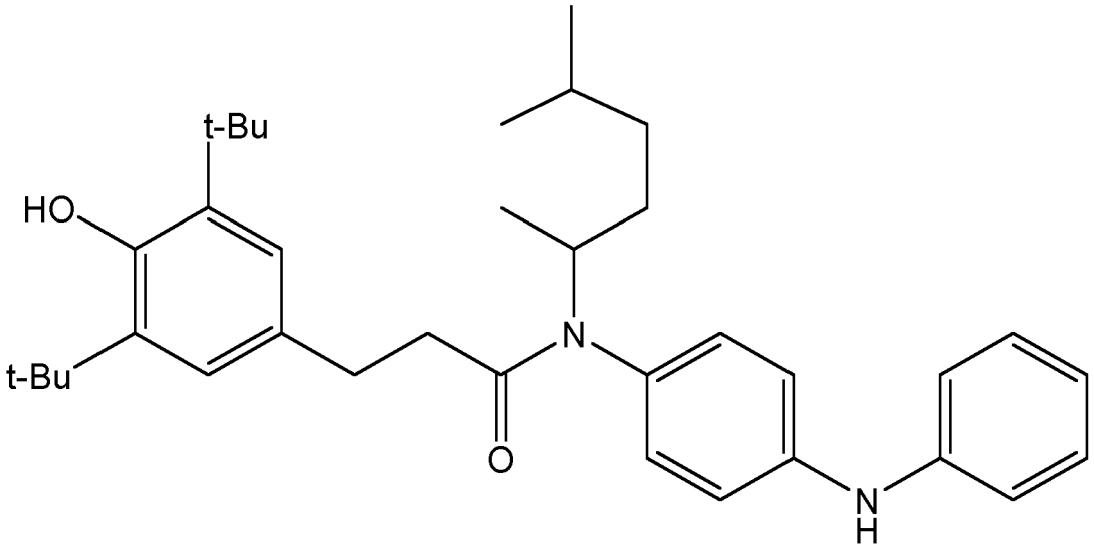


[0026] In other embodiments, the present invention is represented by the following structural formula:

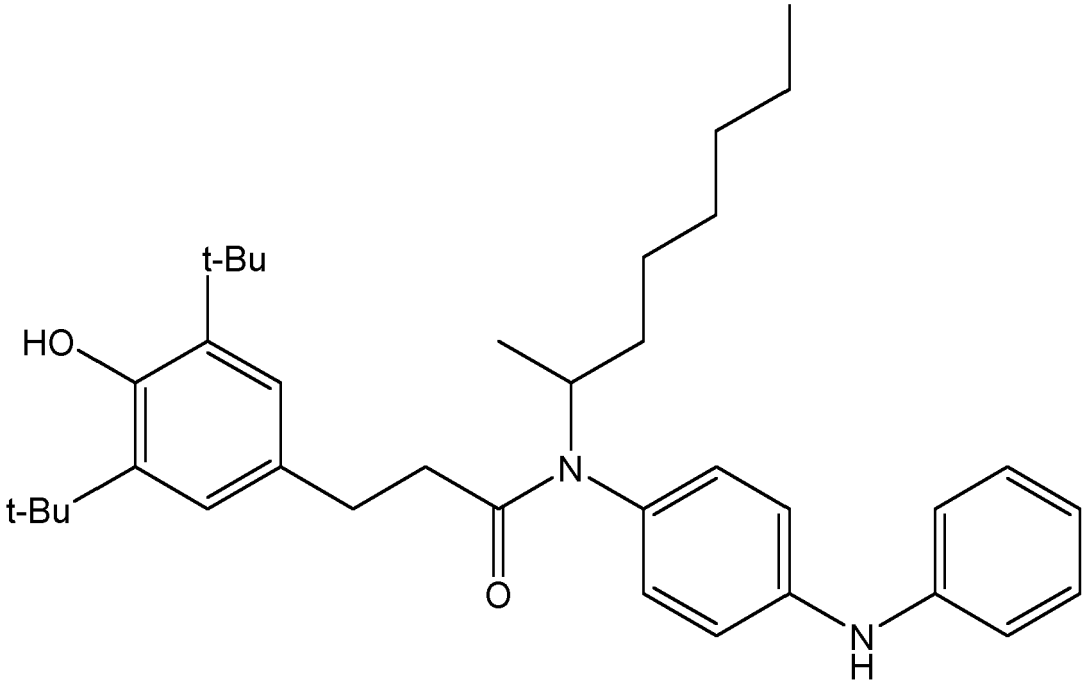


,

[0027] In one embodiments, the present invention is represented by the following structural formula:



[0028] In yet other embodiments, the present invention is represented by the following structural formula:



[0029] The antioxidant compounds of the present invention can be employed to inhibit the oxidation of an oxidizable material, for example by contacting the material with an antioxidant compound made by the methods of the present invention.

[0030] For purposes of the present invention, a method of "inhibiting oxidation" is a method that inhibits the propagation of a free radical-mediated process. Free radicals can be generated by heat, light, ionizing radiation, metal ions and some proteins and enzymes. Inhibiting oxidation also includes inhibiting reactions caused by the presence of oxygen, ozone or another compound capable of generating these gases or reactive equivalents of these gases.

[0031] As used herein the term "oxidizable material" is any material which is subject to oxidation by free-radicals or oxidative reaction caused by the presence of oxygen, ozone or another compound capable of generating these gases or reactive equivalents thereof. In particular the oxidizable material is a lubricant or a mixture of lubricants or fuel (including but not limited to gasoline, kerosene, diesel, biodiesel). The oxidizable material is a polyolefin, polymers, co-polymers, biopolymers, bioplastics, plastics, elastomers, thermoplastics polymers, polyamides, and blends thereof.

[0032] The shelf life of many materials and substances contained within the materials, such as packaging materials, are enhanced by the presence of the antioxidants of the present invention. The addition of an antioxidant of the present invention to a packaging material is believed to provide additional protection to the product contained inside the package. In addition, the properties of many packaging materials themselves, particularly polymers, are enhanced by the presence of an antioxidant regardless of the application (i.e., not limited to use in packaging). Common examples of packaging materials include paper, cardboard and various plastics and polymers. A packaging material can be coated with an antioxidant (e.g., by spraying the antioxidant or by applying as a thin film coating), blended with or mixed with an antioxidant, or otherwise have an antioxidant present within it. In one example, a thermoplastic such as polyethylene, polypropylene or polystyrene can be melted in the presence of an antioxidant in order to minimize its degradation during the polymer processing.

[0033] The lifetime of fuels (including but not limited to gasoline, kerosene, diesel, and biodiesel), lubricants, lubricant oils, mixtures thereof and compositions comprising lubricants and lubricant oils in general can be improved by contacting the lubricant, lubricant oil, mixtures thereof or composition comprising the lubricant or lubricant oil or mixtures thereof with compounds of the present invention, as described herein.

[0034] As used here, the terms "lubricants" and "lubricant oils" can be used interchangeably. Examples of lubricants suitable for use in the compositions and methods of the present invention include, but are not limited to: i) petroleum based oils (Group I, II and III), ii) synthetic oils (Group IV, V) and iii) biolubricant oils (vegetable oils such as canola, soybean, high oleic canola, high oleic soybean oil, corn oil etc.). Group I oils, as defined herein are solvent refined base oils. Group II oils, as defined herein are modern conventional base oils made by hydrocracking and early wax isomerization, or hydroisomerization technologies and have significantly lower levels of impurities than Group I oils. Group III oils, as defined herein are unconventional base oils. Groups I-III differ in impurities, and viscosity index as is shown in Kramer et al. "The Evolution of Base Oil Technology" Turbine Lubrication in the 21st Century ASTM STP #1407 W.R. Herguth and T.M. Wayne, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2001. Group IV

oils as defined herein are "synthetic" lubricant oils, including for example, poly-alpha olefins (PAOs). Biolubricants as defined herein are lubricants which contain at least 51% biomaterial (see Scott Fields, Environmental Health Perspectives, volume 111, number 12, September 2003). Other examples of lubricant oils can be found in Melvyn F. Askew "Biolubricants-Market Data Sheet" IENICA, August 2004 (as part of the IENICA work stream of the IENICA-INFORRM project); Taylor et al. "Engine lubricant Trends Since 1990" paper accepted for publication in the Proceedings I. Mech. E. Part J, Journal of Engineering Tribology, 2005 (Vol. 219 p 1-16); and Desplanches et al. "Formulating Tomorrow's Lubricants" page 49-52 of The Paths to Sustainable Development, part of special report published in October 2003 by Total. Biolubricants are often but not necessarily, based on vegetable oils. Vegetable derived, for example, from rapeseed, sunflower, palm and coconut can be used as biolubricants. They can also be synthetic esters which may be partly derived from renewable resources. They can be made from a wider variety of natural sources including solid fats and low grade or waste materials such as tallows. Biolubricants in general offer rapid biodegradability and low environmental toxicity.

[0035] As used herein, Group I, II and III oils are petroleum base stock oil. The petroleum industry differentiates their oil based on viscosity index and groups them as Group I, II and III. The synthetic oils are Group IV and Group V. In certain embodiments, synthetic oils are polyolesters for example diesters, polyolesters such as neopentyl glycols (NPGs), trimethylolpropanes (TMPs), penterythritols (PEs), and dipentaerythritols (DiPEs). In other embodiments, synthetic oils include monoesters and trimellitates. In other embodiments, synthetic oils include polyalkylene glycols (PAGs). In certain embodiments of the present invention, 50% to 20% by weight of the antioxidants of the present invention are added to lubricant oils. In certain other embodiments of the present invention, 10% to 5% by weight of the antioxidants of the present invention are added to lubricant oils. In certain other embodiments of the present invention, 0.1% to 2% by weight of the antioxidants of the present invention are added to lubricant oils. In certain other embodiments of the present invention, 0.001% to 0.5% by weight of the antioxidants of the present invention is added to lubricant oils. This percentage varies depending upon their end application and type of the base oil.

[0036] In certain embodiments of the present invention the antioxidants of the present invention are usually added to lubricant oils with stirring at between 0 and 100 °C, between 20 and 80°C or between 40-60°C.

[0037] In certain embodiments of the present invention the antioxidants of the present invention are usually added to lubricant and fuel oils (based on petroleum, synthetic, and/or biobased oils) used in automotives and industrial applications such as but not limited to transmission fluid, engine oil, break oil, metal working fluids, greases, gear oils.

[0038] In certain embodiments, the mixture of antioxidants of the present invention is preferred due to improved solubility characteristics as compared to a single component antioxidant.

[0039] In yet other embodiments of the present invention the antioxidants of the present invention are usually added to lubricant and fuel oils along with other additional lubricant additives including but not limited to anti-corrosion, anti-foaming, viscosity modifier, pour point depressants, and other phenolic and aminic antioxidants.

[0040] In one embodiment, the present invention is a composition comprising present invention antioxidant, and at least one additive selected from the group consisting of i) a surface additive; ii) a performance enhancing additive; and iii) a lubricant protective additive.

[0041] In another embodiments the present invention is a lubricant composition comprising: a lubricant or a mixture of lubricants, a present invention antioxidant and at least one additive selected from the group consisting of i) a surface additive; ii) a performance enhancing additive; and iii) a lubricant protective additive.

[0042] In yet another embodiment the present invention is a method of improving a composition comprising combining the composition with present invention antioxidant; and at least one additive selected from the group consisting of i) a surface additive; ii) a performance enhancing additive; and iii) a lubricant protective additive.

[0043] In yet another embodiment the present invention is a method of improving a lubricant or a mixture of lubricants comprising combining the lubricant or mixture of lubricants with present invention antioxidant; and at least one additive selected from the group consisting of i) a surface additive; ii) a performance enhancing additive; and iii) a lubricant protective additive.

[0044] The compositions and methods of the present invention generally provide increased shelf life, increased oxidative resistance, enhanced performance and/or improved quality to materials, such as, for example, lubricants and lubricant oils and fuels. In general it is believed that because of the synergy of the antioxidants with the additives, the compositions described herein have superior oxidation resistance. The additives exhibit several key functions such as corrosion inhibition, detergency, viscosity modification, antiwear performance, dispersant properties, cleaning and suspending ability. The disclosed compositions, in general provide superior performance of lubricants in high temperatures applications due to the presence of antioxidants which are thermally stable at high temperatures with enhanced oxidation resistance.

STABILIZED LUBRICANT OIL COMPOSITIONS

[0045] Lubricants, lubricant oils, mixtures thereof and compositions comprising lubricants and lubricant oils can be improved by the methods of the present invention, by contacting the lubricant, lubricant oil, mixtures thereof or composition

comprising the lubricant or lubricant oil or mixtures thereof with antioxidants, additives and mixtures thereof as described herein.

[0046] As used here, the terms "lubricants" and "lubricant oils" can be used interchangeably. Examples of lubricants suitable for use in the compositions and methods of the present invention include, but are not limited to: i) petroleum based oils (Group I, II and III), ii) synthetic oils (Group IV and V)) and iii) biolubricant oils (vegetable oils such as canola, soybean, corn oil etc.). Group I oils, as defined herein are solvent refined base oils. Group II oils, as defined herein are modern conventional base oils made by hydrocracking and early wax isomerization, or hydroisomerization technologies and have significantly lower levels of impurities than Group I oils. Group III oils, as defined herein are unconventional base oils. Groups I-III differ in impurities, and viscosity index as is shown in Kramer et al. "The Evolution of Base Oil Technology" Turbine Lubrication in the 21st Century ASTM STP #1407 W.R. Herguth and T.M. Wayne, Eds., American Society for Testing and Materials, West Conshohocken, PA, 2001. Group IV oils as defined herein are "synthetic" lubricant oils, including for example, poly-alpha olefins (PAOs). Biolubricants as defined herein are lubricants which contain at least 51% biomaterial (see Scott Fields, Environmental Health Perspectives, volume 111, number 12, September 2003). Other examples of lubricant oils can be found in Melvyn F. Askew "Biolubricants-Market Data Sheet" IENICA, August 2004 (as part of the IENICA work stream of the IENICA-INFORRM project); Taylor et al. "Engine lubricant Trends Since 1990" paper accepted for publication in the Proceedings I. Mech. E. Part J, Journal of Engineering Tribology, 2005 (Vol. 219 p 1-16); and Desplanches et al. "Formulating Tomorrow's Lubricants" page 49-52 of The Paths to Sustainable Development, part of special report published in October 2003 by Total. Biolubricants are often but not necessarily, based on vegetable oils. Vegetable derived, for example, from rapeseed, sunflower, palm and coconut can be used as biolubricants. They can also be synthetic esters which may be partly derived from renewable resources. They can be made from a wider variety of natural sources including solid fats and low grade or waste materials such as tallows. Biolubricants in general offer rapid biodegradability and low environmental toxicity.

ADDITIVES

[0047] Examples of first additives suitable for use in the compositions and methods of the present invention include but are not limited to, surface additives, performance enhancing additives and lubricant protective additives.

[0048] Surface additives: In certain embodiments of the present invention, surface additives can protect the surfaces that are lubricated from wear, corrosion, rust, and frictions. Examples of these surface additives suitable for use in the compositions and methods of the present invention include, but are not limited to: (a) rust inhibitors, (b) corrosion inhibitors, (c) extreme pressure agents, (d) tackiness agents, (e) antiwear agents, (f) detergents and dispersants, (g) compounded oil (like fat or vegetable oil to reduce the coefficient of friction without affecting the viscosity), (h) antimisting, (i) seal swelling agents and (j) biocides.

[0049] Performance Enhancing Additives: In certain embodiments of the present invention, performance enhancing additives improve the performance of lubricants. Examples of these performance enhancing additives suitable for use in the Compositions and methods of the present invention include, but are not limited to: (a) pour-point depressants, (b) viscosity index modifiers (c) emulsifiers, and (d) demulsifiers.

[0050] Lubricant Protective Additives: In certain embodiments of the present invention, lubricant protective additives maintain the quality of oil from oxidation and other thermal degradation processes. Examples of these lubricant protective additives suitable for use in the compositions and methods of the present invention include, but are not limited to: (a) oxidation inhibitors and (b) foam inhibitors.

OTHER LUBRICANT ADDITIVES

[0051] In certain embodiments, a second additive can be used in the compositions and methods of the present invention in combination with the first antioxidant and the first additive as described above. Examples of second additives suitable for use in the compositions and methods of the present invention include, include but are not limited to, for example, dispersants, detergents, corrosion inhibitors, rust inhibitors, metal deactivators, antiwear and extreme pressure agents, antifoam agents, friction modifiers, seal swell agents, demulsifiers, viscosity index improvers, pour point depressants, and the like. See, for example, U.S. Patent No. 5,498,809 for a description of useful lubricating oil composition additives.

[0052] Dispersants: Examples of dispersants suitable for use in the compositions and methods of the present invention include, but are not limited to: polybutenylsuccinic acid-amides, -imides, or -esters, polybutenylphosphonic acid derivatives, Mannich Base ashless dispersants, and the like.

[0053] Detergents: Examples of detergents suitable for use in the compositions and methods of the present invention include, but are not limited to: metallic phenolates, metallic sulfonates, metallic salicylates, metallic phosphonates, metallic thiophosphonates, metallic thiopyrophosphonates, and the like.

[0054] Corrosion Inhibitors: Examples of corrosion inhibitors suitable for use in the compositions and methods of the present invention include, but are not limited to: phosphosulfurized hydrocarbons and their reaction products with an

alkaline earth metal oxide or hydroxide, hydrocarbyl-thio-substituted derivatives of 1,3,4-thiadiazole, thiadiazole polysulphides and their derivatives and polymers thereof, thio and polythio sulphenamides of thiadiazoles such as those described in U.K. Patent Specification 1,560,830, and the like.

[0055] Rust Inhibitors: Examples of rust inhibitors suitable for use in the compositions and methods of the present invention include, but are not limited to: nonionic surfactants such as polyoxyalkylene polyols and esters thereof, anionic surfactants such as salts of alkyl sulfonic acids, and other compounds such as alkoxylated fatty amines, amides, alcohols and the like, including alkoxylated fatty acid derivatives treated with C9 to C16 alkyl-substituted phenols (such as the mono- and di-heptyl, octyl, nonyl, decyl, undecyl, dodecyl and tridecyl phenols).

[0056] Metal Deactivators: Metal deactivators as used herein, are the additives which form an inactive film on metal surfaces by complexing with metallic ions and reducing, for example, the catalytic effect on metal gum formation and other oxidation. Examples of metal deactivators suitable for use in the compositions and methods of the present invention include, but are not limited to: N,N-disubstituted aminomethyl-1,2,4-triazoles, N,N-disubstituted aminomethyl-benzotriazoles, mixtures thereof, and the like.

[0057] Antiwear and Extreme Pressure Additives: Antiwear and extreme pressure additives, as used herein, react with metal surfaces to form a layer with lower shear strength then metal, thereby preventing metal to metal contact and reducing friction and wear. Examples of antiwear additives suitable for use in the compositions and methods of the present invention include, but are not limited to: sulfurized olefins, sulfurized esters, sulfurized animal and vegetable oils, phosphate esters, organophosphites, dialkyl alkylphosphonates, acid phosphates, zinc dialkyldithiophosphates, zinc diaryldithiophosphates, organic dithiophosphates, organic phosphorothiolates, organic thiophosphates, organic dithiocarbamates, dimercaptothiadiazole derivatives, mercaptobenzothiazole derivatives, amine phosphates, amine thiophosphates, amine dithiophosphates, organic borates, chlorinated paraffins, and the like.

[0058] Antifoam Agents: Examples of antifoam agents suitable for use in the compositions and methods of the present invention include, but are not limited to: polysiloxanes and the like.

[0059] Friction Modifiers: Examples of friction modifiers suitable for use in the compositions and methods of the present invention include, but are not limited to: fatty acid esters and amides, organic molybdenum compounds, molybdenum dialkylthiocarbamates, molybdenum dialkyl dithiophosphates, molybdenum dithiolates, copper oleate, copper salicylate, copper dialkyldithiophosphates, molybdenum disulfide, graphite, polytetrafluoroethylene, and the like.

[0060] Seal Swell Agents: Seal swell agents, as used herein, react chemically with elastomers to cause slight swell thus improving low temperature performance especially in, for example, aircraft hydraulic oil. Examples of seal swell agents suitable for use in the compositions and methods of the present invention include, but are not limited to: dioctyl sebacate, dioctyl adipate, dialkyl phthalates, and the like.

[0061] Demulsifiers: Demulsifiers, as used herein promote separation of oil and water in lubricants exposed to water. Examples of demulsifiers suitable for use in the compositions and methods of the present invention include, but are not limited to: the esters described in U.S. Patent Nos. 3,098,827 and 2,674,619.

[0062] Viscosity Index Improvers: Examples of viscosity index improvers suitable for use in the compositions and methods of the present invention include, but are not limited to: olefin copolymers, dispersant olefin copolymers, polymethacrylates, vinylpyrrolidone/methacrylate-copolymers, polyvinylpyrrolidones, polybutanes, styrene/-acrylate-copolymers, polyethers, and the like.

[0063] Pour Point Depressants: Pour point depressants as used herein reduce the size and cohesiveness of crystal structure resulting in low pour point and increased flow at low-temperatures. Examples of pour point depressants suitable for use in the compositions and methods of the present invention include, but are not limited to: polymethacrylates, alkylated naphthalene derivatives, and the like.

OTHER ANTIOXIDANTS AND STABILIZERS

[0064] In certain embodiments, a second antioxidant or a stabilizer can be used in the compositions and methods of the present invention in combination with the first antioxidant and the first additive and optionally the second additive as described above. Examples of second antioxidants suitable for use in the compositions and methods of the present invention include, include but are not limited to:

1. Amine Antioxidants

1.1. Alkylated Diphenylamines, for example octylated diphenylamine; styrenated diphenylamine; mixtures of mono- and dialkylated tert-butyl-tert-octyldiphenylamines; and 4,4'-dicumyldiphenylamine.

1.2. Phenyl Naphthylamines, for example N-phenyl-1-naphthylamine; N-phenyl-2-naphthylamine; tert-octylated N-phenyl-1-naphthylamine.

1.3. Derivatives of para-Phenylenediamine, for example N,N'-diisopropyl-p-phenylenediamine; N,N'-di-sec-butyl-p-phenylenediamine; N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine; N,N'-bis(1-ethyl-3-methyl-

pentyl)-p-phenylenediamine; N,N'-bis(1-methylheptyl)-p-phenylenediamine; N,N'-diphenyl-p-phenylenediamine; N,N'-di-(naphthyl-2)-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; N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine.

1.4. Phenothiazines, for example phenothiazine; 2-methylphenothiazine; 3-octylphenothiazine; 2,8-dimethylphenothiazine; 3,7-dimethylphenothiazine; 3,7-diethylphenothiazine; 3,7-dibutylphenothiazine; 3,7-dioctylphenothiazine; 2,8-dioctylphenothiazine.

1.5. Dihydroquinolines, for example 2,2,4-trimethyl-1,2-dihydroquinoline or a polymer thereof.

2. Phenolic Antioxidants

2.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol; 2,6-di-tert-butylphenol; 2-tert-butyl-4,6-dimethylphenol; 2,6-di-tert-butyl-4-ethylphenol; 2,6-di-tert-butyl-4-n-butylphenol; 2,6-di-tert-butyl-4-isobutylphenol; 2,6-di-tert-butyl-4-sec-butylphenol; 2,6-di-tert-butyl-4-octadecylphenol; 2,6-di-tert-butyl-4-nonylphenol; 2,6-dicyclopentyl-4-methylphenol; 2-(β-methylcyclohexyl)-4,6-dimethylphenol; 2,6-dioctadecyl-4-methylphenol; 2,4,6-tricyclohexylphenol; 2,6-di-tert-butyl-4-methoxymethylphenol; 2,6-di-tert-butyl-4-dimethylaminomethylphenol; o-tert-butylphenol.

2.2. Alkylated hydroquinones, for example 2,6-di-tert-butyl-4-methoxyphenol; 2,5-di-tert-butylhydroquinone; 2,5-di-tert-amylhydroquinone; 2,6-di-phenyl-4-octadecyloxyphenol.

2.3. Hydroxylated thiodiphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methyl-phenol); 2,2'-thiobis(4-octylphenol); 4,4'-thiobis(6-tert-butyl-3-methylphenol); 4,4'-thiobis(6-tert-butyl-2-methylphenol).

2.4. 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'-ethylidenebis(6-tert-butyl-4-isobutylphenol); 2,2'-methylenebis[6-[?]-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-di(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol; 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane; ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxylphenyl)butyrate]; di(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene; di[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl]terephthalate.

2.5. Benzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene; di(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide; 3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetic acid isooctyl ester; bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)dithioterephthalate; 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; 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid dioctadecyl ester; 3,5-di-tert-butyl-4-hydroxybenzylphosphonic acid mono-ethyl ester calcium salt.

2.6. Acylaminophenols, for example 4-hydroxylauric acid anilide; 4-hydroxystearic acid anilide; 2,4-bis-octylmercapto-6-(3,5-di-tert-butyl-4-hydroxyaniline)-s-triazine; N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamic acid octyl ester.

2.7. Esters of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol; octadecanol; 1,6-hexanediol; neopentyl glycol; thiodiethylene glycol; diethylene glycol; triethylene glycol; pentaerythritol; tris(hydroxyethyl)isocyanurate; and di(hydroxyethyl)oxalic acid diamide.

2.8. Esters of β-(5-tert-butyl-4-hydroxy-3-methylphenyl)propionic acid with mono- or polyhydric alcohols, e.g. with methanol; octadecanol; 1,6-hexanediol; neopentyl glycol; thiodiethylene glycol; diethylene glycol; triethylene glycol; pentaerythritol; tris(hydroxyethyl)isocyanurate; and di(hydroxyethyl)oxalic acid diamide.

2.9. Amides of β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionic acid, e.g., N,N'-di(3,5-di-tert-butyl-4-hydroxyphenyl-propionyl)hexamethylenediamine ; N,N'-di(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine; N,N'-di-(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine.

3. Sulfurized organic compounds, for example aromatic, alkyl, or alkenyl sulfides and polysulfines; sulfurized olefins; sulfurized fatty acid esters; sulfurized ester olefins; sulfurized oils; esters of β-thiodipropionic acid; sulfurized Diels-Alder adducts; sulfurized terpene compounds; and mixtures thereof.

4. Organo-borate compounds, for example alkyl- and aryl- (and mixed alkyl, aryl) substituted borates.

5. Phosphite and phosphate antioxidants, for example alkyl- and aryl- (and mixed alkyl, aryl) substituted phosphites, and alkyl- and aryl- (and mixed alkyl, aryl) substituted dithiophosphates such as O,O,S-trialkyl dithiophosphates, O,O,S-triaryldithiophosphates and dithiophosphates having mixed substitution by alkyl and aryl groups, phospho-

rothionyl sulfide, phosphorus-containing silane, polyphenylene sulfide, amine salts of phosphinic acid and quinone phosphates.

6. Copper compounds, for example copper dihydrocarbyl thio- or dithiophosphates, copper salts of synthetic or natural carboxylic acids, copper salts of alkenyl carboxylic acids or anhydrides such as succinic acids or anhydrides, copper dithiocarbamates, copper sulphonates, phenates, and acetylacetonates. The copper may be in cuprous (Cu^{I}) or cupric (Cu") form.

7. Zinc dithiodiphosphates, for example zinc dialkyldithiophosphates, diphenyldialkyldithiophosphates, and di(alkylphenyl)dithiophosphates.

[0065] In one embodiment, the compositions for use in the methods of the present invention, include but are not limited to:

a. a first antioxidant (in the concentration range, from about 0.0001% to about 50%, from about 0.0005% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) with a first additive selected from the group comprising a surface additive, a performance enhancing additive and a lubricant performance additive, for example, in amounts of from about 0.0005% to about 50%, from about 0.0001% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1% by weight, based on the weight of lubricant to be stabilized.

b. the first antioxidant and the first additive as described in a. and a second additive, for example, in concentrations of from about 0.0001% to about 50% by weight, about 0.0005% to about 20% by weight, about 0.001% to about 10% by weight, from about 0.01% to about 5% by weight, from about 0.05% to about 1% by weight from about 0.1% to about 1% by weight based on the overall weight of the lubricant to be stabilized.

c. the first antioxidant and the first additive as described in a. and optionally the second additive as described in b. and a second antioxidant, for example, Irganox® L 57, Irganox® 1010, Irganox® 1330, Irganox® 1076, Irganox® 5057 and Irganox® L 135 in the concentration range, from about 0.0001% to about 50%, from about 0.0005% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) by weight, based on the weight of lubricant to be stabilized.

[0066] In yet another embodiment, the antioxidant compositions for use in the methods of the present invention, includes but is not limited to: the first antioxidant from the present invention and the second antioxidant from the section 'OTHER ANTIOXIDANTS AND STABILIZERS'. The antioxidant composition, where in the weight ratio of the second antioxidant to the first antioxidant of the present invention is from about 1:99 to 99:1, from about 10:90, 20:80, 30:70, 40:60, 50:50, 60:40, 70:30, 80:20, 90:10. The second antioxidant second antioxidant, for example, Irganox® L 57, Irganox® L64, Irganox® 1330, Irganox® 1076, Irganox® 5057 and Irganox® L 135.

[0067] The term "alkyl" as used herein means a saturated straight-chain, branched or cyclic hydrocarbon. When straight-chained or branched, an alkyl group is typically C1-C8, more typically C1-C6; when cyclic, an alkyl group is typically C3-C12, more typically C3-C7 alkyl ester. Examples of alkyl groups include methyl, ethyl, *n*-propyl, *iso*-propyl, *n*-butyl, *sec*-butyl and *tert*-butyl and 1, 1-dimethylhexyl.

[0068] The term "alkoxy" as used herein is represented by -OR**, wherein R** is an alkyl group as defined above.

[0069] The term "carbonyl" as used herein is represented by -C(=O)R**, wherein R** is an alkyl group as defined above.

[0070] The term "alkoxycarbonyl" as used herein is represented by -C(=O)OR**, wherein R** is an alkyl group as defined above.

[0071] The term "aromatic group" includes carbocyclic aromatic rings and heteroaryl rings. The term "aromatic group" may be used interchangeably with the terms "aryl", "aryl ring" "aromatic ring", "aryl group" and "aromatic group".

[0072] Carbocyclic aromatic ring groups have only carbon ring atoms (typically six to fourteen) and include monocyclic aromatic rings such as phenyl and fused polycyclic aromatic ring systems in which a carbocyclic aromatic ring is fused to one or more aromatic rings (carbocyclic aromatic or heteroaromatic)r. Examples include 1-naphthyl, 2-naphthyl, 1-anthracyl and 2-anthracyl. Also included within the scope of the term "carbocyclic aromatic ring", as it is used herein, is a group in which an aromatic ring is fused to one or more non-aromatic rings (carbocyclic or heterocyclic), such as in an indanyl, phthalimidyl, naphthimidyl, phenanthridinyl, or tetrahydronaphthyl, where the radical or point of attachment is on the aromatic ring.

[0073] The term "heteroaryl", "heteroaromatic", "heteroaryl ring", "heteroaryl group" and "heteroaromatic group", used alone or as part of a larger moiety as in "heteroaralkyl" refers to heteroaromatic ring groups having five to fourteen members, including monocyclic heteroaromatic rings and polycyclic aromatic rings in which a monocyclic aromatic ring is fused to one or more other aromatic ring (carbocyclic or heterocyclic). Heteroaryl groups have one or more ring heteroatoms. Examples of heteroaryl groups include 2-furanyl, 3-furanyl, *N*-imidazolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, oxadiazolyl, oxadiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, *N*-pyrazolyl, 3-pyrazolyl, 4-pyrazolyl, 5-pyrazolyl, *N*-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrimidinyl,

4-pyrimidinyl, 5-pyrimidinyl, 3-pyridazinyl, 4-pyridazinyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, triazolyl, tetrazolyl, 2-thienyl, 3-thienyl, carbazolyl, benzothienyl, benzofuranyl, indolyl, quinolinyl, benzothiazole, benzooxazole, benzimidazolyl, isoquinolinyl and isoindolyl. Also included within the scope of the term "heteroaryl", as it is used herein, is a group in which an aromatic ring is fused to one or more non-aromatic rings (carbocyclic or heterocyclic), where the radical or point of attachment is on the aromatic ring.

[0074] The term non-aromatic heterocyclic group used alone or as part of a larger moiety refers to non-aromatic heterocyclic ring groups having three to fourteen members, including monocyclic heterocyclcic rings and polycyclic rings in which a monocyclic ring is fused to one or more other non-aromatic carbocyclic or heterocyclic ring or aromatic ring (carbocyclic or heterocyclic). Heterocyclic groups have one or more ring heteroatoms, and can be saturated or unsaturated. Examples of heterocyclic groups include piperidinyl, piperizinyl, pyrrolidinyl, pyrazolidinyl, imidazolidinyl, tetrahydroquinolinyl, inodolinyl, isoindolinyl, tetrahydrofuranyl, oxazolidinyl, thiazolidinyl, dioxolanyl, dithiolanyl, tetrahydropyranyl, dihydropyranyl, azepanyl and azetidinyl.

[0075] The term "heteroatom" means nitrogen, oxygen, or sulfur and includes any oxidized form of nitrogen and sulfur, and the quaternized form of any basic nitrogen. Also the term "nitrogen" includes substitutable nitrogen of a heteroaryl or non-aromatic heterocyclic group. As an example, in a saturated or partially unsaturated ring having 0-3 heteroatoms selected from oxygen, sulfur or nitrogen, the nitrogen may be N (as in 3,4-dihydro-2H-pyrrolyl), NH (as in pyrrolidinyl) or NR" (as in N-substituted pyrrolidinyl), wherein R" is a suitable substituent for the nitrogen atom in the ring of a non-aromatic nitrogen-containing heterocyclic group, as defined below.

[0076] As used herein the term non-aromatic carbocyclic ring as used alone or as part of a larger moiety refers to a non-aromatic carbon containing ring which can be saturated or unsaturated having three to fourteen atoms including monocyclic and polycyclic rings in which the carbocyclic ring can be fused to one or more non-aromatic carbocyclic or heterocyclic rings or one or more aromatic (carbocyclic or heterocyclic) rings.

[0077] An optionally substituted aryl group as defined herein may contain one or more substitutable ring atoms, such as carbon or nitrogen ring atoms. Examples of suitable substituents on a substitutable ring carbon atom of an aryl group include halogen (e.g., -Br, CI, I and F), -OH, C1-C4 alkyl, C1-C4 haloalkyl, $-NO_2$, C1-C4 alkoxy, C1-C4 haloalkoxy, -CN, $-NH_2$, C1-C4 alkylamino, C1-C4 dialkylamino, $-C(O)NH_2$, -C(O)NH(C1-C4 alkyl), -C(O)(C1-C4 alkyl), -OC(O)(C1-C4 alkyl), -OC(O)(aryl), -OC(O)(substituted aryl), -OC(O)(aralkyl), -OC(O)(substituted aralkyl), -NHC(O)H, -NHC(O)(C1-C4 alkyl), $-C(O)N(C1\text{-}C4\ alkyl)_2$, -NHC(O)O-(C1-C4 alkyl),-C(O)OH, -C(O)O-(C1-C4 alkyl), $-NHC(O)NH_2$, -NHC(O)NH(C1-C4 alkyl), $-NHC(O)N(C1\text{-}C4\ alkyl)_2$, $-NH\text{-}C(=NH)NH_2$, $-SO_2NH_2$ $-SO_2NH(C1\text{-}C3alkyl)$, $-SO_2N(C1\text{-}C3alkyl)_2$, $NHSO_2H$, $NHSO_2(C1\text{-}C4\ alkyl)$ and optionally substituted aryl. Preferred substituents on aryl groups are as defined throughout the specification. In certain embodiments aryl groups are unsubstituted.

[0078] Examples of suitable substituents on a substitutable ring nitrogen atom of an aryl group include C1-C4 alkyl, NH_2, C1-C4 alkylamino, C1-C4 dialkylamino, $-C(O)NH_2$, -C(O)NH(C1-C4 alkyl), -C(O)(C1-C4 alkyl), $-CO_2$ R**, -C(O)C(O)R**, $-C(O)CH_3$, -C(O)OH, -C(O)O-(C1-C4 alkyl), $-SO_2NH_2$ $-SO_2NH(C1\text{-}C3alkyl)$, $-SO_2N(C1\text{-}C3alkyl)_2$, $NHSO_2H$, $NHSO_2(C1\text{-}C4\ alkyl)$, $-C(=S)NH_2$, -C(=S)NH(C1-C4 alkyl), $-C(=S)N(C1\text{-}C4\ alkyl)_2$, $-C(=NH)\text{-}N(H)_2$, -C(=NH)-NH(C1-C4 alkyl) and $-C(=NH)\text{-}N(C1\text{-}C4\ alkyl)_2$,

[0079] An optionally substituted alkyl group or non-aromatic carbocyclic or heterocyclic group as defined herein may contain one or more substituents. Examples of suitable substituents for an alkyl group include those listed above for a substitutable carbon of an aryl and the following: =O, =S, =NNHR**, $=NN(R^{**})_2$, =NNHC(O)R**, $=NNHCO_2$ (alkyl), $=NNHSO_2$ (alkyl), =NR**, spiro cycloalkyl group or fused cycloalkyl group. R** in each occurrence, independently is -H or C1-C6 alkyl. Preferred substituents on alkyl groups are as defined throughout the specification. In certain embodiments optionally substituted alkyl groups are unsubstituted.

[0080] A "spiro cycloalkyl" group is a cycloalkyl group which shares one ring carbon atom with a carbon atom in an alkylene group or alkyl group, wherein the carbon atom being shared in the alkyl group is not a terminal carbon atom.

[0081] Without wishing to be bound by any theory or limited to any mechanism it is believed that macromolecular antioxidants and polymeric macromolecular antioxidants of the present invention exploit the differences in activities (ks, equilibrium constant) of, for example, homo- or hetero- type antioxidant moieties. Antioxidant moieties include, for example, hindered phenolic groups, unhindered phenolic groups, aminic groups and thioester groups, etc. of which there can be one or more present in each macromolecular antioxidant molecule. As used herein a homo- type antioxidant macromolecule comprises antioxidant moieties which are all same, for example, hindered phenolic, -OH groups. As used herein a hetero- type antioxidant macromolecule comprises at least one different type of moiety, for example, hindered phenolic and aminic groups in the one macromolecule.

[0082] This difference in activities can be the result of, for example, the substitutions on neighboring carbons or the local chemical or physical environment (for example, due to electrochemical or stereochemical factors) which can be due in part to the macromolecular nature of molecules.

[0083] In certain embodiments of the present invention, more than two types of antioxidant moieties with different rate constants are used in the methods of the present invention.

[0084] In certain embodiments, the present invention pertains to the use of the disclosed compositions to improve

materials, such as lubricants, lubricant oils, compositions comprising lubricants and lubricant oils and mixtures thereof.

[0085] In certain embodiments, as defined herein improving a material means inhibiting oxidation of an oxidizable material.

[0086] For purposes of the present invention, a method of "inhibiting oxidation" is a method that inhibits the propagation of a free radical-mediated process. Free radicals can be generated by heat, light, ionizing radiation, metal ions and some proteins and enzymes. Inhibiting oxidation also includes inhibiting reactions caused by the presence of oxygen, ozone or another compound capable of generating these gases or reactive equivalents of these gases.

[0087] As used herein the term "oxidizable material" is any material which is subject to oxidation by free-radicals or oxidative reaction caused by the presence of oxygen, ozone or another compound capable of generating these gases or reactive equivalents thereof. In particular the oxidizable material is a lubricant or a mixture of lubricants.

[0088] In certain other embodiments, as defined herein improving a material means inhibiting oxidation, as well as improving performance and/or increasing the quality of a material, such as, a lubricant, lubricant oil, composition comprising a lubricant or lubricant oil or mixtures thereof. Increasing the quality of a material includes reducing friction and wear, increasing viscosity, resistance to corrosion, aging or contamination, etc. In certain embodiments, improving means that the lubricant is more resistant to degradation due to the presence of oxygen, temperature, pressure, water, metal species and other contributing factors to degradation. In certain embodiments, additive as described herein help to promote the shelf life of these oils. In certain embodiments the stability of the lubricants is directly related to their performance. That is the lubricant will not perform well if the lubricant has been degraded. In certain embodiments the performance of the lubricants is related to the additives. That is if antioxidant and additives are used they will result in an improvement in the stability and performance of the lubricants.

[0089] A lubricant, as defined herein is a substance (usually a liquid) introduced between two moving surfaces to reduce the friction and wear between them. Lubricant can be used in, for example, automotive engines, and hydraulic fluids with transmission oils and the like. In addition to automotive and industrial applications, lubricants are used for many other purposes, including biomedical applications (e.g. lubricants for artificial joints), grease, aviation lubricants, turbine engine lubricants, compressor oils, power transformer oils, automatic transmission fluids, metal working fluids, gear oils, sexual lubricants and others.

[0090] In certain other embodiments of the present invention, lubricants are biolubricants that are used as hydraulic fluid (bio hydraulic fluid), metal working fluid, gear oils (bio-gear oil), elevator oil, transformer oil, tractor oil, marine lubricants, grease, rock drill oil, chain saw bar oil, wire, rope and chain lubricants, stern tube lubricant, penetrating oils, aerosols, functional fluids, environmentally acceptable lubricants (EALs), and many other industrial applications. Usually the base oil of biolubricant is bio-oil, synthetically modified bio-oil, biobased oil, and/or mixture of these bio-oils and biobased oils with other Group I-V oils. Biolubricants are normally biodegradable. Extent of biolubricants biodegradability is dependent on the composition of base oil.

[0091] In certain other embodiments, as defined herein improving a material means inhibiting oxidation, as well as improving performance and/or increasing the quality of a material, such as polymers, copolymers and their blends, plastics, elastomers, polyolefins, thermoplastic elastomers, and nylons.

[0092] In one embodiment, of the present invention the compositions for use in stabilization of polyolefins, include but are not limited to:

a. an antioxidant (in the concentration range , from about 0.0001% to about 50%, from about 0.0005% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) with acid scavengers, for example, in amounts of from about 0.0005% to about 50%, from about 0.0001% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1% by weight, based on the weight of polyolefin to be stabilized.

b. an antioxidant (in the concentration range from about 0.0005% to about 50%, from about 0.0001% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) along with organic phosphorus stabilizers. The organic phosphorus stabilizers are used for example, in amounts of, from about 0.001 % to about 30 %, from about 0.005 % to about 20 %, from about 0.01 % to about 5 %, from about 0.05 % to about 2 % or from about 0.1 % to about 1 %, by weight, based on the weight of the polyolefin to be stabilized.

c. an antioxidant (in the concentration range from about 0.0005% to about 50%, from about 0.0001% to about 50%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) along with acid scavengers and organic phosphorus stabilizers in concentrations described in a. and b. above.

d. an antioxidant in combination with other known commercially available antioxidants, such as, for example, Irganox® 1010, Irganox® 1330, Irganox® 1076 and Irganox® 1135 or other antioxidants described above along with the formulations described in a.-c. above.

POLYOLEFINS

[0093] In certain embodiments of the present invention, polyolefins and mixtures of polyolefins can be stabilized by contacting the polyolefin or mixture of polyolefins with a composition of the present invention. These polyolefins and mixtures of polyolefins, include, but are not limited to substituted polyolefins, polyacrylates, polymethacrylates and copolymers of polyolefins. The following are examples of some types of polyolefins which can be stabilized by the methods of the present invention:

1. Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polyisoprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE) and ultra low density polyethylene (ULDPE). Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, for example polyethylene and polypropylene, can be prepared by different, and especially by the following, methods:

i) radical polymerization (normally under high pressure and at elevated temperature).
ii) catalytic polymerization using a catalyst that normally contains one or more than one

metal of groups IVb, Vb, VIb or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alcoholates, esters, ethers, amines, alkyls, alkenyls and/or aryls that may be either p- or s-coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium (III) chloride, and alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerization medium. The catalysts can be used by themselves in the polymerization or further activators may be used, typically metal alkyls, metal hydrides, metal alkyl halides, metal alkyl oxides or metal alkyloxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or silyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

2. Mixtures of the polymers mentioned under 1, for example, mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/but-1-ene copolymers, propylene/isobutylene copolymers, ethylene/but-1-ene copolymers, ethylene/hexene copolymers, ethylene/methylpentene copolymers, ethylene/heptene copolymers, ethylene/octene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (ionomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene; and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylenevinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LLDPE/EVA, LLDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

4. Blends of polymers mentioned under 1 with impact modifiers such as ethylene-propylene-diene monomer copolymers (EPDM), copolymers of ethylene with higher alpha-olefins (such as ethylene-octene copolymers), polybutadiene, polyisoprene, styrene-butadiene copolymers, hydrogenated styrene-butadiene copolymers, styrene-isoprene copolymers, hydrogenated styrene-isoprene copolymers. These blends are commonly referred to in the industry as TPO's (thermoplastic polyolefins).

[0094] In other embodiment polymers of the present invention include biopolymers, bio copolymers, bio-elastomers, bioplastics and their blends with synthetic polymers mentioned in subsections 1-4 of the preceding paragraph.

[0095] In certain particular embodiments polyolefins of the present invention are for example polypropylene homo- and copolymers and polyethylene homo- and copolymers. For instance, some polyolefin Ares polypropylene, high density polyethylene (HDPE), linear low density polyethylene (LLDPE) and polypropylene random and impact (heterophasic) copolymers.

[0096] In certain particular embodiments polyolefins of the present invention are for a wide range of industrial and house hold applications including but not limited to wire and cables, insulators and jackets, carriers and containers for

solids, liquids and powders, packaging, automotive, aviation, and ship components and parts, industrial applications, papers, paints, tires, thin and thick sheets, solids, pipes and tubes, composites with other materials like for example carbon, wood, leather, and metals, electric, housing for wires, electric, electronic and optical components including computers, filters and sponges, geo-membrane liners, housing and building components including roofing shingles, cosmetics, fragrance and toiletries, starch products, textile products and diapers.

STABILIZERS

ACID SCAVENGERS OR ACID STABILIZERS

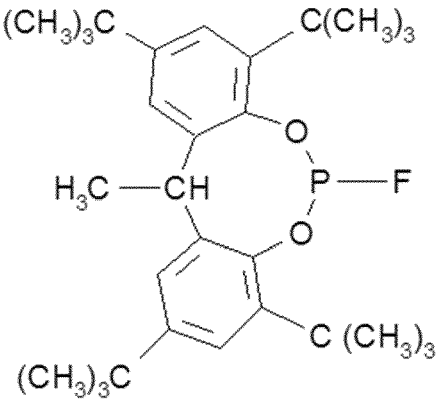
[0097] "Acid scavengers or stabilizers" are defined herein as antacids or co-stabilizers which neutralize the acidic catalysts or other components present in the polymers.

[0098] In certain embodiments, of the present invention the acid scavengers which are suitable for use in the methods of the present invention include but are not limited to: zinc oxide, calcium lactate, natural and synthetic hydrotalcites, natural and synthetic hydrocalumites, and alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium behenate, magnesium stearate, sodium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate and zinc pyrocatecholate. Combinations of acid scavengers may also be employed.

[0099] In certain particular embodiments, the acid scavengers are used for example, in amounts of from about 0.0005 % to about 50 % by weight, about 0.0001 % to about 20 % by weight, about 0.005 % to about 5 % by weight, about 0.01 % to about 3 % by weight, about 0.05 % to about 2 % by weight, or about 0.1 % to about 1 % by weight, based on the weight of polyolefin to be stabilized.

ORGANIC PHOSPHORUS STABILIZERS

[0100] In certain embodiments of the present invention, examples of organic phosphorus stabilizers (or phosphorus stabilizers) include phosphates, phosphites and phosphonites which are suitable for use in the methods of the present invention. Specific examples of phosphorus stabilizers include but are not limited to: 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, ethanamine, 2-[[2,4,8,10-tetrakis(1,1dimethylethyl)dibenzo[d,f][1,2,3]dioxaphosphepin-6-yl]oxy]-N,N-[bis[2-[[2,4,8,10-tetrakis(1,1diemthylethyl)dibenzo[d,f][1,2,3]dioxaphepin-6-yl]oxy]ethyl] (represented by structural formula (B) diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite (represented by structural formula (D) below), bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite (represented by structural formula (E) below), 3,9-bis(octadecylpxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro[5,5undecane (represented by structural formula (F), bisisodecyloxy-pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis¬(2,4,6-tri-tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis ¬(2,4-di-tert-butylphenyl) 4,4'-biphenylene-diphosphonite (represented by structural formula (H) below), 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-dibenzo[d,f][1,3,2]dioxaphosphepin (represented by structural formula (C) below), 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g][1,3,2]dioxaphosphocin (represented by structural formula (A) below), bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite, bis(2,4 di-tert-butyl-6-methylphenyl) ethyl phosphite (represented by structural formula (G) below), (2,4,6-tri-tert-butylphenyl) 2-butyl-2-ethyl-1,3-propanediol phosphate (represented by structural formula (J) below), bis(2,4-di-cumylphenyl) pentaerythritol diphosphite (represented by structural formula (K) below), and structural formula (L) below:



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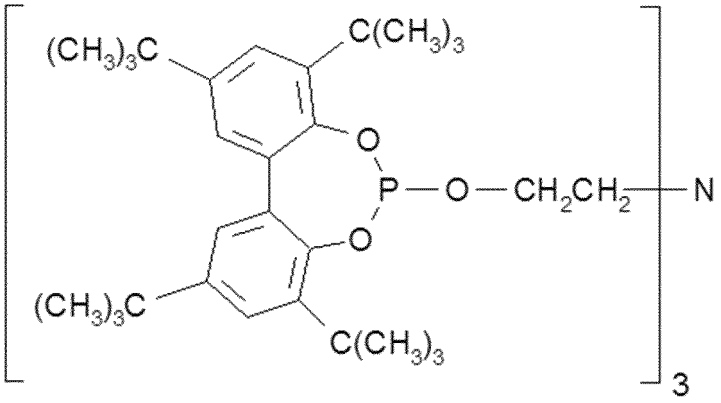

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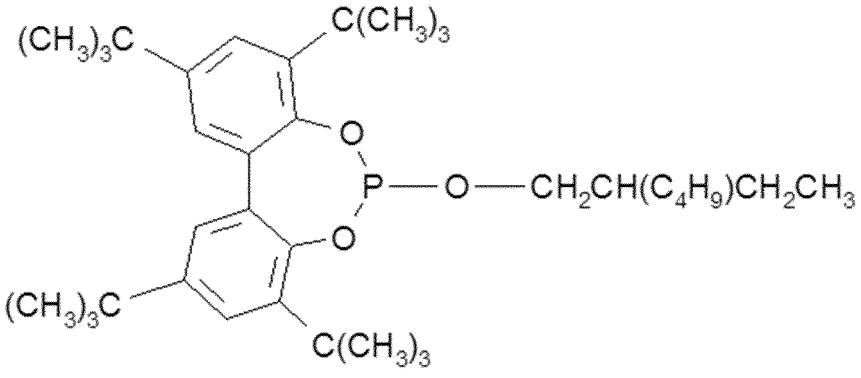

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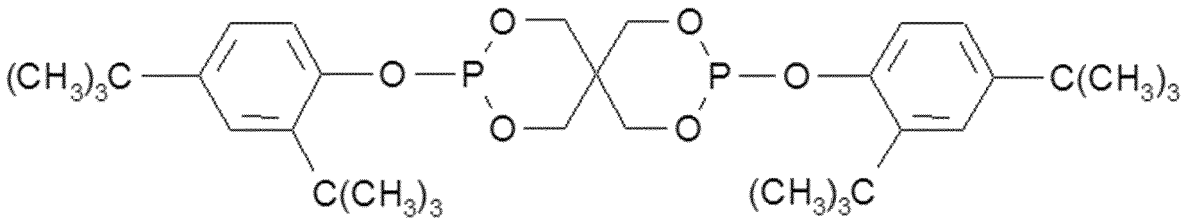

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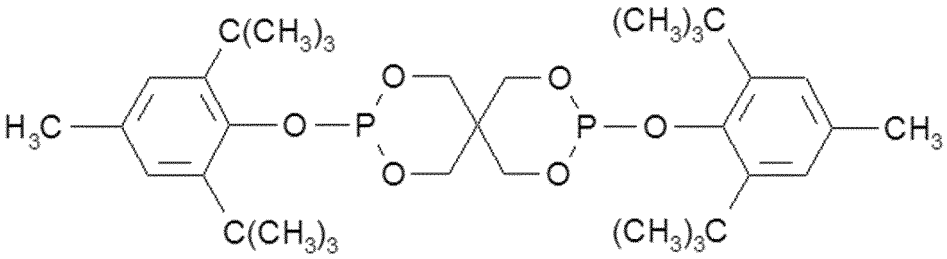

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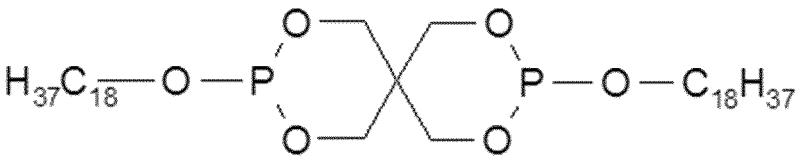

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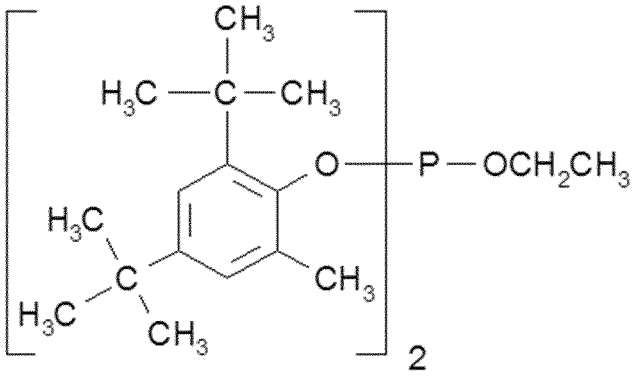

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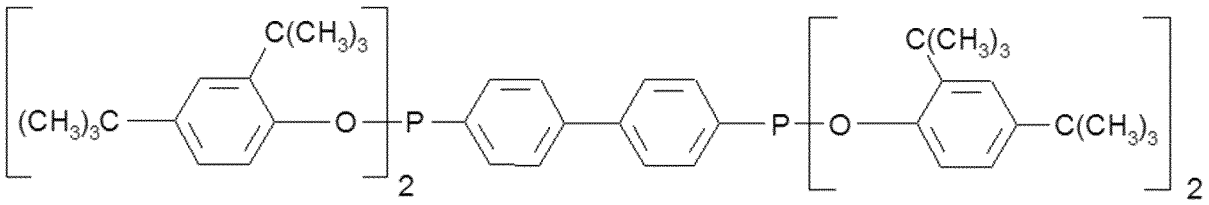

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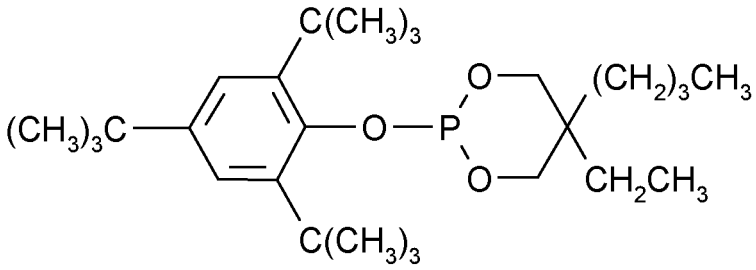

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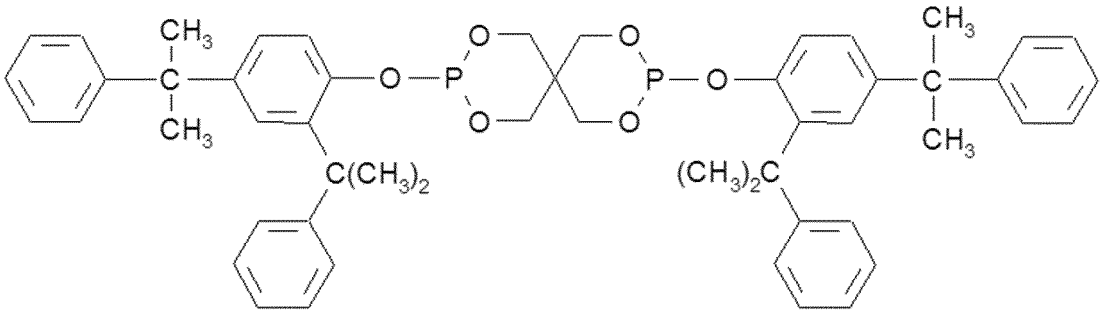

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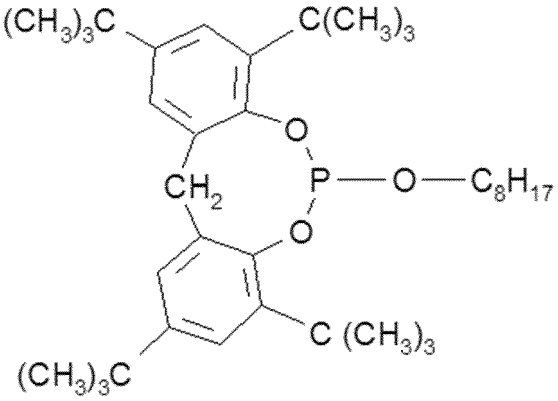


(L)

[0101] In certain other embodiments of the present invention, the following compounds are examples of organic phosphites and phosphonites which are suitable for use in the methods of the present invention as organic phosphorus

stabilizers: tris(2,4-di-tert-butylphenyl) phosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite (formula (D)), tetrakis(2,4-di-tert-butylphenyl)4,4'-biphenylene-diphosphonite (formula (H)), (2,4,6-tri-tert-butylphenyl) 2-butyl-2-ethyl-1,3-propanediol phosphate (formula (J)), or bis(2,4-di-cumylphenyl) pentaerythritol diphosphite (formula (K)).

[0102] The organic phosphorus stabilizers are used, for example, in amounts of from about 0.001 % to about 50 % by weight, about 0.005 % to about 20 % by weight, about 0.01 % to about 5 % by weight, 0.05 % to about 3 % by weight, 0. 1 % to about 2 % by weight or 0.1 % to about 1 % by weight based on the weight of the polyolefin to be stabilized.

CO-STABILIZERS

[0103] In certain embodiments of the present invention, in addition to antioxidants and stabilizers described above the compositions of the present invention may comprise further co-stabilizers (e.g., additives) such as, for example, the following:

1. Antioxidants

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

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

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

1.4. **Tocopherols,** for example α-tocopherol, β-tocopherol, γ-tocopherol, γ-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'-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(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-hydroxy2-methylphenyl)-4-n-dodecylmercaptobutane, 1,1,5,5-tetra-(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane.

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

1.8. **Hydroxybenzylated malonates,** for example dioctadecyl-2,2-bis-(3,5-di-tert-butyl-2-hydroxybenzyl)malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)malonate, 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.

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

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

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

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

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

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

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

1.18. **Ascorbic acid** (vitamin C)

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

As defined herein, "hindered amine stabilizers" are hindered amines which produce nitroxyl radicals that react with alkyl radicals produced during thermo-oxidation of the polymers.

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

The sterically hindered amine may also be one of the compounds described in U.S. Pat. No. 5,980,783, that is compounds of component I-a), I-b), I-c), I-d), I-e), I-f), I-g), I-h), I-i), I-j), I-k) or I-l), in particular the light stabilizer 1-a-1, 1-a-2, 1-b-1, 1-c-1, 1-c-2, 1-d-1, 1-d-2, 1-d-3, 1-e-1, 1-f-1, 1-g-1, 1-g-2 or 1-k-1 listed on columns 64-72 of said U.S. Pat. No. 5,980,783.

The sterically hindered amine may also be one of the compounds described in U.S. Pat. Nos. 6,046,304 and 6,297,299, for example compounds as described in claims 10 or 38 or in Examples 1-12 or D-1 to D-5 therein.

2.2. Sterically hindered amines substituted on the N-atom by a hydroxy-substituted alkoxy group, for example compounds such as 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-hexadecanoyloxy-2,2,6,6-tetra-methylpiperidine, the reaction product of 1-oxyl-4-hydroxy-2,2,6,6-tetramethylpiperidine with a carbon radical from t-amylalcohol, 1-(2-hydroxy-2-methylpropoxy)-4-hydroxy-2,2,6,6-tetramethylpiperidine, 1-(2-hydroxy-2-methylpropoxy)-4-oxo-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, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethyl-piperidin-4-yl) succinate, bis(1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl) glutarate and 2,4-bis{N-[1-(2-hydroxy-2-methylpropoxy)-2,2,6,6-tetramethylpiperidin-4-yl]-N-butyl-amino}-6-(2-hydroxyethylamino)-s-triazine.

3. Ultraviolet Absorbers

As defined herein "ultraviolet absorbers" essentially absorb the harmful UV radiation and dissipate it so that is does not lead to photosensitization i.e., dissipation as heat.

3.1. 2-(2-Hydroxyphenyl)-2H-benzotriazoles, for example known commercial hydroxyphenyl-2H-benzotriazoles and benzotriazoles as disclosed in, U.S. Pat. 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; 5,436,349; 5,516,914; 5,554,760; 5,563,242; 5,574,166; 5,607,987 and 5,977,219, such as 2-(2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-tert-butylphenyl)-2H-benzotriazole, 2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole, 5-chloro-2-(3,5-di-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole, 5-chloro-2-(3-tert-butyl-2-hydroxy-5-methylphenyl)-2H-benzotriazole, 2-(3-sec-butyl-5-tert-butyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(2-hydroxy-4-octyloxyphenyl)-2H-benzotriazole, 2-(3,5-di-tert-amyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3,5-bis-a-cumyl-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-tert-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-tert-butyl-2-hydroxy-5-(2-octyloxycarbonyl)ethylphenyl)-2H-benzotriazole, dodecylated 2-(2-hydroxy-5-methylphenyl)-2-H-benzotriazole, 2-(3-tert-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-tert-butyl-2-hydroxy-5-(2-methoxycarbonylethyl)phenyl)-5-chloro-2H-benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-(2-methoxycarbonylethyl)phenyl)-2H-benzotriazole, 2-(3-tert-butyl-5-(2-(2-ethylhexyloxy)carbonylethyl)-2-hydroxyphenyl)-2H-benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-(2-isooctyloxycarbonylethyl)phenyl-2H-benzotriazole, 2,2'-methylene-bis(4-tert-octyl-(6-2H-benzotriazol-2-yl)phenol), 2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole, 2-(2-hydroxy-3-tert-octyl-5-a-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-tert-octylphenyl)-2H-benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-(2-isooctyloxycarbonylethyl)phenyl)-5-chloro-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-5-tert-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-octylphenyl)-2H-benzo-triazole, methyl 3-(5-trifluoromethyl-2H-benzotriazol-2-yl)-5-tert-butyl-4-hydroxyhydrocinnamate, 5-butylsulfonyl-2-(2-hydroxy-3-α-cumyl-5-tert-octylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3-α-cumyl-5-tert-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole, 5-trifluoromethyl-2-(2-hydroxy-3,5-di-α-cumylphenyl)-2H-benzotriazole, 5-butylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole and 5-phenylsulfonyl-2-(2-hydroxy-3,5-di-tert-butylphenyl)-2H-benzotriazole.

3.2. **2-Hydroxybenzophenones,** for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives.

3.3. **Esters of substituted and unsubstituted benzoic acids,** as for example 4-tert-butylphenyl 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.

3.4. **Acrylates and malonates,** for example, α-cyano-β,β-diphenylacrylic acid ethyl ester or isooctyl ester, α-carbomethoxy-cinnamic acid methyl ester, α-cyano-β-methyl-p-methoxy-cinnamic acid methyl ester or butyl ester, α-carbomethoxy-p-methoxy-cinnamic acid methyl ester, N-(β-carbomethoxy-β-cyanovinyl)-2-methyl-indoline, Sanduvor® PR 25, (Clariant), dimethyl p-methoxybenzylidenemalonate (CAS#7443-25-6), and Sanduvor® PR 31 (Clariant), di-(1,2,2,6,6-pentamethylpiperid- in-4-yl) p-methoxybenzylidenemalonate (CAS #147783-69-5).

3.5. **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-disubtituted oxanilides and mixtures of o- and p-ethoxy-disubstituted oxanilides.

3.6. **Tris-aryl-o-hydroxyphenyl-s-triazines,** for example known commercial tris-aryl-o-hydroxyphenyl-s-triazines and triazines as disclosed in, WO 96/28431, EP 434608, EP 941989, GB 2,317,893, U.S. Pat. Nos. 3,843,371; 4,619,956; 4,740,542; 5,096,489; 5,106,891; 5,298,067; 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; 5,942,626; 5,959,008; 5,998,116 and 6,013,704, 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-(4-chlorophenyl)-s-triazine, 2,4-bis[2-hydroxy-4-(2-hydroxpethoxy)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-biphenylyl)-6-(2-hydroxy-4-octyloxycarbonylethylideneoxyphenyl)-s-triazine, 2-phenyl-4-[2-hydroxy-4-(3-sec-

butyloxy-2-hydroxypropyloxy)phenyl]-6-[2-hydroxy-4-(3-sec-amyloxy-2-hydroxy-propyloxy)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-butyloxyphenyl)-s-triazine, 2,4-bis(2,4-dimethylphenyl)-6-[2-hydroxy-4-(3-nonyloxy*-2-hydroxypropyloxy)-5-a-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-isooctyloxycarbonylsopropylideneoxy-phenyl)-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-hydroxapropyloxy)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.

4. **Metal deactivators,** as used herein are compounds which form stable complexes with metal ions and inhibit their reaction with peroxides, for example, N,N'-diphenyloxamide, N-salicylal-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl) hydrazine, 3-salicyloylamino-1,2,4-triazole, bis(benzylidene)oxalyl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-diacetyladipoyl dihydrazide, N,N'-bis(salicyloyl)oxalyl dihydrazide, N,N'-bis(salicyloyl)thiopropionyl dihydrazide.

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

6. **Hydroxylamines** for example, N,N-dihydrocarbylhydroxylamines selected from the group consisting of N,N-dibenzylhydroxylamine, N,N-dimethylhydroxylamine, N,N-diethylhydroxylamine, N,N-bis(2-hydroxypropyl)hydroxylamine, N,N-bis(3-hydroxypropyl)hydroxylamine, N,N-bis(2-carboxyethyl)hydroxylamine, N,N-bis(benzylthiomethyl)hydroxylamine, N,N-dioctylhydroxylamine, N,N-dilaurylhydroxylamine, N,N-didodecylhydroxylamine, N,N-ditetradecylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N-hexadecyl-N-tetradecylhydroxylamine, N-hexadecyl-N-heptadecylhydroxylamine, N-hexadecyl-N-octadecylhydroxylamine, N-heptadecyl-N-octadecylhydroxylamine, N-methyl-N-octadecylhydroxylamine, and N,N-di(hydrogenated tallow)hydroxylamine. The hydroxylamine may be for example the N,N-di(alkyl)hydroxylamine produced by the direct oxidation of N,N-di(hydrogenated tallow)amine. For example, the hydroxylamine prepared by direct hydrogen peroxide oxidation of bis(hydrogenated tallow alkyl) amines that are N, N-di (hydrogenated tallow) hydroxylamine, CAS # 143925-92-2. N,N-di(hydrogenated tallow)hydroxylamine is prepared as in the working Examples of U.S. Pat. No. 5,013,510.

7. **Nitrones,** for example, N-benzyl-α-phenyl-nitrone, N-ethyl-α-methyl-nitrone, N-octyl-α-heptyl-nitrone, N-lauryl-α-undecyl-nitrone, N-tetradecyl-α-tridecyl-nitrone, N-hexadecyl-α-pentadecyl-nitrone, N-octadecyl-α-heptadecyl-nitrone, N-hexadecyl-α-heptadecyl-nitrone, N-ocatadecyl-α-pentadecyl-nitrone, N-heptadecyl-α-heptadecyl-nitrone, N-octadecyl-α-hexadecyl-nitrone, nitrone derived from N,N-di(hydrogenated tallow)hydroxylamine.

8. **Amine-N-oxides,** for example Genox™ EP, a di(C_{16}-C_{18})alkyl methyl amine oxide, CAS# 204933-93-7, Crompton Corporation.

9. **Benzofuranones and indolinones,** for example those disclosed in U.S. Pat. Nos. 4,325,863; 4,338,244; 5,175,312; 5,216,052; 5,252,643; 5,369,159; 5,488,117; 5,356,966; 5,367,008; 5,428,162; 5,428,177; 5,516,920; 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.

10. Polyhydric alcohols, for example pentaerythritol and glycerol.

11. Basic co-stabilizers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triallyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides and polyurethanes.

12. 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, lithium benzoate, disodium bicycle[2.2.1]heptane 2,3-dicarboxylate; organic phosphates and salts thereof, e.g. sodium 2,2'-methylenebis(4,6-di-tert-butylphenyl)phosphate, and polymeric compounds such as ionic copolymers (ionomers).

13. Clarifiers, for example substituted and unsubstituted bisbenzylidene sorbitols.

14. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibers, glass bulbs, asbestos, talc, wollastonite, nanoclays, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours or fibers of other natural products, synthetic fibers.
15. Dispersing Agents, as used herein are compounds which when added to a colloidal solution disperse the particles uniformly, such as, for example, polyethylene oxide waxes or mineral oil.
16. Other additives, for example, plasticizers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flame retardants, antistatic agents, antimicrobials and blowing agents.

[0104] In certain embodiments of the present invention the co-stabilizers are added, for example, in concentrations of from about 0.0001% to about 50% by weight, about 0.0005% to about 20% by weight, about 0.001% to about 10% by weight, from about 0.01% to about 5% by weight, from about 0.05% to about 1% by weight from about 0.1% to about 1% by weight based on the overall weight of the polyolefin to be stabilized.

[0105] In certain other embodiments of the present invention the fillers and reinforcing agents, for example talc, calcium carbonate, mica or kaolin, are added to the polyolefins in concentrations of about 0.001% to about 80% by weight, about 0.005% to about 60% by weight, about 0.01% to about 40% by weight, of about 0.05% to about 20% by weight, of about 0. 1% to about 10% by weight, of about 0.5% to about 5% by weight, based on the overall weight of the polyolefins to be stabilized.

[0106] In certain particular embodiments of the present invention the fillers and reinforcing agents, for example metal hydroxides, especially aluminum hydroxide or magnesium hydroxide, are added to the polyolefins in concentrations of about 0.001% to about 80% by weight, about 0.005% to about 70% by weight, about 0.01% to about 60% by weight, about 0.1% to about 50% by weight about 0.5% to about 40% by weight about 1% to about 20% by weight based on the overall weight of the polyolefins to be stabilized.

[0107] In certain particular embodiments of the present invention carbon black as filler is added to the polyolefins in concentrations, judiciously, of from about 0.001% to about 30% by weight, 0.005% to about 10% by weight, 0.01% to about 5% by weight, of from about 0.05% to about 3% by weight of from about 0.1% to about 2% by weight of from about 0.1% to about 1% by weight based on the overall weight of the polyolefins to be stabilized.

[0108] In certain particular embodiments of the present invention glass fibers as reinforcing agents are added to the polyolefins in concentrations, judiciously, of from of about 0.001% to about 80% by weight, about 0.005% to about 60% by weight, about 0.01% to about 40% by weight, of about 0.05% to about 20% by weight, of about 0. 1% to about 10% by weight, based on the overall weight of the polyolefins to be stabilized.

[0109] The term "alkyl" as used herein means a saturated straight-chain, branched or cyclic hydrocarbon. When straight-chained or branched, an alkyl group is typically C1-C8, more typically C1-C6; when cyclic, an alkyl group is typically C3-C12, more typically C3-C7 alkyl ester. Examples of alkyl groups include methyl, ethyl, n propyl, iso propyl, n butyl, sec butyl and tert butyl and 1,1-dimethylhexyl.

[0110] The term "alkoxy" as used herein is represented by -OR**, wherein R** is an alkyl group as defined above.

[0111] The term "acyl" as used herein is represented by -C(O)R**, wherein R** is an alkyl group as defined above.

[0112] The term "alkyl ester" as used herein means a group represented by -C(O)OR**, where R** is an alkyl group as defined above.

[0113] The term "aromatic group" used alone or as part of a larger moiety as in "aralkyl", includes carbocyclic aromatic rings and heteroaryl rings. The term "aromatic group" may be used interchangeably with the terms "aryl", "aryl ring" "aromatic ring", "aryl group" and "aromatic group".

[0114] Carbocyclic aromatic ring groups have only carbon ring atoms (typically six to fourteen) and include monocyclic aromatic rings such as phenyl and fused polycyclic aromatic ring systems in which a carbocyclic aromatic ring is fused to one or more aromatic rings (carbocyclic aromatic or heteroaromatic). Examples include 1-naphthyl, 2-naphthyl, 1-anthracyl and 2-anthracyl. Also included within the scope of the term "carbocyclic aromatic ring", as it is used herein, is a group in which an aromatic ring is fused to one or more non-aromatic rings (carbocyclic or heterocyclic), such as in an indanyl, phthalimidyl, naphthimidyl, phenanthridinyl, or tetrahydronaphthyl, where the radical or point of attachment is on the aromatic ring.

[0115] The term "heteroaryl", "heteroaromatic", "heteroaryl ring", "heteroaryl group" and "heteroaromatic group", used alone or as part of a larger moiety as in "heteroaralkyl" refers to heteroaromatic ring groups having five to fourteen members, including monocyclic heteroaromatic rings and polycyclic aromatic rings in which a monocyclic aromatic ring is fused to one or more other aromatic ring (carbocyclic aromatic or heteroaromatic). Heteroaryl groups have one or more ring heteroatoms. Examples of heteroaryl groups include 2-furanyl, 3-furanyl, N-imidazolyl, 2-imidazolyl, 4-imidazolyl, 5-imidazolyl, 3-isoxazolyl, 4-isoxazolyl, 5-isoxazolyl, 2-oxadiazolyl, 5-oxadiazolyl, 2-oxazolyl, 4-oxazolyl, 5-oxazolyl, 3-pyrazolyl, 4-pyrazolyl, 1-pyrrolyl, 2-pyrrolyl, 3-pyrrolyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 2-pyrimidinyl, 4-pyrimidinyl, 5-pyrimidinyl, 3-pyridazinyl, 2-thiazolyl, 4-thiazolyl, 5-thiazolyl, 2-triazolyl, 5-triazolyl, tetrazolyl, 2-thienyl, 3-thienyl, carbazolyl, 2 benzothienyl, 3 benzothienyl, 2 benzofuranyl, 3 benzofuranyl, 2 indolyl, 3 indolyl, 2 quinolinyl, 3 quinolinyl, 2 benzothiazole, 2 benzooxazole, 2 benzimidazolyl, 2 quinolinyl, 3 quinolinyl, 1 isoquinolinyl, 3 quinolinyl, 1 isoindolyl and

3 isoindolyl. Also included within the scope of the term "heteroaryl", as it is used herein, is a group in which an aromatic ring is fused to one or more non-aromatic rings (carbocyclic or heterocyclic), where the radical or point of attachment is on the aromatic ring.

[0116] The term "heteroatom" means nitrogen, oxygen, or sulfur and includes any oxidized form of nitrogen and sulfur, and the quaternized form of any basic nitrogen. Also the term "nitrogen" includes substitutable nitrogen of a heteroaryl or non-aromatic heterocyclic group. As an example, in a saturated or partially unsaturated ring having 0-3 heteroatoms selected from oxygen, sulfur or nitrogen, the nitrogen may be N (as in 3,4-dihydro-2H-pyrrolyl), NH (as in pyrrolidinyl) or NR" (as in N-substituted pyrrolidinyl), wherein R" is a suitable substituent for the nitrogen atom in the ring of a non-aromatic nitrogen-containing heterocyclic group, as defined below.

[0117] An "aralkyl group", as used herein is an alkyl groups substituted with an aryl group as defined above.

[0118] An optionally substituted aryl group as defined herein may contain one or more substitutable ring atoms, such as carbon or nitrogen ring atoms. Examples of suitable substituents on a substitutable ring carbon atom of an aryl group include -OH, C1-C3 alkyl, C1-C3 haloalkyl, $-NO_2$, C1-C3 alkoxy, C1-C3 haloalkoxy, -CN, $-NH_2$, C1-C3 alkylamino, C1-C3 dialkylamino, $-C(O)NH_2$, -C(O)NH(C1-C3 alkyl), -C(O)(C1-C3 alkyl), -NHC(O)H, -NHC(O)(C1-C3 alkyl), -C(O)N(C1-C3 alkyl)$_2$, -NHC(O)O-(C1-C3 alkyl), -C(O)OH, -C(O)O-(C1-C3 alkyl), $-NHC(O)NH_2$, -NHC(O)NH(C1-C3 alkyl), -NHC(O)N(C1-C3 alkyl)$_2$, $-SO_2NH_2$ $-SO_2NH$(C1-C3alkyl), $-SO_2N$(C1-C3alkyl)$_2$, $NHSO_2H$ or $NHSO_2$(C1-C3 alkyl). Preferred substituents on aryl groups are as defined throughout the specification. In certain embodiments optionally substituted aryl groups are unsubstituted.

[0119] Examples of suitable substituents on a substitutable ring nitrogen atom of an aryl group include C1-C3 alkyl, NH_2, C1-C3 alkylamino, C1-C3 dialkylamino, $-C(O)NH_2$, -C(O)NH(C1-C3 alkyl), -C(O)(C1-C3 alkyl), $-CO_2$ R**, -C(O)C(O)R**, $-C(O)CH_3$, -C(O)OH, -C(O)O-(C1-C3 alkyl), $-SO_2NH_2$ $-SO_2NH$(C1-C3alkyl), $-SO_2N$(C1-C3alkyl)$_2$, $NHSO_2H$, $NHSO_2$(C1-C3 alkyl), $-C(=S)NH_2$, -C(=S)NH(C1-C3 alkyl), -C(=S)N(C1-C3 alkyl)$_2$, -C(=NH)-N(H)$_2$, -C(=NH)-NH(C1-C3 alkyl) and -C(=NH)-N(C1-C3 alkyl)$_2$.

[0120] An optionally substituted alkyl group as defined herein may contain one or more substituents. Examples of suitable substituents for an alkyl group include those listed above for a substitutable carbon of an aryl and the following: =O, =S, =NNHR**, =NN(R**)$_2$, =NNHC (O) R**, $=NNHCO_2$ (alkyl), $=NNHSO_2$ (alkyl), =NR**, spiro cycloalkyl group or fused cycloalkyl group. R** in each occurrence, independently is -H or C1-C6 alkyl. Preferred substituents on alkyl groups are as defined throughout the specification. In certain embodiments optionally substituted alkyl groups are unsubstituted.

[0121] A "spiro cycloalkyl" group is a cycloalkyl group which shares one ring carbon atom with a carbon atom in an alkylene group or alkyl group, wherein the carbon atom being shared in the alkyl group is not a terminal carbon atom.

[0122] The polyamide is generally known as nylon having the formula

$$-NH-(CH2)_x-CO-$$

where x is an integer, preferably 6, 9, 10, 11 or 12. Any suitable nylon may be employed as the base resin in the composition according to the invention. Preferred nylons are Nylon-6 (polycaprolactam), Nylon-6,6 (polyhexamethylene adipamide), Nylon-6,9 (polyhexamethylene azelaamide), Nylon-6,10 (polyhexamethylene sebacamide), Nylon-6,12(polyhexamethylene dodecanoamide), Nylon-1(polyundecanoamide) and Nylon-12 (polydodecanoamide).The nylon base resin will be preferably 100% of the units represented by the formula, but it may also contain non-polyamide units, e.g. an olefin homopolymer or copolymer. In such polycopolyamides, polyamides generally comprise at least 25%, preferably at least 75%, particularly essentially 100% units having the above formula.

[0123] In another embodiment the polymer is selected from the group consisting of polyamide, polyester and combination thereof; preferably polymer is selected from the group consisting of polyamide, such as nylon 6, nylon 66, nylon 10, nylon1010, nylon 12, nylon1212, nylon610, nylon 612, PPA, PA6T, PA9T and combination thereof; and preferably the polymer is selected from the group consisting of PET, PBT, PTT and combinations thereof.

[0124] As disclosed in Kirk-Othmer Encyclopedia of Chemical Technology, Volume 19, pages 772- 797, nylon may be compounded with a wide range of additives that include lubricants to improve the melt flow, screw feeding and mold release; nucleants which are finely dispersed seed the molten nylon and result in a higher density of small uniformly sized spherulites to increase the tensile strength and stiffness; stabilizers to slow down the rate of oxidation and UV aging by adding antioxidants, ultraviolet stabilizers, hydro-peroxide decomposers, or metal salts mostly in the form of copper halide mixtures; impact modifiers to improve the notched impact strength and ductility by adding rubbers, olefin copolymers silicones, polyurethanes or modified acrylics; flame retardants to aid inhibiting the combustion process and eliminating burning drips by adding halogenated organics; plastisizers to increase the flexibility of nylon and to improve the impact strength, and reinforcement by adding such as glass fibers or nylon mixing with nanometer size silicates to make nanocomposites to improve the tensile strength and stiffness. To balance the properties nylon are sometimes blended with other polymers e.g. polyethylene or polypropylene.

Description of Polyamides:

[0125] Examples of thermoplastic polyamides useful in the compositions of the present invention include semicrystalline or amorphous aliphatic and semi-aromatic polyamides as well as mixtures thereof.

[0126] Suitable aliphatic polyamides are derived from aliphatic lactams or aliphatic diamines and dicarboxylic acids and include, for example, polyamide 6, polyamide 11, polyamide 12, polyamide 6,6, polyamide 4,6, polyamide 6,10, polyamide 6,12. Suitable aliphatic polyamides also include copolyamides derived from mixtures of aliphatic diamines, aliphatic dicarboxylic acids, and aliphatic lactams.

[0127] Suitable semi-aromatic polyamides are derived from at least one aromatic diamine and/or aromatic dicarboxylic acid monomer and other aliphatic monomers, which may include aliphatic diamines, aliphatic dicarboxylic acids, and aliphatic lactams. Specific examples include PA-6,1, PA-6,I/6,6-copolyamide, PA-6,T, PA-6,T/6-copolyamide, PA-6,T/6,6-copolyamide, PA-6,I/6,T-copolyamide, PA-6,6/6,T/6,1-copolyamide, PA-6,T/2-MPMD,T-copolyamide (2-MPMD=2-methylpentamethylene diamine), PA-9,T, and PA-9T/2-MOMD,T (2-MOMD=2-methyl-1,8-octamethylenediamine).

Description of Stabilizers for Polyamides:

[0128] Heat stabilizing systems for polyamides typically comprise one or more additives selected from the groups of phenolic antioxidants, low-valent phosphorus compounds, aromatic amines, copper salts alone or in combination with one or more alkali or alkaline earth metal halide salts metal salts, and the transition metals and their oxides.

[0129] Phenolic antioxidants suitable for use in polyamides are well known in the art and are described by K. Schwarzenbach et al. in "Plastic Additives Handbook", 5th ed., H. Zweifel, Ed., Hanser Publishers, Chapter 1. Examples of preferred phenolic antioxidants for use in polyamides include:

N,N'-Hexamethylenebis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionamide], Chemical Abstract Service Registry No. 23128-74-7, available from BASF as Irganox® 1098,
[1,2-Bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionoyl]hydrazine, Chemical Abstract Service Registry No. 32687-87-8, available from BASF as Irganox® MD 1024,
Pentaerythritol tetrakis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate], Chemical Abstract Service Registry No. 6683-19-8, available from BASF as Irganox® 1010,
1,3,5-Trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene, Chemical Abstract Service Registry No. 1709-70-2, available from Albemarle Corporation as Ethanox® 330,
Butylated reaction product of p-cresol and dicyclopentadiene, Chemical Abstract Service Registry No. 68610-51-5, available from ELIOKEM as Wingstay® L,
N-(4-hydroxyphenyl)octadecanamide, Chemical Abstract Service Registry No. 103-99-1,
2-*tert*-butyl-6-(3-*tert*-butyl-2-hydroxy-5-methyl) benzyl-4-methylphenyl acrylate, Chemical Abstract Service Registry No. 61167-58-6, available from Sumitomo as Sumilizer® GM,
2-[1-(2-hydroxy-3,5-di-*tert*-pentylphenyl)ethyl]-4, 6-di-*tert*-pentylphenyl acrylate, Chemical Abstract Service Registry No. 123968-25-2, available from Sumitomo as Sumilizer® GS, and
2,6-Di-*tert*-butyl-4-[4,6-bis(octylthio)-1,3,5-triazin-2-ylamino]phenol, Chemical Abstract Service Registry No. 991-84-4, available from BASF as Irganox® 565.

[0130] Low-valent phosphorus compounds suitable for use in polyamides include organic phosphites and phosphonites, salts of phenylphosphinic acid, and hypophosphite salts. Organic phosphites and phosphonites suitable for use in polyamides are well known in the art and are described by K. Schwarzenbach et al. in "Plastic Additives Handbook", 5th ed., H. Zweifel, Ed., Hanser Publishers, Chapter 1. Examples of preferred organic phosphites and phosphonites for use in polyamides include:

Tris(2,4-di-tert-butylphenyl)phosphite, Chemical Abstract Service Registry No. 31570-04-4, available from BASF as Irgafos® 168,
Bis(2,4-dicumylphenyl) pentaerythritol diphosphite, Chemical Abstract Service Registry No. 154862-43-8, available from Dover Chemical as Doverphos® S-9228,
Bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, available from Amfine Chemical as ADK Stab® PEP-36, and
Tetrakis(2,4-di-tert-butylphenyl)[1,1'-biphenyl]4,4'-diylbisphosphonite, Chemical Abstract Service Registry No. 119345-01-6, available from Clariant as Hostanox® P-EPQ.

[0131] Examples of salts of phenylphosphinic acid suitable for use in polyamides include sodium phenylphosphinate

(Chemical Abstract Service Registry No. 4297-95-4), zinc phenylphosphinate (Chemical Abstract Service Registry No. 25070-22-8), and other phenylphosphinate salts of alkali metals and alkaline earth metals.

[0132] Examples of hypophosphite salts include sodium hypophosphite (Chemical Abstract Service Registry No. 7681-53-0), sodium hypophosphite monohydrate (Chemical Abstract Service Registry No. 10039-56-2) and other hypophosphite salts of alkali metals and alkaline earth metals and their hydrates.

[0133] Aromatic amine antioxidants suitable for use in polyamides are well known in the art and are described by K. Schwarzenbach et al. in "Plastic Additives Handbook", 5th ed., H. Zweifel, Ed., Hanser Publishers, Chapter 1. Examples of preferred aromatic amine antioxidants for use in polyamides include:

4,4'-Bis(α, α-dimethylbenzyl)diphenylamine, Chemical Abstract Service Registry No. 10081-67-1, available from Chemtura as Naugard® 445,
Acetone-diphenylamine condensation product, Chemical Abstract Service Registry No. 9003-79-6, available from Chemtura as Naugard® A, and
Styrenated diphenylamines, Chemical Abstract Service Registry No. 68442-68-2, available from ELIOKEM as Wingstay® 29.

[0134] Examples of suitable copper salts include copper (I) and copper (II) salts, for example, copper phosphates, copper halides, and copper acetates. Suitable alkali metal halides for use in combination with the copper salts include the chlorides, bromides and iodides of lithium, sodium, potassium, and cesium. Examples of suitable alkaline earth metal halides for use in combination with the copper salts include the chlorides, bromides, and iodides of calcium. Suitable copper (I) halide / alkali metal halide combinations include, for example, CuI / KI and CuI / KBr. When used in combination, preferred ratios of the copper salt to the alkali metal or alkaline earth salt range from about 1:50 to about 2:1 by weight.

[0135] Examples of suitable transition metals and their oxides include iron, copper, and the iron oxides.

[0136] The preferred concentration of component of the heat stabilizing system ranges from about 0.05% to about 10 % by weight, from about 0.01% to about 5%, from about 0.01% to about 3 %, from about 0.01% to about 1%, based on the weight of thermoplastic polyamide polymer being stabilized.

[0137] In one embodiment, of the present invention the compositions for use in stabilization of polyamides, copolyamides, polyesters, copolyesters and blend of polymer or copolymer with one or more other polymers include but are not limited to:

a. an antioxidant of the instant invention (in the concentration range , from about 0.0001% to about 50%, from about 0.0005% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) with acid scavengers, for example, in amounts of from about 0.0005% to about 50%, from about 0.0001% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1% by weight, based on the weight of polymer or copolymer or blend of polymer with the other polymers or copolymers and blend of polymer or copolymer with one or more other polymers to be stabilized.

b. an antioxidant of the instant invention (in the concentration range from about 0.0005% to about 50%, from about 0.0001% to about 20%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) along with organic phosphorus stabilizers. The organic phosphorus stabilizers are used for example, in amounts of, from about 0.001 % to about 30 %, from about 0.005 % to about 20 %, from about 0.01 % to about 5 %, from about 0.05 % to about 2 % or from about 0.1 % to about 1 %, by weight, based on the weight of the polymer to be stabilized.

c. an antioxidant of the instant invention (in the concentration range from about 0.0005% to about 50%, from about 0.0001% to about 50%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) along with low valent phosphorus compounds, aromatic amine antioxidants, copper salts alone or in combination with one or more alkali or alkaline earth metal halide salts, and transition metals and their oxides in a. and b. above. These additives are used for example, in amounts of, from about 0.001 % to about 30 %, from about 0.005 % to about 20 %, from about 0.01 % to about 5 %, from about 0.05 % to about 2 % or from about 0.1 % to about 1 %, by weight, based on the weight of the polymer to be stabilized.

d. an antioxidant of the instant invention (in the concentration range from about 0.0005% to about 50%, from about 0.0001% to about 50%, from about 0.005% to about 10%, from about 0.05% to about 5% or from about 0.01% to about 1%) along with polyfunctional epoxides, polyhydric alcohols, and polyfunctional carboxylic acids and anhydrides. These additives are used for example, in amounts of, from about 0.001 % to about 30 %, from about 0.005 % to about 20 %, from about 0.01 % to about 5 %, from about 0.05 % to about 2 % or from about 0.1 % to about 1 %, by weight, based on the weight of the polymer to be stabilized.

e. an antioxidant of the instant invention in combination with other known commercially available antioxidants, such as, for example, Irganox® 1010, Irganox® 1330, Irganox® 1076 , Irganox® 1135, aromatic amines antioxidants Naugard 445, Naugard A, Winstay 29 or other antioxidants described above along with the formulations described

in a.-d. above.

Exemplification:

Example 1: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,4-dimethyl-pentyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride

[0138] In a one liter of 3-neck round bottom flask, 25.0g of N-(1,4-Dimethyl-pentyl)-N'-phenyl-benzene-1,4-diamine was dissolved in 200 ml of anhydrous toluene under argon atmosphere. 25 ml of triethyl amine was added drop wise. 30 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride was dissolved in 200 ml of anhydrous toluene and was transferred drop wise to the round bottom flask containing N-(1,4-Dimethyl-pentyl)-N'-phenyl-benzene-1,4-diamine under argon atmosphere. Reactants were heated to reflux temperature of toluene (111°C). The reaction was completed in 6 hours. The crude product thus obtained was purified by washing with cold hexane to get 29.5g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,4-dimethyl-pentyl)-N-(4-phenylaminophenyl)-propionamide and the structure was confirmed by 500 MHz ^{1}H NMR spectroscopy with resonance peaks at 0.9-1.1 (m), 1.33(m), 1.41 (s), 1.61 (m), 1.91 (m), 2.3 (t), 2.85 (t), 3.88 (m), 6.81 (m), 6.86 (s), 7.01 (m), 7.13-7.15 (m), 7.32-7.35 (m) ppm.

Example 2: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride

[0139] In a 100 ml of 3-neck round bottom flask, 1.0g of N-(1,3-Dimethyl-butyl)-N'-phenylbenzene-1,4-diamine was dissolved in 20 ml of anhydrous toluene under argon atmosphere. 0.75 ml of triethyl amine was added drop wise. 1.4 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride was dissolved in 20 ml of anhydrous toluene and was transferred drop wise to the round bottom flask containing N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine under argon atmosphere. Reactants were heated to reflux temperature of toluene (111°C). The reaction was completed in 5 hours. The crude product thus obtained was purified by washing with cold hexane to get 1.5g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide and the structure was confirmed by 500 MHz ^{1}H NMR with peaks appearing at 0.9-1.1 (m), 1.42 (s), 1.61 (m), 1.94 (m), 2.28 (t), 2.83 (t), 3.89 (m), 6.83 (m), 6.88 (s), 7.03 (m), 7.13-7.15 (m), 7.32-7.35 (m) ppm.

Example 3: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-isopropyl-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride

[0140] In a 100 ml of 3-neck round bottom flask, 1.0g of N-Isopropyl-N'-phenyl-benzene-1,4-diamine is dissolved in 20 ml of anhydrous toluene under argon atmosphere. 0.75 ml of triethyl amine is added drop wise. 1.3 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride is dissolved in 20 ml of anhydrous toluene and is transferred drop wise to the round bottom flask containing N-Isopropyl-N'-phenyl-benzene-1,4-diamine. Reactants are heated to reflux temperature of toluene (111°C). The reaction is completed in 5 hours. The crude product thus obtained is purified by washing with cold hexane to get 1.4g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-isopropyl-N-(4-phenylamino-phenyl)-propionamide.

Example 4: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(4-phenylaminophenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride

[0141] In a 100 ml of 3-neck round bottom flask, 1.0g of N-Phenyl-benzene-1,4-diamine is dissolved in 20 ml of anhydrous toluene under argon atmosphere. 0.75 ml of triethyl amine is added drop wise. 1.2 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride is dissolved in 20 ml of anhydrous toluene and is transferred drop wise to the round bottom flask containing N-Phenylbenzene-1,4-diamine. Reactants are heated to reflux temperature of toluene (111°C). The reaction is completed in 4 hours. The crude product thus obtained is purified by washing with cold hexane to get 1.2g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(4-phenylamino-phenyl)-propionamide.

Example 5: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,4-dimethyl-pentyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid

[0142] In a set-up of Dean-Stark apparatus, 1.0 g of N-(1,4-Dimethyl-pentyl)-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.4 g of 3-(3,5-di*tert*-butyl-4-hydroxyphenyl) propanoic acid and a catalytic amount of boric acid (0.024g) are added to the flask. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,4-dimethyl-pentyl)-N-(4-phe-

nylaminophenyl)-propionamide.

Example 6: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid

[0143] In a set-up of Dean-Stark apparatus, 1.0 g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-di*tert*-butyl-4-hydroxyphenyl) propanoic acid and a catalytic amount of boric acid (0.024g) are added to the flask. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylaminophenyl)-propionamide.

Example 7: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-isopropyl-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid

[0144] In a set-up of Dean-Stark apparatus, 1.0 g of N-Isopropyl-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-di*tert*-butyl-4-hydroxyphenyl) propanoic acid and a catalytic amount of boric acid (0.024g) are added to the flask. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-isopropyl-N-(4-phenylamino-phenyl)-propionamide.

Example 8: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(4-phenylaminophenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid

[0145] In a set-up of Dean-Stark apparatus, 1.0 g of N-Phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-di*tert*-butyl-4-hydroxyphenyl) propanoic acid and a catalytic amount of boric acid (0.024g) are added to the flask. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(4-phenylamino-phenyl)-propionamide.

Example 9: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,4-dimethyl-pentyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester

[0146] In a set-up of Dean-Stark apparatus, 1.0 g of N-(1,4-Dimethyl-pentyl)-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.4 g of 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)-propionic acid methyl ester and a catalytic amount of boric acid (0.024g) are added to the flask. 10 g of 4 A° molecular sieves are added in the dean stark to absorb the eliminated methanol during the course of reaction. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,4-dimethyl-pentyl)-N-(4-phenylamino-phenyl)-propionamide.

Example 10: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester

[0147] In a set-up of Dean-Stark apparatus, 1.0 g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)-propionic acid methyl ester and a catalytic amount of boric acid (0.024g) are added to the flask. 10 g of 4 A° molecular sieves are added in the dean stark to absorb the eliminated methanol during the course of reaction. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide.

Example 11: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-isopropyl-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester

[0148] In a set-up of Dean-Stark apparatus, 1.0 g of N-Isopropyl-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester and a catalytic amount of boric acid (0.024g) are added to the flask. 10 g of 4 A° molecular sieves are added in the dean stark to absorb the eliminated methanol during the course of reaction. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-isopropyl-N-(4-phenylamino-phenyl)-propionamide.

Example 12: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(4-phenylaminophenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester

[0149] In a set-up of Dean-Stark apparatus, 1.0 g of N-Phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester and a catalytic amount of boric acid (0.024g) are added to the flask. 10 g of 4 A° molecular sieves are added in the dean stark to absorb the eliminated methanol during the course of reaction. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(4-phenylamino-phenyl)-propionamide.

Example 13: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methyl-heptyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride

[0150] In a 100 ml of 3-neck round bottom flask, 1.0g of N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine was dissolved in 20 ml of anhydrous toluene under argon atmosphere. 0.75 ml of triethyl amine was added drop wise. 1.4 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride was dissolved in 20 ml of anhydrous toluene and was transferred drop wise to the round bottom flask containing N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine under argon atmosphere. Reactants were heated to reflux temperature of toluene (111°C). The reaction was completed in 5 hours. The crude product thus obtained was purified by washing with cold hexane to get 1.5g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methyl-heptyl)-N-(4-phenylamino-phenyl)-propionamide. The structure was confirmed by 500 MHz ^{1}H NMR with peaks appearing at 0.91 (m), 1.3 - 1.41 (m), 1.44 (s), 1.61 (m), 2.3 (t), 2.85 (t), 3.88 (m), 6.81 (m), 6.86 (s), 7.01 (m), 7.13-7.15 (m), 7.32-7.35 (m) ppm.

Example 14: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methyl-heptyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid

[0151] In a set-up of Dean-Stark apparatus, 1.0 g of N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-di*tert*-butyl-4-hydroxyphenyl) propanoic acid and a catalytic amount of boric acid (0.024g) are added to the flask. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methyl-heptyl)-N-(4-phenylaminophenyl)-propionamide.

Example 15: Synthesis of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methyl-heptyl)-N-(4-phenylamino-phenyl)-propionamide using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester

[0152] In a set-up of Dean-Stark apparatus, 1.0 g of N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine is dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)-propionic acid methyl ester and a catalytic amount of boric acid (0.024g) are added to the flask. 10 g of 4 A° molecular sieves are added in the dean stark to absorb the eliminated methanol during the course of reaction. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methyl-heptyl)-N-(4-phenylamino-phenyl)-propionamide.

Example 16: Reaction product of synthesis of mixture of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine and N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride

[0153] In a 100 ml of 3-neck round bottom flask, 0.5g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine and 0.5g of N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine were dissolved in 20 ml of anhydrous toluene under argon atmosphere. 0.8 ml of triethyl amine was added. 1.5 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionyl chloride was dissolved in 20 ml of anhydrous toluene and was transferred drop wise to the round bottom flask containing N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine and N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine under argon atmosphere. Reactants were heated to reflux temperature of toluene (111°C). The reaction was completed in 1 hour. The crude product thus obtained was purified by washing with cold hexane to get 1.4g of reaction product of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide and 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)-N-(1-methyl-heptyl)-N-(4-phenylamino-phenyl)-propionamide. The structure was confirmed by 500 MHz ^{1}H NMR with peaks appearing at 0.9-1.1 (m), 1.3 - 1.41 (m), 1.44 (s), 1.61 (m), 1.94 (m), 2.3 (t), 2.85 (t), 3.88 (m), 6.81 (m), 6.86 (s), 7.01 (m), 7.13-7.15 (m), 7.32-7.35 (m) ppm.

Example 17: Reaction product of synthesis of mixture of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine and N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid

[0154] In a set-up of Dean-Stark apparatus, 0.5g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine and 0.5g of N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine are dissolved in 40 ml of anhydrous toluene. 1.4 g of 3-(3,5-di*tert*-butyl-4-hydroxyphenyl) propanoic acid and a catalytic amount of boric acid (0.024g) are added to the flask. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get reaction product of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide and 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methyl-heptyl)-N-(4-phenylaminophenyl)-propionamide.

Example 18: Reaction product of synthesis of mixture of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine and N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine using 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester

[0155] In a set-up of Dean-Stark apparatus, 0.5g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine and 0.5g of N-(1-Methyl-heptyl)-N'-phenyl-benzene-1,4-diamine are dissolved in 40 ml of anhydrous toluene. 1.3 g of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-propionic acid methyl ester and a catalytic amount of boric acid (0.024g) are added to the flask. 10 g of 4 A° molecular sieves are added in the dean stark to absorb the eliminated methanol during the course of reaction. The reaction mixture is refluxed under argon atmosphere for 15 hours. The crude product thus obtained is purified to get reaction product of 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1,3-dimethyl-butyl)-N-(4-phenylamino-phenyl)-propionamide and 3-(3,5-Di-tert-butyl-4-hydroxy-phenyl)-N-(1-methylheptyl)-N-(4-phenylamino-phenyl)-propionamide.

Example 19: Synthesis of 4-(3-{4,6-Bis-[(1,3-dimethyl-butyl)-(4-phenylamino-phenyl)-amino]-[1,3,5]triazin-2-yloxy)-propyl)-2,6-di-tert-butyl-phenol using 2,4,6-Trichloro-[1,3,5]triazine

[0156] In a 100 ml of 3-neck round bottom flask, 1.0 g of *2,4,6-Trichloro-[1,3,5]triazine* was dissolved in 25 ml of anhydrous tetrahydrofuran under nitrogen atmosphere. 3.1 ml of triethyl amine was added. 4.45g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine was transferred to the round bottom flask under nitrogen atmosphere. Reactants were heated to reflux temperature of tetrahydrofuran (65°C). The reaction was completed in 20 hours. The crude product thus obtained was purified to get 4.1g of 4-(3-{4,6-Bis-[(1,3-dimethyl-butyl)-(4-phenylamino-phenyl)-amino]-[1,3,5]triazin-2-yloxy}-propyl)-2,6-di-*tert*-butyl-phenol. The structure was confirmed by 500 MHz ^{1}H NMR with peaks appearing at 1.34 (s), 2.54 (t), 2.64 (t), 6.72 (s), 6.77 (d), 6.81 (s), 6.98 (d) ppm.

Example 20: Synthesis of 4-[3-({4,6-bis[3-(3,5-ditert-butyl-4-hydroxyphenyl)propoxy]-1,3,5-triazin-2-yl}oxy)propyl]-2,6-ditert-butylphenol using 2,4,6-Trichloro-[1,3,5]triazine

[0157] In a 100 ml of 3-neck round bottom flask, 1.0 g of *2,4,6-Trichloro-[1,3,5]triazine* is dissolved in 25 ml of anhydrous tetrahydrofuran under nitrogen atmosphere. 3.1 ml of triethyl amine is added. 4.3g of 2,6-Di-tert-butyl-4-(3-hydroxy-propyl)-phenol is transferred to the round bottom flask under nitrogen atmosphere. Reactants are heated to reflux temperature of tetrahydrofuran (65°C). The reaction is completed in 15 hours. The crude product thus obtained is purified to get 4-[3-({4,6-bis[3-(3,5-di*tert*-butyl-4-hydroxyphenyl)propoxy]-1,3,5-triazin-2-yl}oxy)propyl]-2,6-di*tert*-butylphenol.

Example 21: Synthesis of 4-[3-({4,6-bis[(4-anilinophenyl)(1,3-dimethylbutyl)amino]-1,3,5-triazin-2-yl}oxy)propyl]-2,6-ditert-butylphenol using 2,4,6-Trichloro-[1,3,5]triazine

[0158] In a 100 ml of 3-neck round bottom flask, 1.0 g of *2,4,6-Trichloro-[1,3,5]triazine* is dissolved in 25 ml of anhydrous tetrahydrofuran under nitrogen atmosphere. Flask is kept in ice bath maintained at 0°C using salt. 3.1 ml of triethyl amine is added. 1.6g of 2,6-Di-tert-butyl-4-(3-hydroxypropyl)-phenol is transferred to the round bottom flask under nitrogen atmosphere. It is stirred for 4 hours at 0°C. Now 3.1g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine is transferred to the round bottom flask under nitrogen atmosphere. Reactants are heated to reflux temperature of tetrahydrofuran (65°C). The reaction is completed in 15 hours. The crude product thus obtained is purified to get 4-[3-({4,6-bis[(4-anilinophenyl)(1,3-dimethylbutyl)amino]-1,3,5-triazin-2-yl}oxy)propyl]-2,6-di*tert*-butylphenol.

Example 22: Synthesis of 4-[3-({4-[(4-anilinophenyl)(1,3-dimethylbutyl)amino]-6-[3-(3,5-ditert-butyl-4-hydroxyphenyl)-propoxy]-1,3,5-triazin-2-yl}oxy)propyl]-2,6-ditert-butylphenol using 2,4,6-Trichloro-[1,3,5]triazine

[0159] In a 100 ml of 3-neck round bottom flask, 1.0 g of *2,4,6-Trichloro-[1,3,5]triazine* is dissolved in 25 ml of anhydrous

tetrahydrofuran under nitrogen atmosphere. Flask is kept in ice bath maintained at 0°C using salt. 3.1 ml of triethyl amine is added. 1.7g of N-(1,3-Dimethyl-butyl)-N'-*phenyl-benzene-1,4-diamine* is transferred to the round bottom flask under nitrogen atmosphere. It is stirred for 4 hours at 0°C. Now 3.0g of 2,6-Di-tert-butyl-4-(3-hydroxy-propyl)-phenol is transferred to the round bottom flask under nitrogen atmosphere. Reactants are heated to reflux temperature of tetrahydrofuran (65°C). The reaction is completed in 15 hours. The crude product thus obtained is purified to get 4-[3-({4-[(4-anilinophenyl)(1,3-dimethylbutyl)amino]-6-[3-(3,5-di*tert*-butyl-4-hydroxyphenyl)-propoxyl-1,3,5-triazin-2-yl}oxy)propyl]-2,6-di*tert*-butylphenol.

Example 23: Synthesis of N, N',N"-Tris-(1,3-dimethyl-butyl)-N, N', N"-tris-(4-phenylaminophenyl)-propane-1,2,3-triamine using 1,2,3-Trichloro-propane

[0160] In a 100 ml of 3-neck round bottom flask, 1.0 g of 1,2,3-Trichloro-propane is dissolved in 25 ml of anhydrous toluene under nitrogen atmosphere. 3.0 ml of triethyl amine is added. 5.8g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine is transferred to the round bottom flask under nitrogen atmosphere. Reactants are heated to reflux temperature of toluene (110°C). The reaction is completed in 20 hours. The crude product thus obtained is purified to get 4.8g of N, N',N"-Tris-(1,3-dimethyl-butyl)-N, N', N"-tris-(4-phenylamino-phenyl)-propane-1,2,3-triamine.

Example 24: Synthesis of 4-[3-({3,5-bis[3-(3,5-ditert-butyl-4-hydroxyphenyl)propoxy] pentyl}oxy)propyl]-2,6-ditert-butyl-phenol using 1,2,3-Trichloro-propane

[0161] In a 100 ml of 3-neck round bottom flask, 1.0 g of 1,2,3-Trichloro-propane is dissolved in 25 ml of anhydrous toluene under nitrogen atmosphere. 3.2 ml of triethyl amine is added. 5.7g of 2,6-Di-tert-butyl-4-(3-hydroxy-propyl)-phenol is transferred to the round bottom flask under nitrogen atmosphere. Reactants are heated to reflux temperature of toluene (110°C). The reaction is completed in 20 hours. The crude product thus obtained is purified to get 4-[3-({3,5-bis[3-(3,5-di*tert*-butyl-4-hydroxyphenyl)propoxy]pentyl}oxy)propyl]-2,6-di*tert*-butylphenol.

Example 25: Synthesis of 2,6-Di-tert-butyl-4-[3-(2-[(1,3-dimethyl-butyl)-(4-phenylaminophenyl)-amino]-1-{[(1,3-dimethyl-butyl)-(4-phenylamino-phenyl)-amino]-methyl}-ethoxy)-propyl]-phenol using 1,2,3-Trichloro-propane

[0162] In a 100 ml of 3-neck round bottom flask, 1.0 g of 1,2,3-Trichloro-propane is dissolved in 25 ml of anhydrous tetrahydrofuran under nitrogen atmosphere. Flask is kept in ice bath maintained at 0°C using salt. 3.2 ml of triethyl amine is added. 3.1g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine is transferred to the round bottom flask under nitrogen atmosphere. It is stirred for 10 hours at 0°C. Now 1.5g of 2,6-Di-tert-butyl-4-(3-hydroxy-propyl)-phenol is transferred to the round bottom flask under nitrogen atmosphere. Reactants are heated to reflux temperature of toluene (110°C). The reaction is completed in 5 hours. The crude product thus obtained is purified to get 2,6-Di-tert-butyl-4-[3-(2-[(1,3-dimethyl-butyl)-(4-phenylamino-phenyl)-amino]-1-{[(1,3-dimethyl-butyl)-(4-phenylamino-phenyl)-amino]-methyl}-ethoxy)-propyl]-phenol.

Example 26: Synthesis of 4-[3-({3-[(4-anilinophenyl)(1,3-dimethylbutyl)amino]-5-[3-(3,5-ditert-butyl-4-hydroxyphenyl)propoxy]pentyl}oxy)propyl]-2,6-ditert-butylphenol using 1,2,3-Trichloro-propane

[0163] In a 100 ml of 3-neck round bottom flask, 1.0 g of 1,2,3-Trichloro-propane is dissolved in 25 ml of anhydrous toluene under nitrogen atmosphere. Flask is kept in ice bath maintained at 0°C using salt. 3.2 ml of triethyl amine is added. 3.0g of 2,6-Di-tert-butyl-4-(3-hydroxy-propyl)-phenol is transferred to the round bottom flask under nitrogen atmosphere. It is stirred for 10 hours at 0°C. Now 1.6g of N-(1,3-Dimethyl-butyl)-N'-phenyl-benzene-1,4-diamine is transferred to the round bottom flask under nitrogen atmosphere. Reactants are heated to reflux temperature of toluene (110°C). The reaction is completed in 5 hours. The crude product thus obtained is purified to get 4-[3-({3-[(4-anilinophenyl)(1,3-dimethylbutyl)amino]-5-[3-(3,5-di*tert*-butyl-4-hydroxyphenyl)propoxy]pentyl}oxy)propyl]-2,6-di*tert*-butylphenol.

[0164] The performance of the compound of the present invention (Example 2) was assessed by measuring the oxidative induction time of stabilized samples of vegetable oil at elevated temperature (150°C) and under high oxygen pressure (500 psi). This is a standard test method in the lubricant industry and is described in ASTM D 6186. Testing was conducted in biolubricant base oils, canola and soybean oil. These base oils differ mainly in their content of polyunsaturated fatty acids which are especially unstable to oxidation, with soybean oil having the highest concentration and hence the lowest inherent oxidative stability.

[0165] The performance of the compound in Example 2 was assessed vs. the commercial antioxidant Irganox® L 135 (CAS No. 125643-61-0, BASF) as a control.

[0166] The testing results are summarized in Table 1. The antioxidant of Example 2 outperformed the commercial control Irganox® L 135 by a significant margin in both bio-based oils.

[0167] In canola oil, the performance enhancement factor for compound of Example 2 over the commercial antioxidant was approximately 3x (compare results for 0.5% Example 2 vs. 1.5% Irganox® L 135). At higher treat levels, the new antioxidant provided a level of performance that could not be achieved with state-of-the-art commercial antioxidants. This result once again suggests that the new antioxidant of this instant invention may enable the use of bio-lubricants based on canola oil in higher performance applications from which they are currently excluded.

[0168] In the more oxidatively unstable soybean oil, the performance enhancement factor for compound of Example 2 over the commercial antioxidant was approximately 1.5x (compare results for 1.0% Example 2 with 1.5% Irganox® L 135).

Table 1. Performance of antioxidants in biolubricant oils: canola and soybean oils.

	Oxidative Induction Time (min), 150°C, 500 psi O_2,					
	Canola oil			Soybean oil		
Additive	0.5%	1.0%	1.5%	0.5%	1.0%	1.5%
Example 2	31.3	34.1	44.0	12.3	17.3	24.1
Irganox® L 135	15.7	23.5	31.2	9.8	14.9	17.6

[0169] The performance of the present invention was also assessed in ester oils. These synthetic base oils are classified as part of Group V base oil groups according to American Petroleum Institute (API 1509, Appendix E). Synthetic esters are used in different lubricant formulations to improve the properties. The test method described for vegetable and biolubricant oils, ASTM D 6186 method was used to test and compare the performance of the present invention in ester oils of different kinds. The test temperature was 180 °C and oxygen pressure was 500 psi. Both trimethylolpropane (TMP) based polyols ester oil (TruVis Teknor 810TMP) and neopentyl glycols (NPG) polyols ester oil (HATCOL 2957) were added 1000 ppm of antioixdant and tested using ASTM D6186 method at 180 °C and 500 psi O_2.

[0170] The performance of the compounds in Examples 2, 13, and 16 was assessed vs. the commercial antioxidant Irganox® L 135 (CAS No. 125643-61-0, BASF) as a control in TMP and NPG oils.

[0171] The testing results are summarized in Tables 2 and 3. The antioxidants of the present invention Examples 2, 13, and 16 outperformed the commercial control Irganox® L 135 by a significant margin in both ester oils.

Table 2. Performance of antioxidants in Group V oils: Polyolester oil, TMP based oil

	Oxidative Induction Time (min), 180°C, 500 psi O_2
	Oil: TMP polyol ester oil,
Additive	1000 ppm
Example 2	104.8
Irganox® L 135	18.3

[0172] In synthetic polyolester oil (TMP base oil), the performance enhancement factor for compound of Example 2 over the commercial antioxidant was approximately 5.7 x (Table 2). This result once again suggests that the new antioxidant of this instant invention may enable the use of synthetic base lubricant oil in higher performance applications from which they are currently excluded.

Table 3. Performance of antioxidants in Group V oils: Polyolester oil, NPG based oil

	Oxidative Induction Time (min), 180°C, 500 psi O_2
	Oil: NPG polyol ester oil
Additive	1000 ppm
Example 2	59.5
Example 13	60.6
Example 16	61.4
Irganox® L 135	12.2

[0173] Table 3 shows all three antioxidants of the present invention outperform over the commercial antioxidant in another type of polyolester, NPG based oil.. The performance enhancement factor was approximately 5x.

[0174] The performance of the present invention compound (Example 2) was assessed by measuring the oxidative induction time (OIT) of polyolefin samples at elevated temperature (170°C) and under high oxygen pressure (500 psi). This is a standard test method and is described in ASTM D 5885. The performance of the compound in Example 2 was assessed vs. the commercial antioxidant Irganox® 1010 (CAS No.6683-19-8) as a control. The stabilized polyolefin samples were prepared by extruding polypropylene (PH350, LyondellBasell) with 1000 ppm antioxidant, 100ppm of calcium stearate (CaS) (CAS No. 1592-23-0) and 1000 ppm of Irganox 168 (CAS No. 31570-04-4) using a Randcastle extruder (RCP-0250) at 250 °C in into mini size pellets. These mini pellets were used to test and compare performance of antioxidants in polyolefin.

[0175] The testing results are summarized in Table 3. The antioxidant of Example 2 outperformed the commercial control Irganox® 1010 by a significant margin (3X) in stabilized polypropylene.

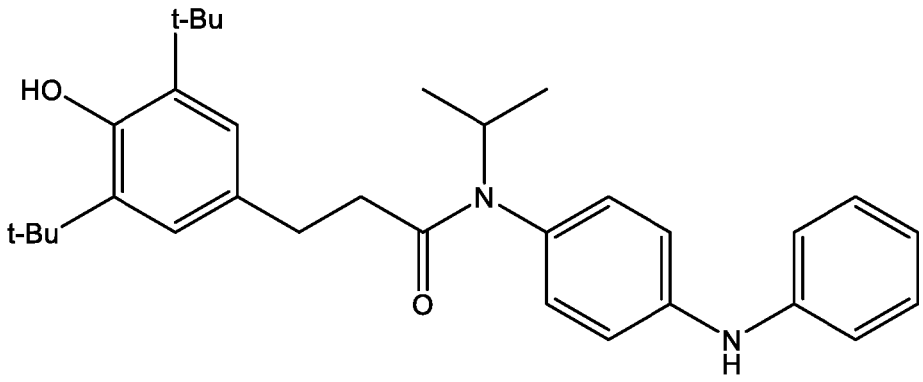
Table 4. Performance of antioxidants in polyolefin: polypropylene.

	Oxidative Induction Time (min), ASTM D5185 Method 170°C, 500 psi O_2 Sample: Polypropylene (PP)
Additive*	1000 ppm
Example 2	24.1
Irganox® 1010	8.4
*formulation: antioxidant 1000ppm+calcium stearate 1000 ppm+1000ppm Irganox® 168	

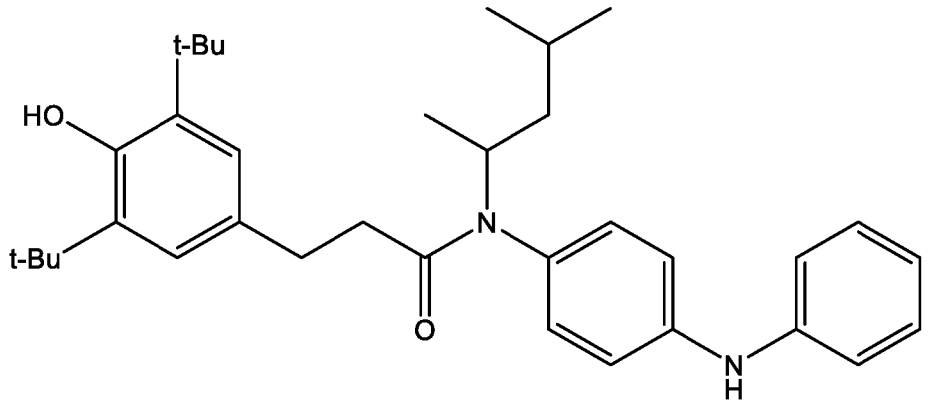
[0176] The OIT of the stabilized polyolefin samples (polypropylene,(PP)) was determined according to the procedure of ASTM D 5885. The system used to measure the OIT was TA Instruments Model Q10. The sample and the reference are heated at a constant rate of 20 °C/min to reach 170 °C. The heating was held isothermally after reaching 170 °C. The zero time was taken when the heating was started. The sample cell was purged with oxygen and pressurized to 500 psi of oxygen. The end of the induction period was signaled by an abrupt increase in the sample's evolved heat as recorded by the instrument. OIT was measured from the start of isothermal conditions to the inflection point of the exothermic peak.

Claims

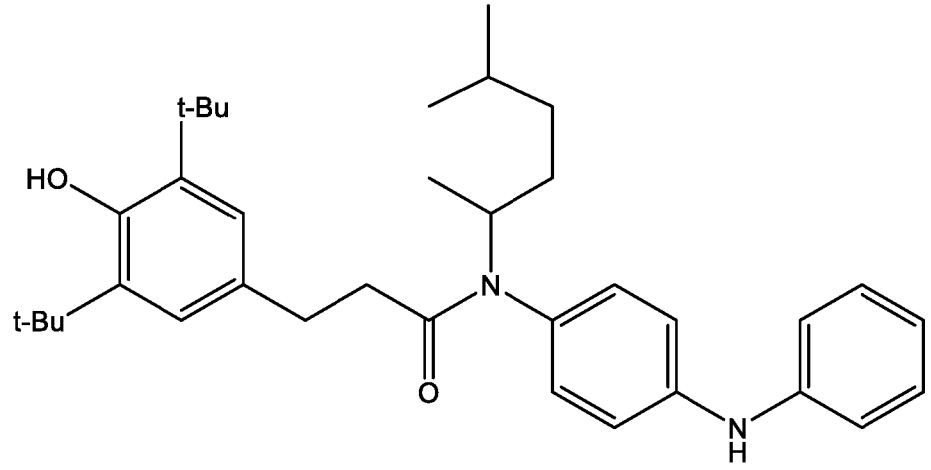
1. A composition comprising a mixture of the following compounds:



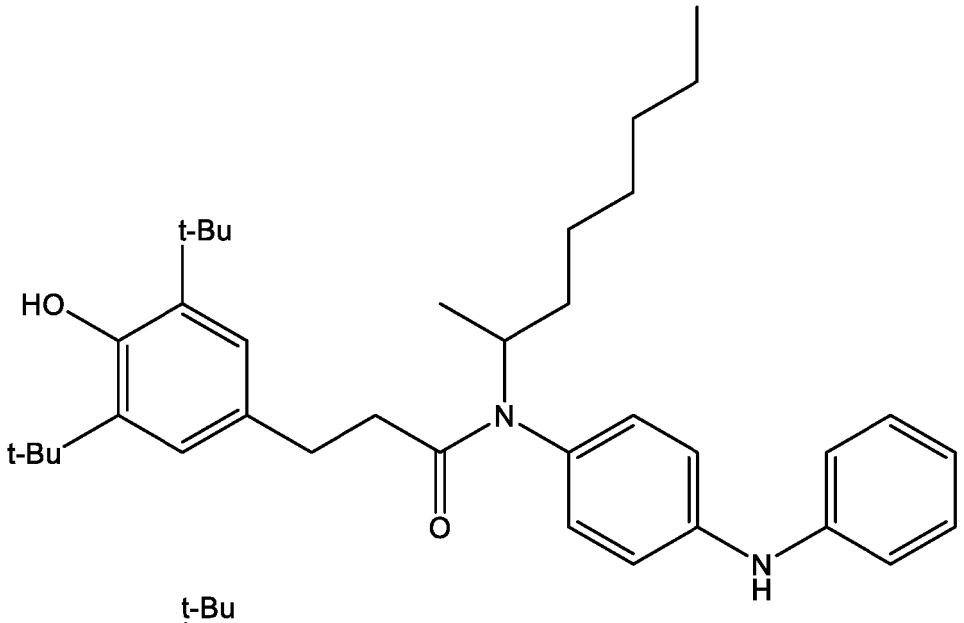
(i)



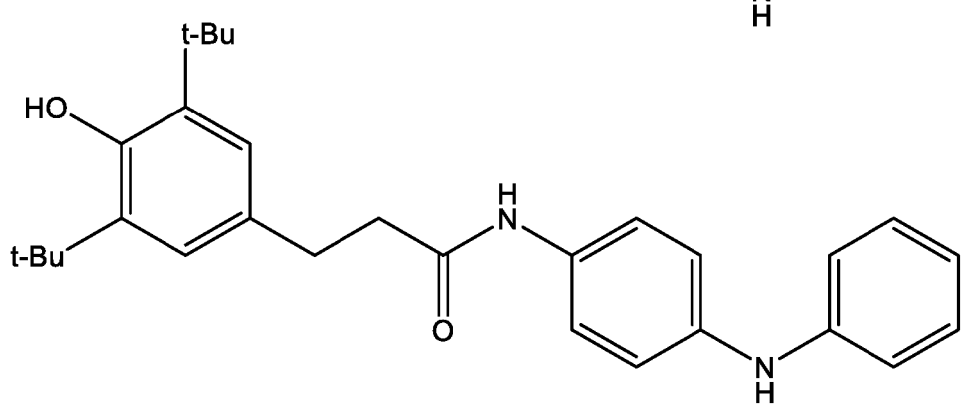
(ii)



(iii)



(iv)

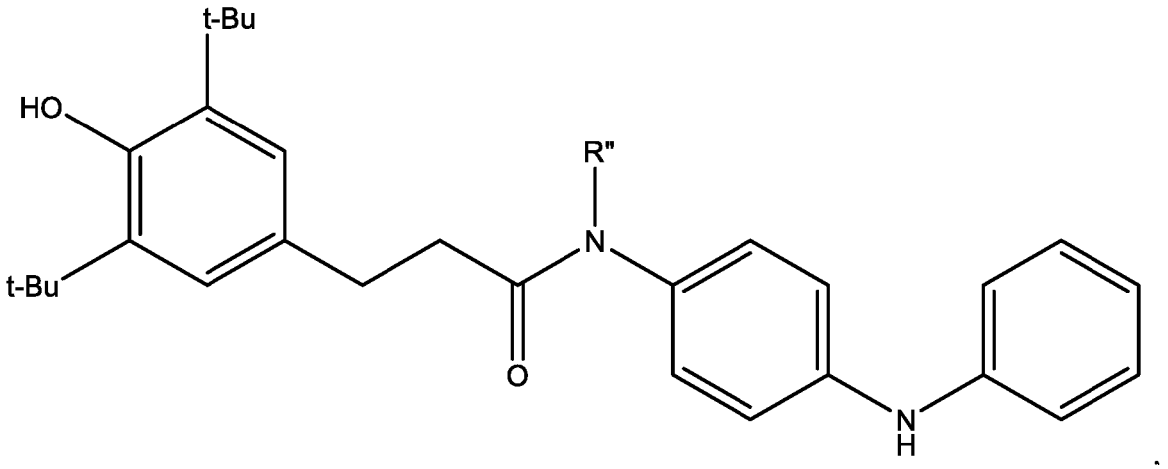


(v)

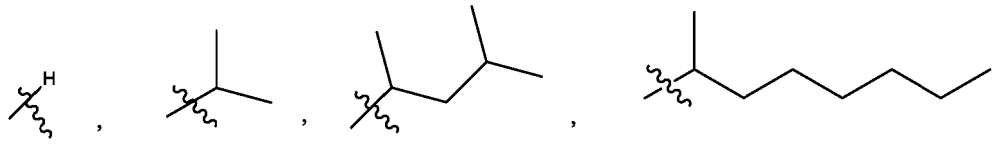
2. The composition of Claim 1, where the composition (i):(ii):(iii):(iv) by weight of 1:1:1:1, 0:1:1:1, 1:0:1:1, 1:1:0:1, 1:1:1:0.

3. The composition of Claim 1, where the composition by weight of (i):(ii), (i):(iii), (i):(iv), (ii):(iii), (ii): (iv), (iii) : (iv), (v): (i), (v): (ii), (v):(iii), (v):(iv) is 10:90, 20:80, 30:70,40:60,50:50, 60:40, 70:30, 80:20, 90:10; preferably wherein the composition by weight (i):(ii), (i):(iii), (ii):(iii), (ii): (iv), (iii) : (iv), (v): (i), (v): (ii), (v):(iii), (v):(iv) is 50:50.

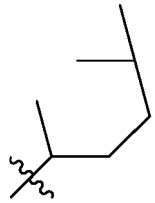
4. A method of making a mixture of compounds having the following structure:



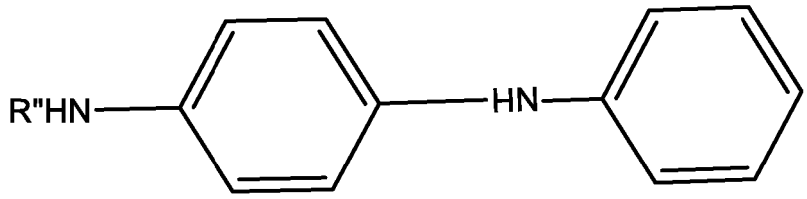
wherein R" is represented by the following formula:



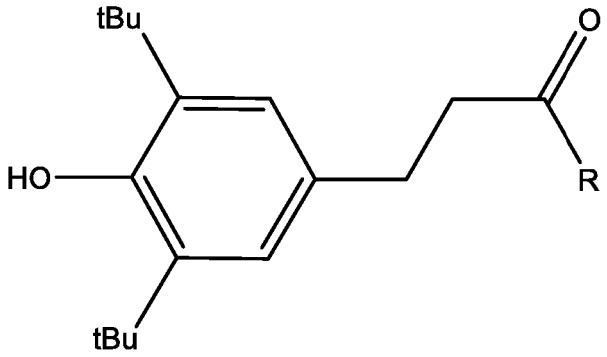
and



, the method comprising combining a mixture of amine compounds having the following formula:



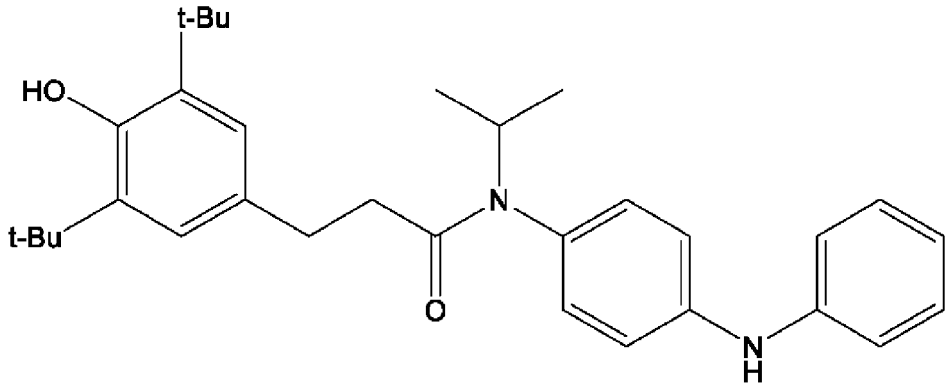
with an equimolar amount of a phenol compound having the following formula:



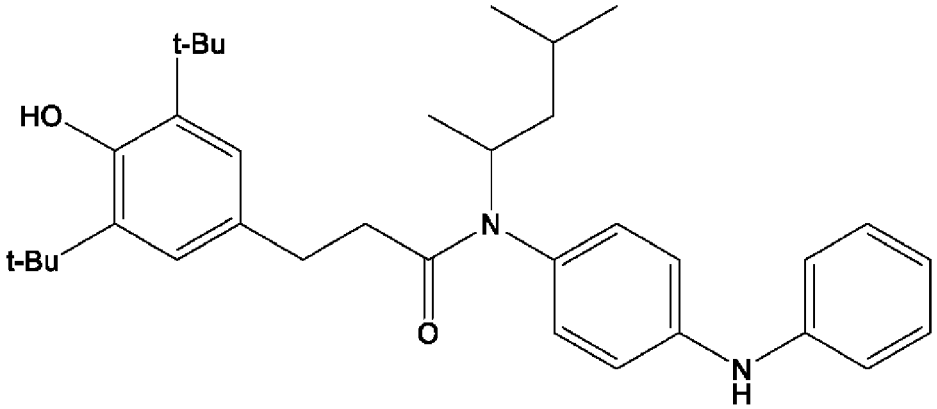
wherein R is -H or OH or OCH3 or Cl.

5. The method of Claim 4, where the phenol compound is 3-(3,5-ditert-butyl-4-hydroxyphenyl)propionyl chloride and a mixture of at least two amines selected from N-phenyl-1,4-phenylene-diamine; N1-isopropyl-N4-phenylbenzene-1,4-diamine; N1-(1,3-dimethylbutyl)-N4-phenylbenzene-1,4-diamine; N1-(1,4-dimethylpentyl)-N4-phenylbenzene-1,4-diamine; N-sec-octyl-N'-phenyl-p-phenylenediamine.

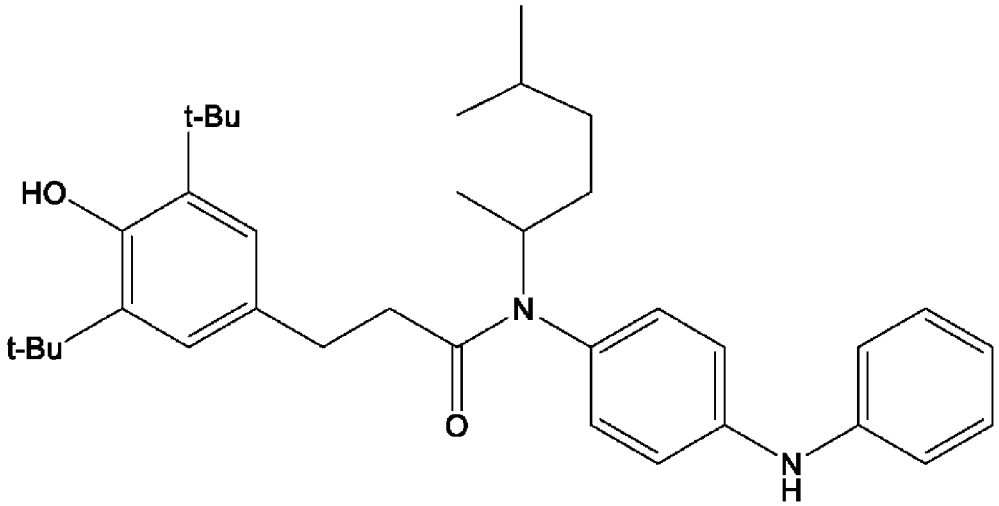
6. A method for preventing oxidation in an oxidizable material, comprising combining the oxidizable material with a mixture of compounds having the following structured formulae:



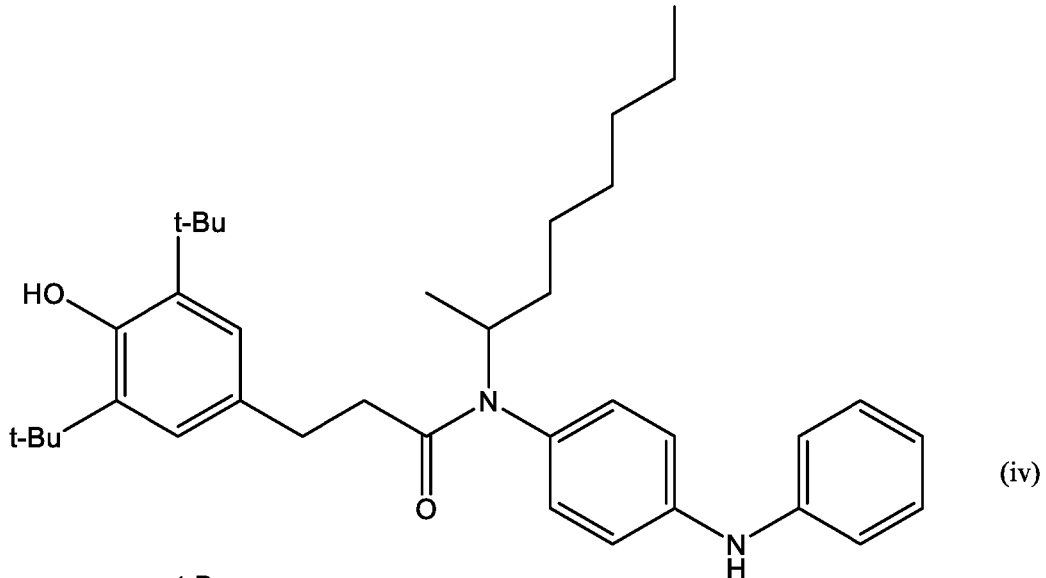
(i)



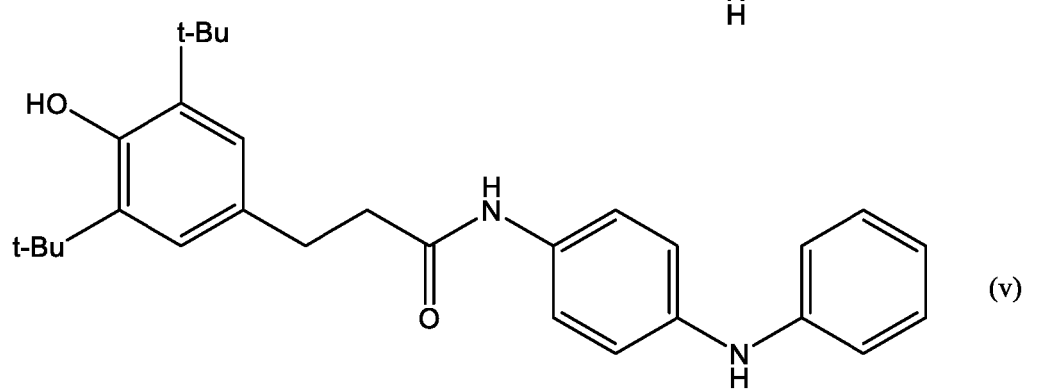
(ii)



(iii)



(iv)



(v)

7. The method of Claim 6, wherein the oxidizable material is bio-oil or modified bio-oil, vegetable oil and/or animal fat, polyolesters, petroleum based Group I, II, III, IV, and V oil, or mixture thereof; lubricants, biolubricants, biobased lubricants, plastics, bioplastics, polyolefins, nylons, polyamides, elastomers, thermoplastic elastomers, polymers copolymers, gasoline, kerosene, diesel, and biodiesel.

8. A stabilized lubricant composition comprising

(a) a lubricant or a mixture of lubricants,
(b) a mixture of compounds according to Claim 1.

9. The stabilized lubricant composition of Claim 8, wherein the antioxidant composition is in an amount 0.05% to 5% by weight of the lubricant composition.

10. The stabilized lubricant composition of Claim 9, further containing at least one lubricant additive in an amount 0.05% to 5% by weight of the lubricant composition selected from the group consisting of anti-wear additives, metal deactivating agents, antioxidants, detergents, rust inhibitors, friction modifiers, viscosity modifiers, pour point depressants, corrosion inhibitors, demulsifying regents, anti-foaming agents.

11. A stabilized lubricant composition of Claim 9, wherein the lubricant is selected from the group consisting of petroleum based oils, synthetic oils, biolubricant oils, and biobased oils, and mixture thereof.

12. A method of forming a stabilized lubricant composition, comprising combining a lubricant or mixture of lubricants to form a lubricant composition consisting essentially of:

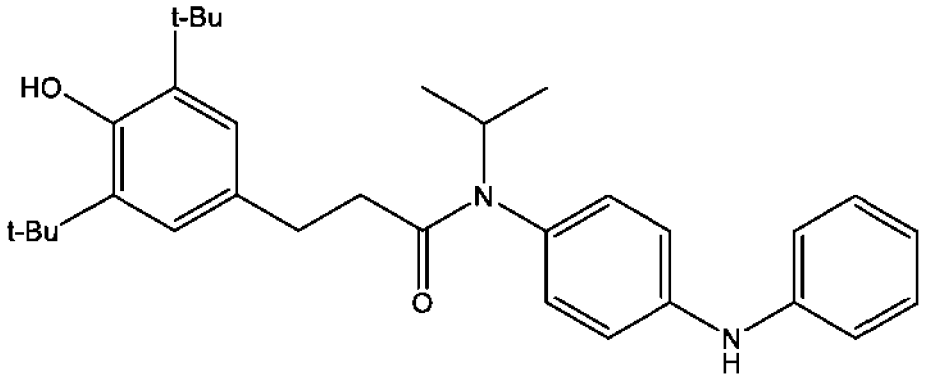
a) a mixture of compounds according to Claim 1;
b) at least one additive selected from the group consisting of: anti-wear additives, metal deactivating agents,

antioxidants, detergents, rust inhibitors, friction modifiers, viscosity modifiers, pour point depressants, corrosion inhibitors, demulsifying regents, anti-foaming agents,

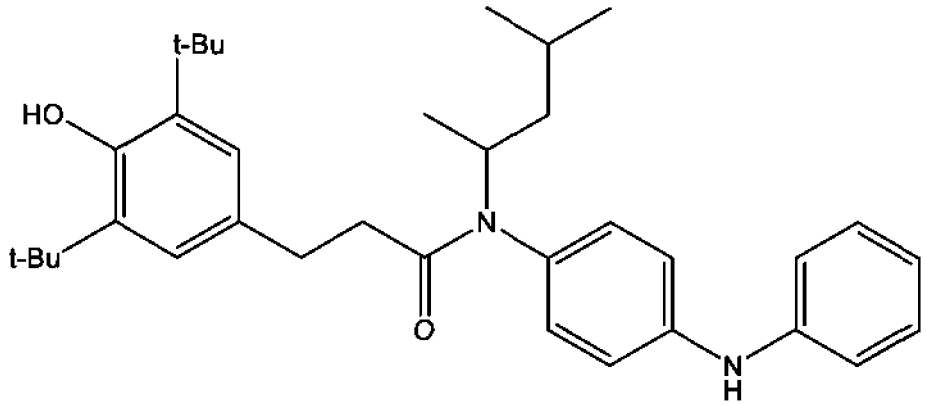
to thereby form a lubricant composition, wherein the concentration of the first antioxidant is between about 0.05 % to about 5 % by weight of the lubricant composition and the concentration of the first additive is between about 0.05 % and about 5 % by weight of the lubricant composition.

Patentansprüche

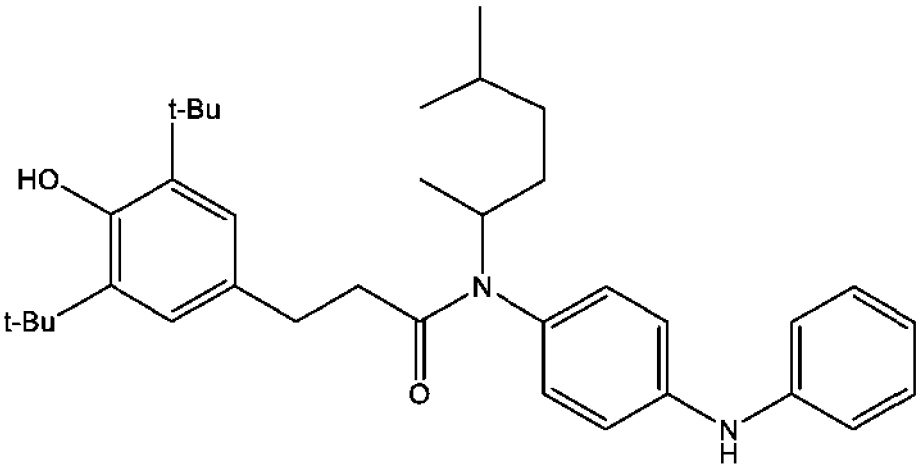
1. Zusammensetzung, die eine Mischung der folgenden Verbindungen umfasst:



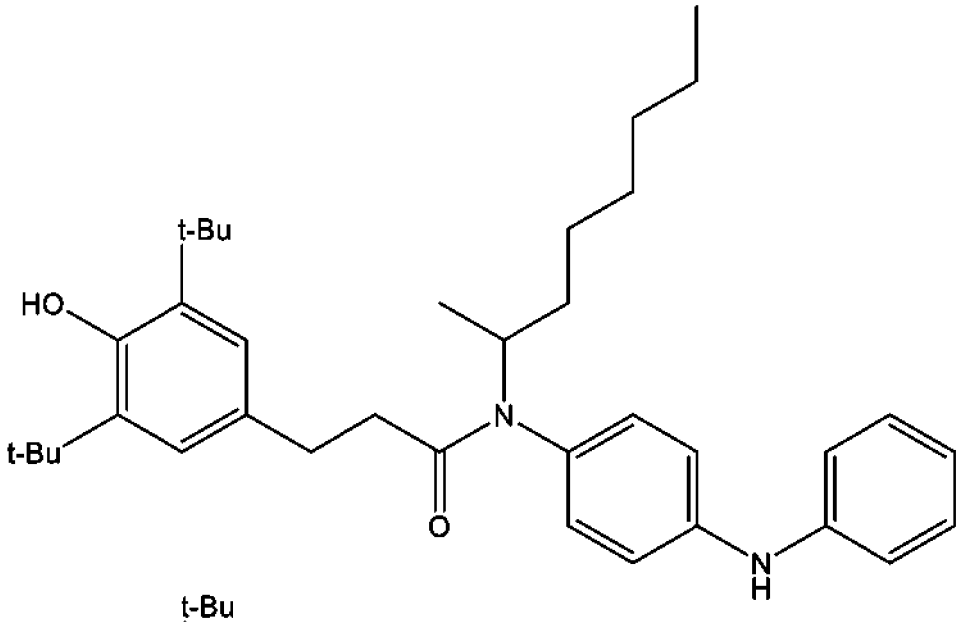
(i)



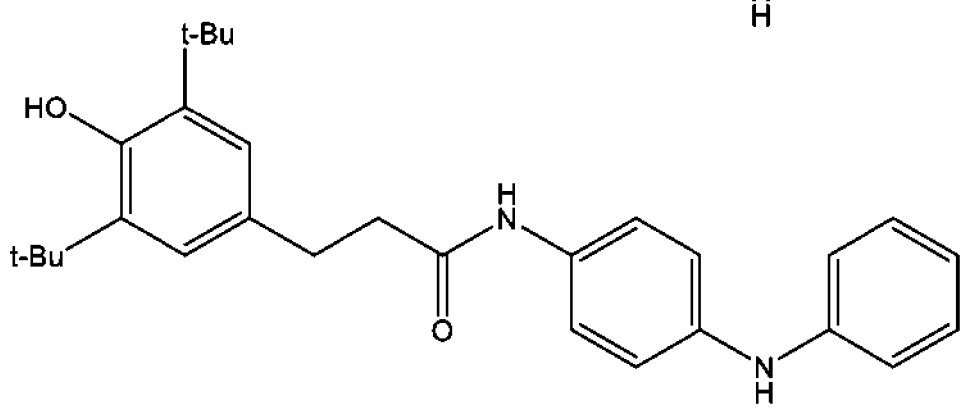
(ii)



(iii)



(iv)

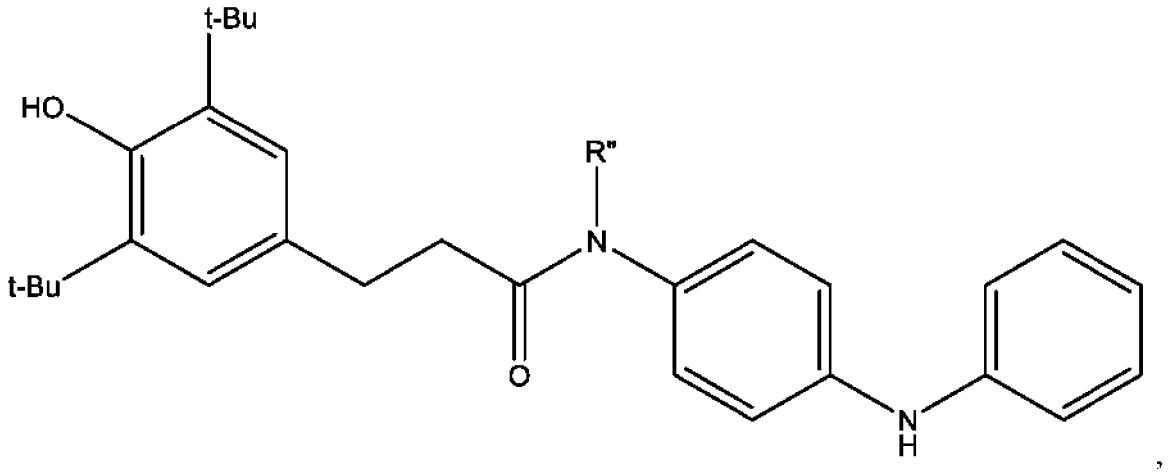


(v)

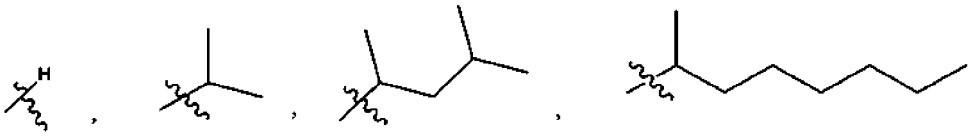
2. Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung (i) : (ii) : (iii) : (iv) nach Gewicht 1 : 1 : 1 : 1, 0 : 1 : 1 : 1, 1 : 0 : 1 :1, 1 : 1: 0 : 1, 1 : 1 : 1 : 0 beträgt.

3. Zusammensetzung nach Anspruch 1, wobei die Zusammensetzung nach Gewicht (i) : (ii), (i) : (iii), (i) : (iv), (ii) : (iii), (ii) : (iv), (iii) : (iv), (v) : (i), (v) : (ii), (v) : (iii), (v) : (iv) 10 : 90, 20 : 80, 30 : 70, 40 : 60, 50 : 50, 60 : 40, 70 : 30, 80 : 20, 90 : 10 beträgt; vorzugsweise
wobei die Zusammensetzung nach Gewicht (i) : (ii), (i) : (iii), (ii) : (iii), (ii) : (iv), (iii) : (iv), (v) : (i), (v) : (ii), (v) : (iii), (v) : (iv) 50 : 50 beträgt.

4. Verfahren zum Herstellen einer Mischung von Verbindungen, die die folgende Struktur aufweisen:

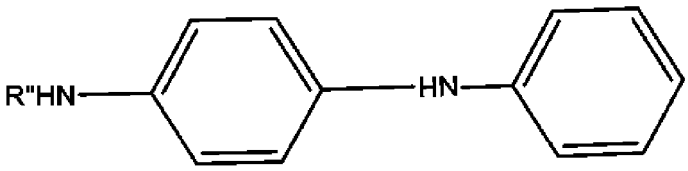


wobei R" durch die folgende Formel dargestellt wird:

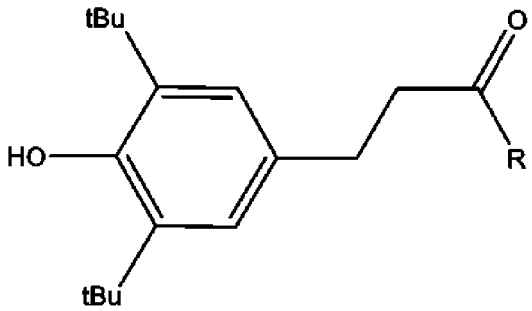


und

, wobei das Verfahren ein Kombinieren einer Mischung von Aminverbindungen, die die folgende Formel aufweist:



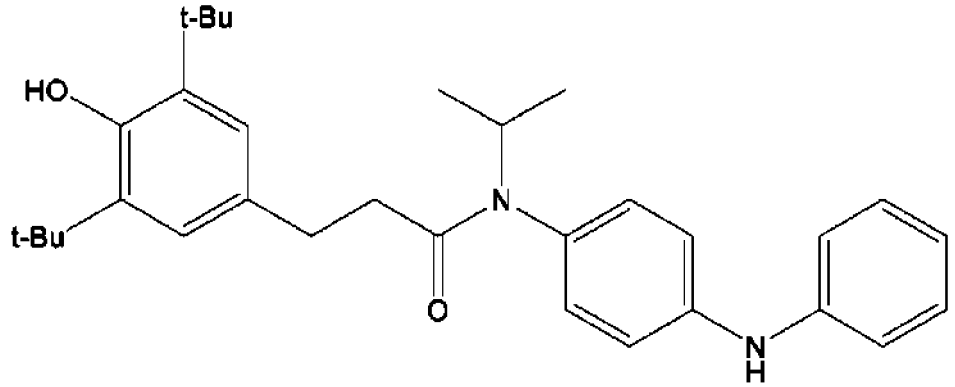
mit einer äquimolaren Menge einer Phenolverbindung umfasst, die die folgende Formel aufweist:



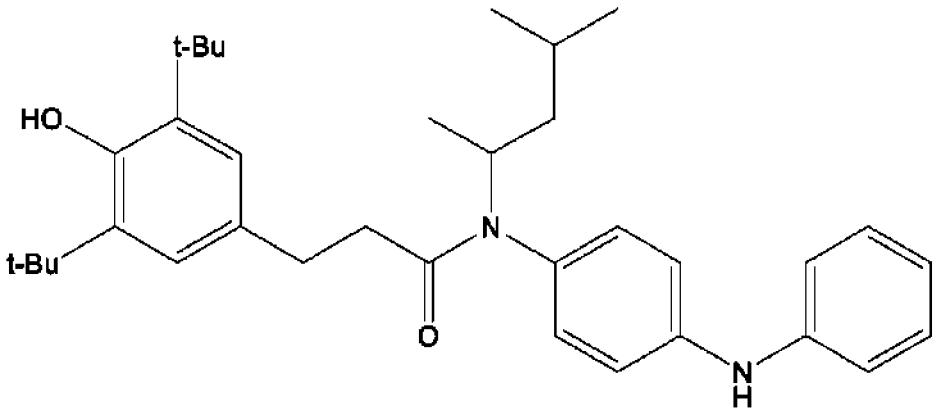
wobei R -H oder OH oder OCH3 oder Cl ist.

5. Verfahren nach Anspruch 4, wobei die Phenolverbindung 3-(3,5-Di-tert-butyl-4-hydroxyphenyl)propionylchlorid und eine Mischung von wenigstens zwei Aminen ist, die aus N-Phenyl-1,4-phenylendiamin; N1-Isopropyl-N4-phenyl-benzol-1,4-diamin; N1-(1,3-Dimethylbutyl)-N4-phenylbenzol-1,4-diamin; N1-(1,4-Dimethylpentyl)-N4-phenylbenzol-1,4-diamin; N-sec-Octyl-N'-phenyl-p-phenylendiamin ausgewählt sind.

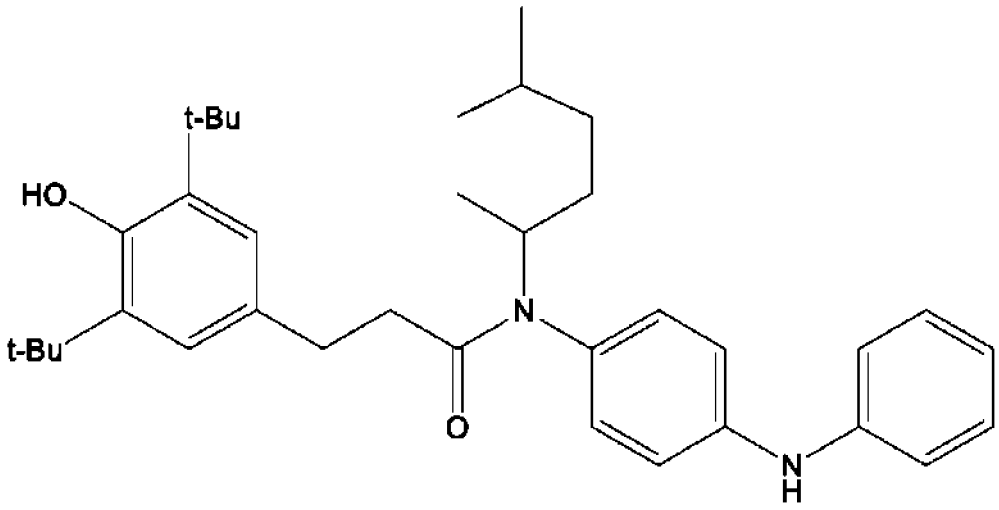
6. Verfahren zum Verhindern von Oxidation in einem oxidierbaren Material, das das Kombinieren des oxidierbaren Materials mit einer Mischung von Verbindungen umfasst, die die folgenden gegliederten Formeln aufweisen:



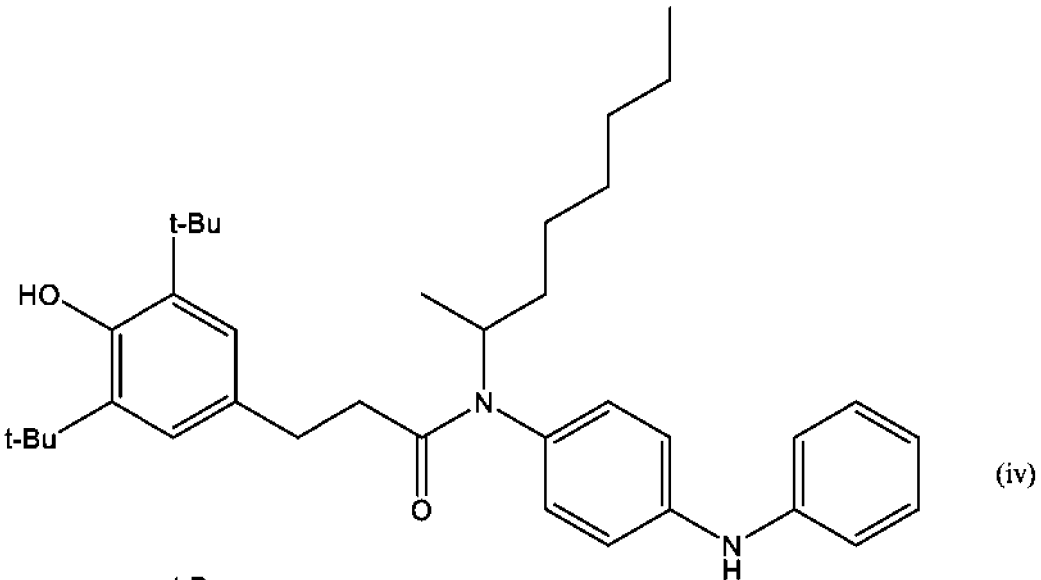
(i)



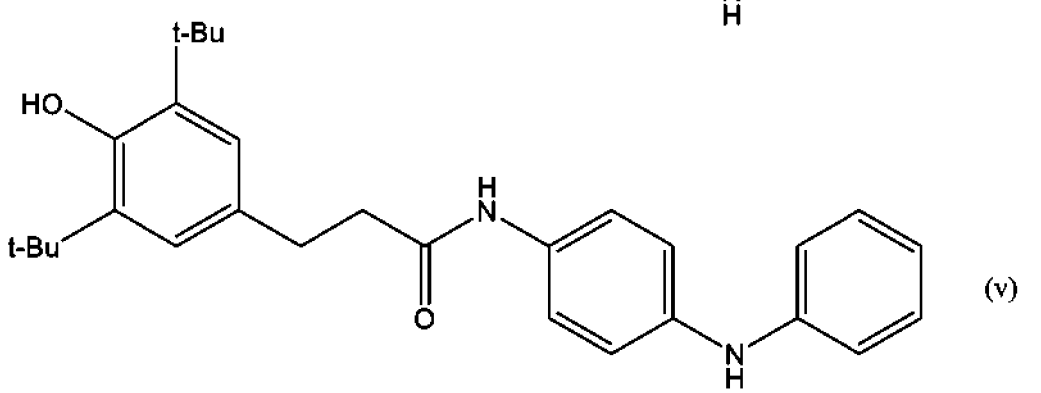
(ii)



(iii)



(iv)



(v)

7. Verfahren nach Anspruch 6, wobei das oxidierbare Material Bioöl oder modifiziertes Bioöl, Pflanzenöl und/oder tierisches Fett, Polyolester, Öl der Gruppe I, II, III, IV und V auf Erdölbasis oder eine Mischung davon; Schmierstoffe, Bioschmierstoffe, biobasierte Schmierstoffe, Kunststoffe, Biokunststoffe, Polyolefine, Nylons, Polyamide, Elastomere, thermoplastische Elastomere, Polymercopolymere, Benzin, Kerosin, Diesel und Biodiesel ist.

8. Stabilisierte Schmiermittelzusammensetzung, die Folgendes umfasst:

(a) ein Schmiermittel oder eine Mischung von Schmiermitteln,
(b) eine Mischung von Verbindungen nach Anspruch 1.

9. Stabilisierte Schmiermittelzusammensetzung nach Anspruch 8, wobei die Antioxidanszusammensetzung in einer Menge von 0,05 bis 5 Gew.-% der Schmiermittelzusammensetzung vorliegt.

10. Stabilisierte Schmiermittelzusammensetzung nach Anspruch 9, die ferner wenigstens ein Schmiermitteladditiv in einer Menge von 0,05 bis 5 Gew.-% der Schmiermittelzusammensetzung enthält, die aus der Gruppe ausgewählt ist, die aus Antiverschleißadditiven, Metalldeaktivatoren, Antioxidantien, Detergentien, Rostschutzmitteln, Reibungsminderern, Viskositätsmodifizierern, Stockpunkterniedrigern, Korrosionsinhibitoren, Demulgatoren, Antischaummittel besteht.

11. Stabilisierte Schmiermittelzusammensetzung nach Anspruch 9, wobei das Schmiermittel aus der Gruppe ausgewählt ist, die aus Ölen auf Erdölbasis, synthetischen Ölen, Bioschmierölen und biobasierten Ölen und Mischungen davon besteht.

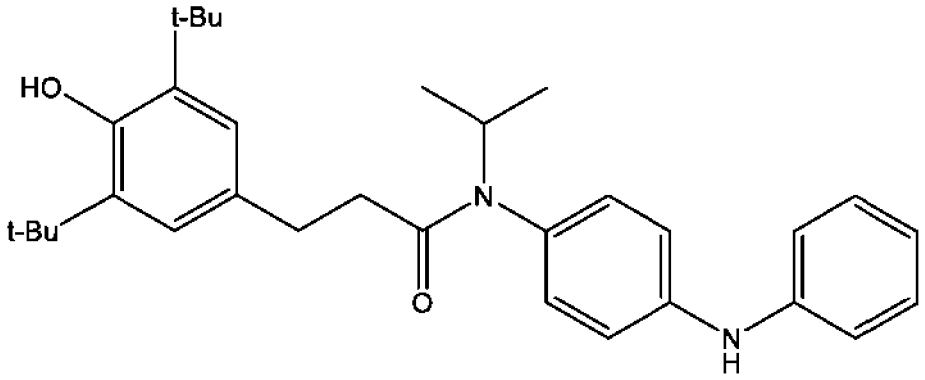
12. Verfahren zum Ausbilden einer stabilisierten Schmiermittelzusammensetzung, die das Kombinieren eines Schmiermittels oder einer Mischung von Schmiermitteln umfasst, um eine Schmiermittelzusammensetzung auszubilden, die im Wesentlichen aus Folgendem besteht:

a) einer Mischung von Verbindungen nach Anspruch 1;
b) wenigstens einem Additiv, das aus der Gruppe ausgewählt ist, die aus Folgendem besteht: Antiverschleißadditiven, Metalldeaktivatoren, Antioxidantien, Detergentien, Rostschutzmitteln, Reibungsminderern, Viskositätsmodifizierern, Stockpunkterniedrigern, Korrosionsinhibitoren, Demulgatoren, Antischaummitteln,

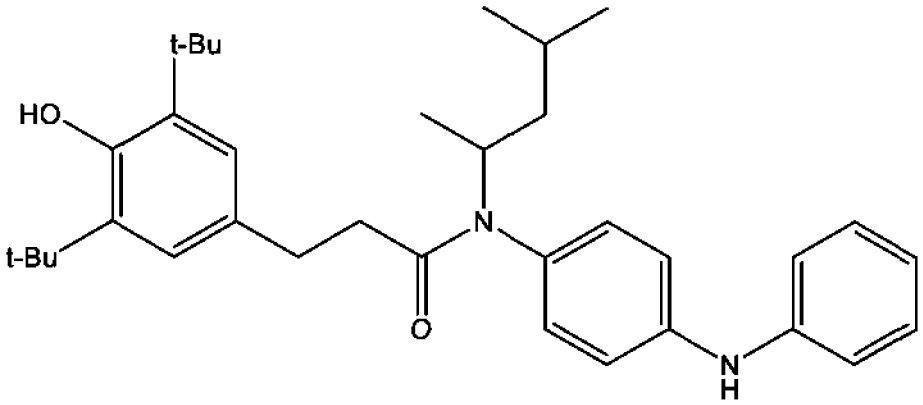
wobei dadurch eine Schmiermittelzusammensetzung ausgebildet wird, wobei die Konzentration des ersten Antioxidans zwischen etwa 0,05 Gew.-% bis etwa 5 Gew.-% der Schmiermittelzusammensetzung beträgt und die Konzentration des ersten Additivs zwischen etwa 0,05 Gew.-% und etwa 5 Gew.-% der Schmiermittelzusammensetzung beträgt.

Revendications

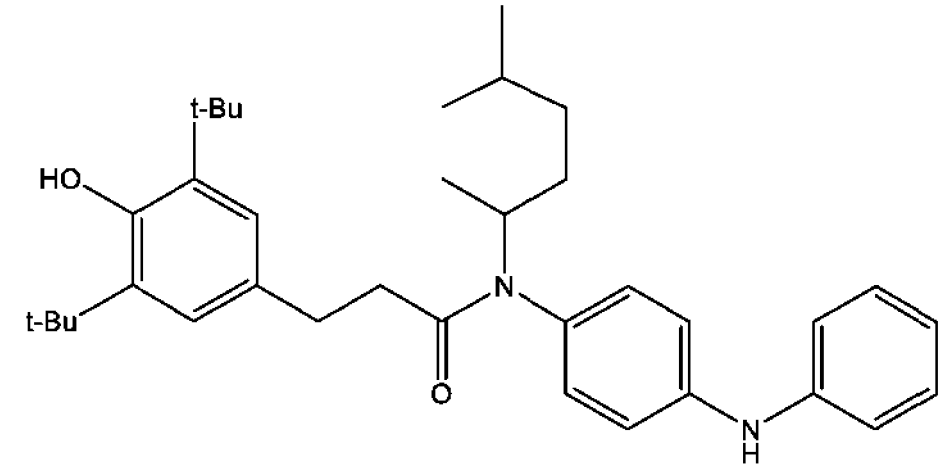
1. Composition comprenant un mélange des composés suivants :



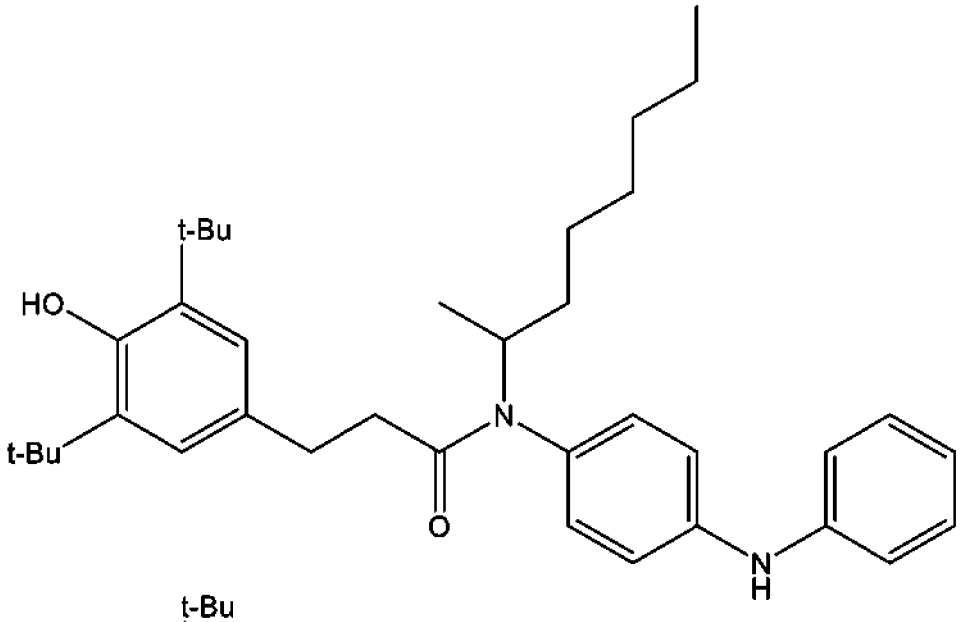
(i)



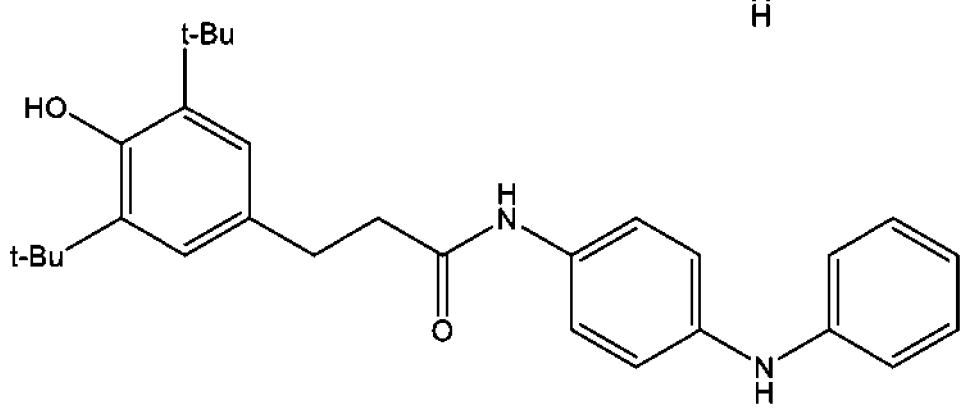
(ii)



(iii)



(iv)

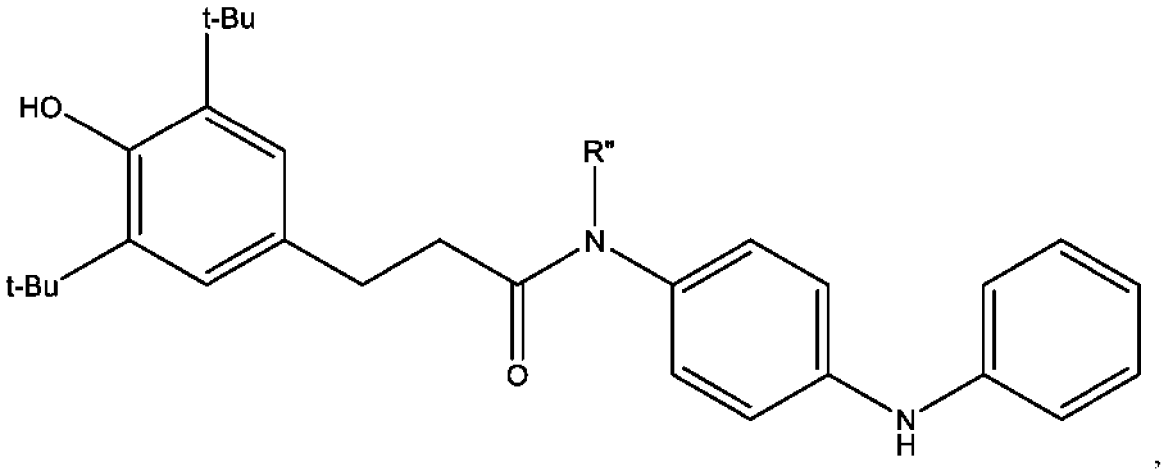


(v)

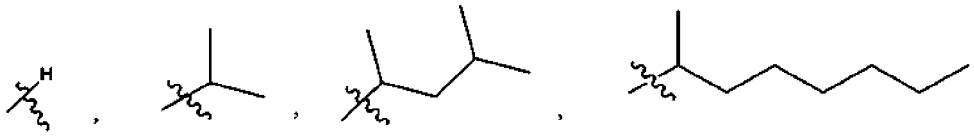
2. Composition selon la revendication 1, dans laquelle la composition (i):(ii):(iii):(iv) en poids de 1:1:1:1, 0:1:1:1, 1:0:1:1, 1:1:0:1, 1:1:1:0.

3. Composition selon la revendication 1, dans laquelle la composition en poids de (i):(ii), (i):(iii), (i):(iv), (ii):(iii), (ii): (iv), (iii) : (iv), (v): (i), (v): (ii), (v):(iii), (v):(iv) est 10:90, 20:80, 30:70,40:60,50:50, 60:40, 70:30, 80:20, 90:10 ; de préférence la composition en poids (i):(ii), (i):(iii), (ii):(iii), (ii): (iv), (iii) : (iv), (v): (i), (v): (ii), (v):(iii), (v):(iv) étant 50:50.

4. Procédé de fabrication d'un mélange de composés ayant la structure suivante :

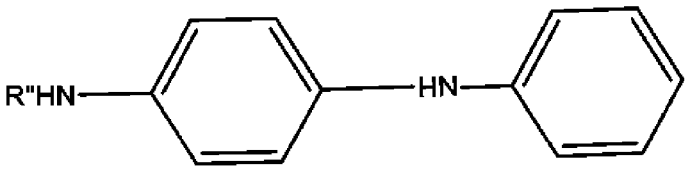


R" étant représenté par la formule suivante :

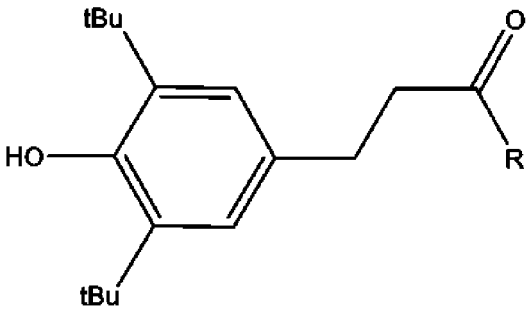


et

, le procédé comprenant la combinaison d'un mélange de composés aminés ayant la formule suivante :



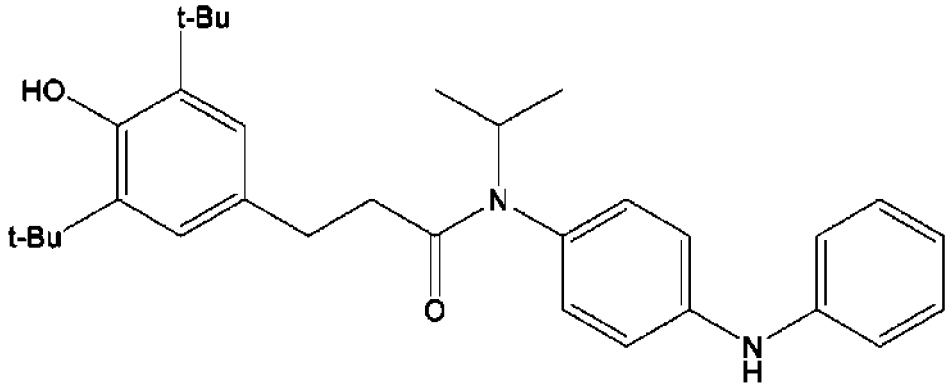
avec une quantité équimolaire d'un composé phénolique ayant la formule suivante :



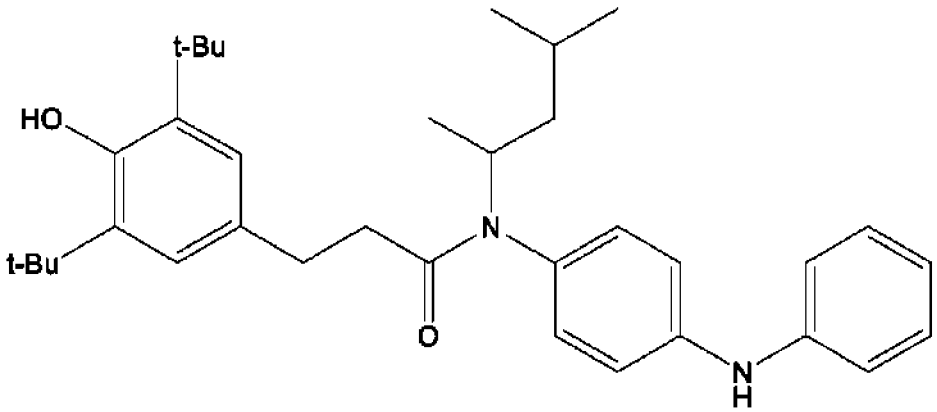
R étant -H ou OH ou OCH3 ou Cl.

5. Procédé selon la revendication 4, dans lequel le composé phénolique est le chlorure 3-(3,5-ditert-butyl-4-hydroxyphényl)propionyle et un mélange d'au moins deux amines choisies parmi N-phényl-1,4-phénylène-diamine ; N1-isopropyl-N4-phénylbenzène-1,4-diamine ; N1-(1,3-diméthylbutyl)-N4-phénylbenzène-1,4-diamine ; N1-(1,4-diméthylpentyl)-N4-phénylbenzène-1,4-diamine ; N-sec-octyl-N'-phényl-p-phénylènediamine.

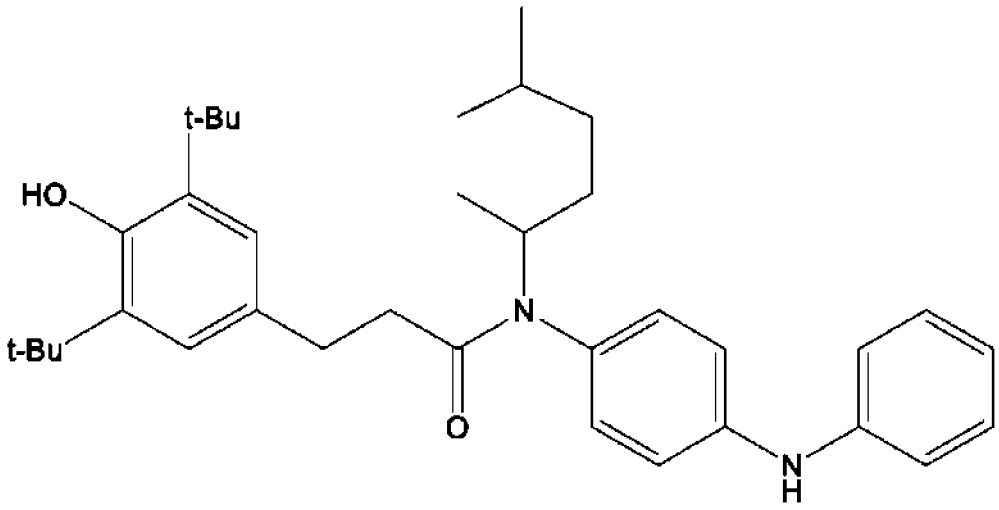
6. Procédé destiné à empêcher l'oxydation dans un matériau oxydable, comprenant la combinaison du matériau oxydable avec un mélange de composés ayant les formules structurées suivantes :



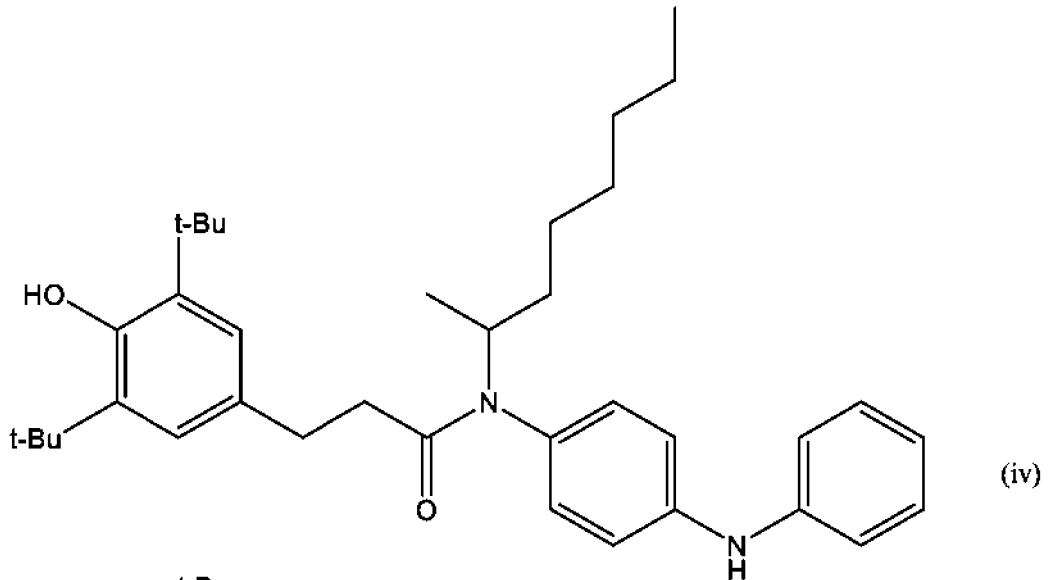
(i)



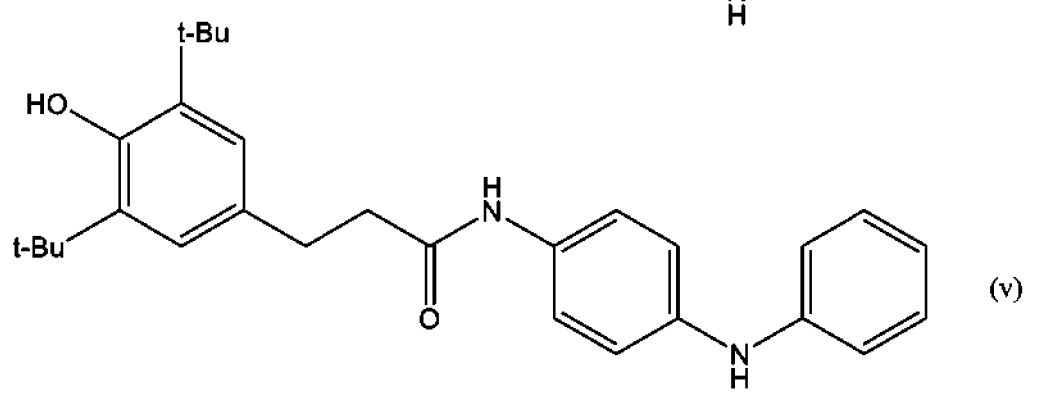
(ii)



(iii)



(iv)



(v)

7. Procédé selon la revendication 6, dans lequel la matière oxydable est de l'huile biologique ou de l'huile biologique modifiée, de l'huile végétale et/ou de la graisse animale, des polyolesters, de l'huile des groupes I, II, III, IV et V à base de pétrole, ou un mélange de ceux-ci ; des lubrifiants, des biolubrifiants, des lubrifiants biosourcés, des plastiques, des bioplastiques, des polyoléfines, des nylons, des polyamides, des élastomères, des élastomères thermoplastiques, des copolymères de polymères, de l'essence, du kérosène, du diesel et du biodiesel.

8. Composition lubrifiante stabilisée comprenant

(a) un lubrifiant ou un mélange de lubrifiants,
(b) un mélange de composés selon la revendication 1.

9. Composition lubrifiante stabilisée selon la revendication 8, dans laquelle la composition antioxydante est en une quantité de 0,05 % à 5 % en poids de la composition lubrifiante.

10. Composition lubrifiante stabilisée selon la revendication 9, contenant en outre au moins un additif lubrifiant en une quantité de 0,05 % à 5 % en poids de la composition lubrifiante choisie dans le groupe constitué d'additifs anti-usure, d'agents de désactivation de métaux, d'antioxydants, de détergents, d'inhibiteurs d'oxydation, de modificateurs de friction, de modificateurs de viscosité, d'améliorants de point d'écoulement, d'inhibiteurs de corrosion, de réactifs démulsifiants, d'agents anti-mousse.

11. Composition lubrifiante stabilisée selon la revendication 9, dans laquelle le lubrifiant est choisi dans le groupe constitué d'huiles à base de pétrole, d'huiles synthétiques, d'huiles biolubrifiantes et d'huiles biosourcées, et le mélange de celles-ci.

12. Procédé de formation d'une composition lubrifiante stabilisée, comprenant la combinaison d'un lubrifiant ou d'un mélange de lubrifiants pour former une composition lubrifiante constituée essentiellement :

a) d'un mélange de composés selon la revendication 1 ;
b) d'au moins un additif choisi dans le groupe constitué : d'additifs anti-usure, d'agents de désactivation de métaux, d'antioxydants, de détergents, d'inhibiteurs d'oxydation, de modificateurs de friction, de modificateurs de viscosité, d'améliorants de point d'écoulement, d'inhibiteurs de corrosion, de réactifs démulsifiants, d'agents anti-mousse,

pour former ainsi une composition lubrifiante, la concentration du premier antioxydant étant comprise entre environ 0,05 % et environ 5 % en poids de la composition lubrifiante et la concentration du premier additif est comprise entre environ 0,05 % et environ 5 % en poids du lubrifiant composition.

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