

THIOSYNERGIST, ANTIOXIDANT COMPOSITION COMPRISING THE SAME AND POLYMER COMPOSITION COMPRISING THE ANTIOXIDANT COMPOSITION

5 TECHNICAL FIELD

The present disclosure relates to a thiosynergist, to an antioxidant composition comprising the same, to a polymer composition comprising the antioxidant composition, to use of the antioxidant composition for stabilizing polymer, and to a process of synthesizing the thiosynergist.

10

BACKGROUND

Thiosynergist as secondary antioxidant are often combined with primary antioxidant for improving long term thermal stability of polymers. However, most of the thiosynergists are solids, which limits the possibility when a liquid antioxidant solution is required. For those thiosynergists that are liquid, volatility can be too high, which reduces long term performance. Therefore, there is still a need in the art to provide a liquid thiosynergist having good performance.

15

SUMMARY OF THE INVENTION

20

It is an object of this disclosure to provide a liquid thiosynergist (liquid compound of formula (I)), which shows good performance.

Another object of this disclosure is to provide an antioxidant composition comprising the liquid thiosynergist of the present invention.

25

A further object of this disclosure is to provide use of the antioxidant composition of the present invention for stabilizing polymer.

A further object of this disclosure is to provide a polymer composition comprising the antioxidant composition.

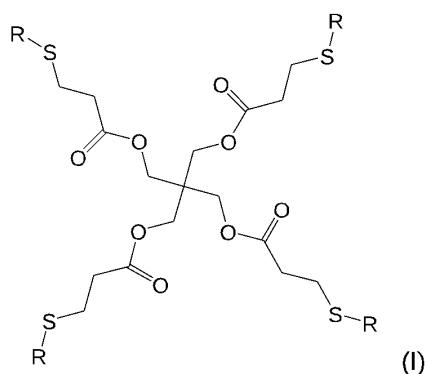
30

A further object of this disclosure is to provide a process of synthesizing the liquid compound of formula (I) of the present invention.

35

It has been surprisingly found that the above objects can be achieved by following embodiments:

1. A liquid compound of formula (I):



wherein each R is a branched C8 alkyl.

2. The liquid compound of formula (I) according to item 1, wherein each R has one branch point.

5

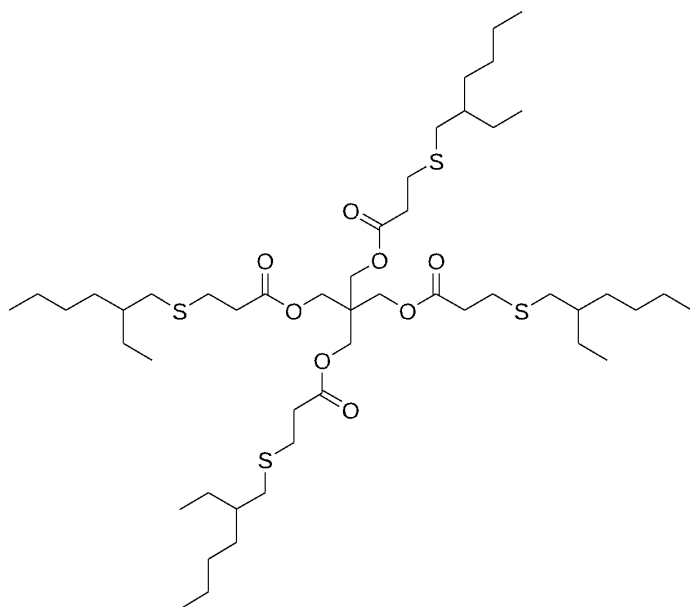
3. The liquid compound of formula (I) according to item 1, wherein each R has one branch point on the second carbon atom starting from the S atom.

4. The liquid compound of formula (I) according to any of items 1 to 3, wherein branched chain

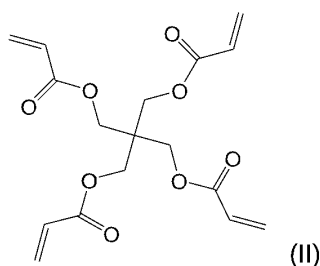
10 in R has 2 or 3 carbon atoms, preferably 2 carbon atoms.

5. The liquid compound of formula (I) according to any of items 1 to 4, wherein each R in formula (I) is the same.

15 6. The liquid compound of formula (I) according to any of items 1 to 5, which has the structure of formula (I-1):



7. An antioxidant composition comprising the liquid compound of formula (I) according to any of items 1 to 6.
- 5 8. The antioxidant composition according to item 7, which further comprises at least one of hindered phenol, hindered amine, and combinations thereof.
9. The antioxidant composition according to item 8, wherein weight ratio of the liquid compound of formula (I) according to any of items 1 to 6 to the at least one of hindered phenol, hindered
- 10 amine, and combinations thereof is in the range from 10:1 to 1:10, preferably from 5:1 to 1:5.
10. The antioxidant composition according to any of items 7 to 9, which further comprises at least one phosphite and/or phosphonite.
- 15 11. The antioxidant composition according to any of items 7 to 10, wherein the antioxidant composition comprises a second thiosynergist which is different from the liquid compound of formula (I), and the liquid compound of formula (I) is present as a first thiosynergist and the amount of the liquid compound of formula (I) is in the range from 50 to 100 wt%, preferably from 80 to 100 wt%, based on the total weight of the thiosynergist present in the antioxidant composition.
- 20 12. The antioxidant composition according to any of items 7 to 11, wherein the antioxidant composition is present in a form of liquid, preferably emulsion.
13. Use of the antioxidant composition according to any of items 7 to 12 for stabilizing polymer.
- 25 14. A polymer composition comprising the antioxidant composition according to any of items 7 to 12.
15. A process of synthesizing the liquid compound of formula (I) according to any of items 1 to 6, which comprises:
- 30 (i) reacting acrylic acid with pentaerythritol to obtain a compound of formula (II)



(ii) reacting the compound of formula (II) with a thiol of formula (III)

R-SH (III)

wherein R is as defined in any of items 1 to 6.

- 5 The advantageous technical effects brought by the thiosynergist of the present invention (liquid compound of formula (I)) include but are not limited to:
1. low odor; 2. low volatility; 3. liquid form; 4. high thermal stability; 5. good solvent solubility; 6. applicable in all kinds of polymers and 7. producing synergistic stabilizing effect when combining with hindered phenol and/or hindered amine and 8. easily mixing. The process for synthesizing
- 10 the liquid compound of formula (I) of the present invention is simple and cheap, and the starting materials are easy to obtain.

It should be understood that the part of summary of the invention is not intended to limit scope of this disclosure. Other features of this disclosure will become easily understandable in accordance with below description.

15

DETAILED DESCRIPTION OF THE INVENTION

In the below description, further explanations to the present disclosure are made with reference to embodiments so as to facilitate sufficient understanding for skilled person in the art. It should be understood that these embodiments are provided merely for better understanding the subject matter of the present disclosure, not for making any limitations to the protection scope, applicability or embodiments as described in the present claims set. It should be understood that, skilled person in the art can omit, replace, or add various technical features to each embodiment based on actual needs, subject to the premise of without departing from the spirit of the present disclosure. In addition, technical features described in some embodiments can be combined with technical features described in other embodiments.

20

25

Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by skilled person in the art to which the present disclosure belongs.

30

In the present disclosure, terms "comprise", "comprising", "include", "including" and various variants thereof can be understood as open-ended terms, which means "include but are not limited to"; in contrast, the term "consisting of" and various variants thereof excludes any component, step or procedure not specifically listed; the term "an embodiment" can be understood as "at least one embodiment"; the term "another embodiment" may be understood as "at least one other embodiment." Other terms that may appear but are not mentioned here, unless explicitly stated, should not be interpreted or limited in a manner that is contrary to the concept on which the embodiments of the present disclosure are based.

35

40

Throughout the present disclosure, expressions "a", "an", "the" and "one or more" are used interchangeably and are intended to include both the plural and the singular except in cases

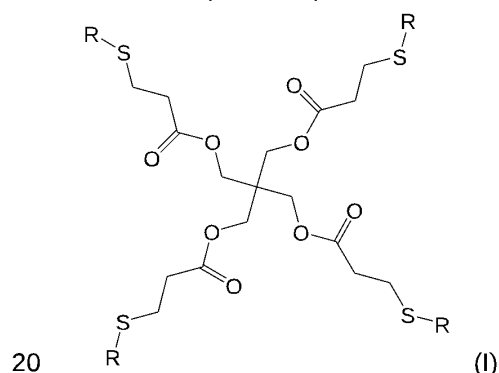
where the singular alone is explicitly specified or is clearly indicated by the context. When the singular alone is intended for, the term "one" is typically used. The term "or" is generally intended to include the sense of "and/or" unless the content clearly dictates otherwise. "Preferred", "preferable" and "preferably" as used herein refer to embodiments of the present disclosure that may bring certain advantages under certain situations. However, other embodiments may also be preferred, under the same situations. Further, the recitation of one or more preferred embodiments does not mean that other embodiments are not useful and is not intended to exclude other embodiments from the scope of the present disclosure.

- 10 All percentages, ppm, parts and ratios are by weight, unless otherwise specified. And the recitation of numerical ranges by end values includes all numbers subsumed within that range (e.g., 5 to 10 includes 5, 5.1, 5.2, 5.55, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10).

- 15 In the context of the present disclosure, any specific values mentioned for a feature (comprising the specific values mentioned in a range as the end point) can be re-combined to form a new range.

Liquid compound of formula (I)

In a first aspect, the present disclosure provides a liquid compound of formula (I):



wherein each R is a branched C8 alkyl.

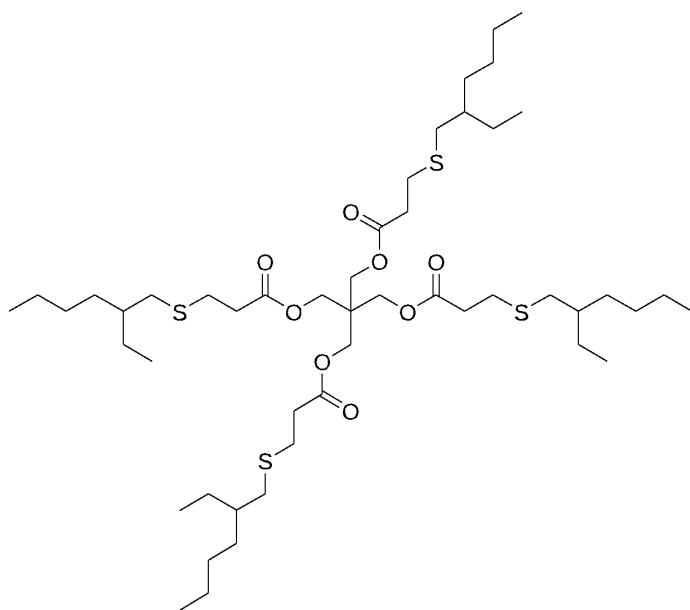
- The liquid compound of formula (I) is a liquid thiosynergist. In some embodiments, the liquid compound of formula (I) can act as a secondary antioxidant combining with other primary antioxidant(s) to improve polymer's long-term thermal stability. The advantages of being liquid includes that such liquid secondary antioxidant can be easily mixed with other liquid and/or solid primary antioxidant(s) which greatly broadens its scope of use. In addition, the liquid compound of formula (I) has relatively low volatility yet showing excellent anti-oxidative properties.
- 30 The liquid compound of formula (I) of the present invention is liquid at room temperature (for example from 25 to 35 °C). In some specific embodiments, it is liquid at a temperature in the range from -18 °C to 50 °C.

In an embodiment, each R has one branch point. In an embodiment, each R has one branch point on the second carbon atom starting from the S atom. Here, the S atom is connected with R.

- 5 In an embodiment, the branched chain in R has 2 or 3 carbon atoms, preferably 2 carbon atoms.

In an embodiment, each R in formula (I) is the same.

In a preferred embodiment, the liquid compound of formula (I) of the present invention has the structure of formula (I-1):



The liquid compound of formula (I-1) of the present invention is in the form of liquid at a temperature even in the range from -18 °C to 300 °C. That is particularly advantageous from the perspective of storage and operation.

15

Antioxidant composition

Another aspect of this disclosure relates to an antioxidant composition comprising the liquid compound of formula (I) of the present invention.

- 20 According to the present invention, the antioxidant composition further comprises at least one of hindered phenol, hindered amine, and combinations thereof.

In an embodiment, the weight ratio of the liquid compound of formula (I) according to the present invention to the at least one hindered phenol and/or hindered amine is in the range from

- 25 10:1 to 1:10 (for example 9:1, 8:1, 7:1, 6:1, 5:1, 4:1, 3:1, 2:1, 1.5:1, 1:1, 1:1.5, 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8 and 1:9), preferably from 5:1 to 1:5, or from 5:1 to 1:2, or from 5:1 to 1:1.5 or from 3:1 to 1:3.

In an embodiment, the liquid compound of formula (I) of the present invention is present as a thiosynergist and the amount of the liquid compound of formula (I) is in the range from 50 to 100 wt% (for example 60 wt%, 70 wt%, 80 wt%, 90 wt%, or 95 wt%), preferably from 80 to 100 wt%, based on the total weight of the thiosynergist present in the antioxidant composition. In an embodiment, the liquid compound of formula (I) of the present invention is the only thiosynergist in the antioxidant composition of the present invention.

In an embodiment, the antioxidant composition is present in a form of liquid, for example, emulsion or suspoemulsion. Preferably, the antioxidant composition is present in a form of emulsion.

The amount of the liquid compound of formula (I) of the present invention can be in the range from 8 to 80 wt% (for example 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%), or from 10 to 70 wt% or from 15 to 60 wt%, based on the total weight of the antioxidant composition.

The amount of hindered phenol and/or hindered amine (preferably hindered phenol) can be in the range from 8 to 80 wt% (for example 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, 50 wt%, 60 wt%, 70 wt%), or from 10 to 70 wt% or from 15 to 60 wt%, based on the total weight of the antioxidant composition.

Hindered phenol

The hindered phenol, i.e., sterically hindered phenol includes phenols that have one or more phenolic hydroxyl groups on the aromatic ring, and preferably those that have a substituent, preferably an alkyl group (for example C₁ to C₆ or C₁ to C₄ alkyl), in the ortho positions, most preferably in the ortho and para positions, to the phenolic hydroxyl group(s).

It should be understood that above description is not intended to limit the scope of hindered phenols that are suitable for the present disclosure. The present disclosure has no limitation on the sterically hindered phenols as long as they have antioxidant properties.

Examples of suitable phenols include alkylphenols, for example, o-, m- or p-cresol (methylphenol), 2-tert-butyl-4-methylphenol, 6-tert-butyl-2,4-dimethylphenol, 2,6-di-tert-butyl-4-methylphenol, 2-tert-butylphenol, 4-tert-butylphenol, 2,4-di-tert-butylphenol, 2-methyl-4-tert-butylphenol, 4-tert-butyl-2,6-dimethylphenol, or 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 4,4'-oxydiphenol, 3,4-methylenedioxydiphenol (sesamol), 3,4-dimethylphenol, hydroquinone, tert-butylhydroquinone, 2,5-di-tert-butylhydroquinone, 2-methyl-p-hydroquinone, 2,3-dimethylhydroquinone, trimethylhydroquinone, pyrocatechol (1,2-dihydroxybenzene), 2-(1'-methylcyclohex-1'-yl)-4,6-dimethylphenol, 2- or 4-(1'-phenyleth-1'-yl)phenol, 2-tert-butyl-6-methylphenol, 2,4,6-tris-tert-butylphenol, 2,6-di-tert-butylphenol, nonylphenol [11066-49-2], octylphenol [140-66-9], 2,6-dimethylphenol, bisphenol A, bisphenol F, bisphenol B, bisphenol C, bisphenol S, 3,3',5,5'-tetrabromobisphenol A, methyl 3,5-di-tert-butyl-4-hydroxybenzoate, 4-tert-butylpyrocatechol, 2-hydroxybenzyl alcohol, 2-methoxy-4-methylphenol, 2,3,6-trimethylphenol, 2,4,5-trimethylphenol, 2,4,6-trimethylphenol, 2-isopropylphenol, 4-isopropylphenol, 6-isopropyl-

m-cresol, n-octadecyl β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 1,1,3-tris-(2-methyl-4-hydroxy-5-tert-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)benzene, 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5,-tris-(3,5-di-tert-butyl-4-hydroxyphenyl)propionyloxyethyl isocyanurate, 1,3,5-tris-(2,6-dimethyl-3-hydroxy-4-tert-butylbenzyl) isocyanurate or pentaerythritol tetrakis[β-(3,5,-di-tert-butyl-4-hydroxyphenyl)propionate], 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 6-isobutyl-2,4-dinitrophenol, 6-sec-butyl-2,4-dinitrophenol, 2,6-di-tert-butyl-4-(4,6-bis(octylthio)-1,3,5-triazin-2-ylamino) phenol, octadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, hexadecyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, octyl 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate, 3-thia-1,5-pentanediol bis[(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate], 4,8-dioxa-1,11-undecanediol bis[(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate], 4,8-dioxa-1,11-undecanediol bis[(3'-tert-butyl-4'-hydroxy-5'-methylphenyl)propionate], 1,9-nonanediol bis[(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionate], 1,7-heptanediaminebis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionamide], 1,1-methanediaminebis[3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionamide], 3-(3',5'-di-tert-butyl-4'-hydroxyphenyl)propionoic hydrazide, 3-(3',5'-dimethyl-4'-hydroxyphenyl)propionoic hydrazide, bis(3-tert-butyl-5-ethyl-2-hydroxyphen-1-yl)methane, bis(3,5-di-tert-butyl-4-hydroxyphen-1-yl)methane, bis[3-(1'-methylcyclohex-1'-yl)-5-methyl-2-hydroxyphen-1-yl]methane, bis(3-tert-butyl-2-hydroxy-5-methylphen-1-yl)methane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphen-1-yl)ethane, bis(5-tert-butyl-4-hydroxy-2-methylphen-1-yl) sulfide, bis(3-tert-butyl-2-hydroxy-5-methylphen-1-yl) sulfide, 1,1-bis(3,4-dimethyl-2-hydroxyphen-1-yl)-2-methylpropane, 1,1-bis(5-tert-butyl-3-methyl-2-hydroxyphen-1-yl)butane, 1,3,5-tris[1'-(3",5"-di-tert-butyl-4"-hydroxyphen-1"-yl)-meth-1'-yl]-2,4,6-trimethylbenzene, 1,1,4-tris(5'-tert-butyl-4'-hydroxy-2'-methylphen-1'-yl)butane; aminophenols, such as para-aminophenol, 3-diethylaminophenol; nitrosophenols, such as para-nitrosophenol, p-nitroso-o-cresol; alkoxyphenols, such as 2-methoxyphenol (Guajacol, pyrocatechol monomethyl ether), 4-methoxyphenol (hydroquinone monomethyl ether), 2-ethoxyphenol, 4-ethoxyphenol, 2-isopropoxyphenol, 4-butoxyphenol, mono- or di-tert-butyl-4-methoxyphenol, 3,5-di-tert-butyl-4-hydroxyanisole, 3-hydroxy-4-methoxybenzyl alcohol, 2,5-dimethoxy-4-hydroxybenzyl alcohol (syringa alcohol), 4-hydroxy-3-methoxybenzaldehyde (vanillin), 4-hydroxy-3-ethoxybenzaldehyde (ethyl vanillin), 3-hydroxy-4-methoxybenzaldehyde (isovanillin), 1-(4-hydroxy-3-methoxyphenyl)ethanone (acetovanillon), eugenol, dihydroeugenol, isoeugenol, tocopherols, such as α-, β-, γ-, δ- and ε-tocopherol, α-tocopherolhydroquinone, 4-methylpyrocatechol, 3-methylpyrocatechol, hydroquinone monobenzyl ether, p-phenoxyphenol, 2,5-di-tert-amylhydroquinone, 2,3-dihydro-2,2-dimethyl-7-hydroxybenzofuran (2,2-dimethyl-7-hydroxycoumaran), 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox®), and derivatives thereof.

Corresponding sterically hindered phenol products are available, for example, under the trade names Irganox® (BASF), such as pentaerythritol tetrakis[β-(3,5,-di-tert-butyl-4-hydroxyphenyl)propionate] (e.g., Irganox® 1010), 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-1,3,5-triazine-2,4,6(1H,3H,5H)trione (e.g., Irganox® 3114), thiodiethylenebis[3-[3,5-di-tert-butyl-4-hydroxyphenyl]propionate] (e.g., Irganox® 1035), 3,5-bis(1,1-dimethylethyl)-4-benzenepropanoic acid, branched C₇-C₉-alkyl ester (e.g., Irganox® 1135), octadecyl 3-(3,5-di-

tert-butyl-4-hydroxyphenyl) propionate (e.g., Irganox® 1076), esters of polyglycol ether terminated with phenol derivatives (e.g., Irganox® 2000), 4,6-bis(octylthiomethyl)-o-cresol (e.g., Irganox® 1520); 3,5-bis(1,1-dimethylethyl)-4-hydroxy-benzenepropanoic acid, branched C₁₃-C₁₅-alkyl esters (e.g., Anox® 1315), butylated products of p-cresol and dicyclopentadiene (Wingstay L).

In an embodiment, the hindered phenol is selected from pentaerythritol tetrakis[β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate] and butylated products of p-cresol and dicyclopentadiene (Wingstay L).

Hindered amine

Sterically hindered amines can include for example bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl) n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethyl-4-piperidyl)nitrilotriacetate, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 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]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, linear or cyclic condensates of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di-(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidine-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 condensate of N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensate 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]); a condensate of 1,6-hexanediamine and 2,4,6-trichloro-1,3,5-triazine as well as N,N-dibutylamine and 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [192268-64-7]); N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimide, 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, a diester of 4-methoxymethylenemalononic acid with 1,2,2,6,6-pentamethyl-4-hydroxypiperidine,

poly[methylpropyl-3-oxy-4-(2,2,6,6-tetramethyl-4-piperidyl)]siloxane, a reaction product of maleic acid anhydride- α -olefin copolymer with 2,2,6,6-tetramethyl-4-aminopiperidine or 1,2,2,6,6-pentamethyl-4-aminopiperidine, 2,4-bis[N-(1-cyclohexyloxy-2,2,6,6-tetramethylpiperidine-4-yl)-N-butylamino]-6-(2-hydroxyethyl)amino-1,3,5-triazine, 1-(2-hydroxy-2-methylpropoxy)-4-octadecanoyloxy-2,2,6,6-tetramethylpiperidine, 5-(2-ethylhexanoyl)-oxymethyl-3,3,5-trimethyl-2-morpholinone, Sanduvor (Clariant; CAS Reg. No. 106917-31-1), 5-(2-ethylhexanoyl)oxymethyl-3,3,5-trimethyl-2-morpholinone, the reaction product of 2,4-bis-[(1-cyclohexyloxy-2,2,6,6-piperidine-4-yl)butylamino]-6-chloro-s-triazine with N,N'-bis(3-aminopropyl)ethylenediamine), 1,3,5-tris(N-cyclohexyl-N-(2,2,6,6-tetramethylpiperazine-3-one-4-yl)amino)-s-triazine, 1,3,5-tris(N-cyclohexyl-N-(1,2,2,6,6-pentamethylpiperazine-3-one-4-yl)- amino)-s-triazine.

Phosphite and/or phosphonite

In an embodiment, the antioxidant composition further comprises at least one phosphite and/or phosphonite.

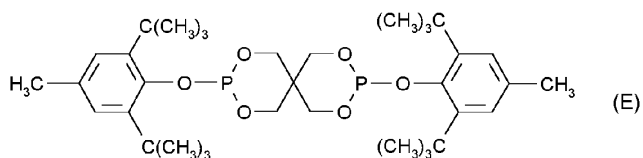
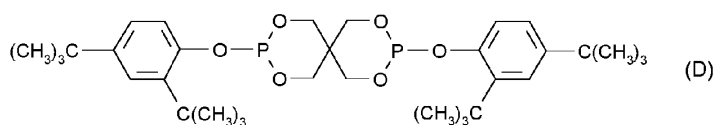
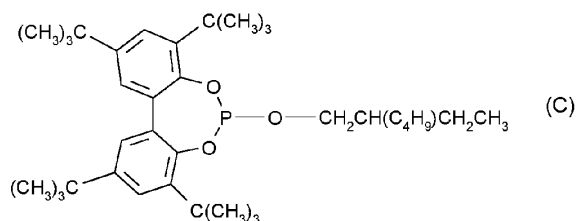
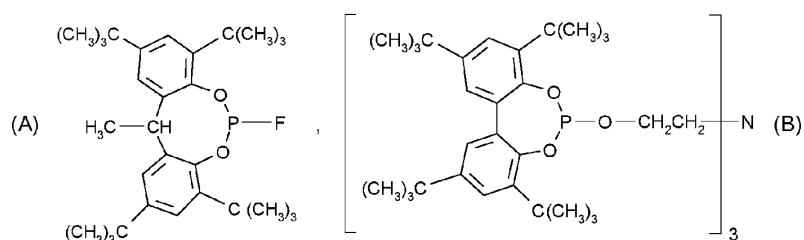
15

Phosphites and phosphonites, can include for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,4-di-cumylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, diisodecyl oxypentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl)ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2''-nitrilo[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-di-oxaphosphirane, phosphorous acid, mixed 2,4-bis(1,1-dimethylpropyl)phenyl and 4-(1,1-dimethylpropyl)phenyl triesters (CAS: 939402-02-5), phosphorous acid triphenyl ester, polymer with α -hydro- ω -hydroxypoly[oxy(methyl-1,2-ethanediyl)], C10-16-alkyl esters (CAS: 1227937-46-3).

The following phosphites are especially preferred:

35 Tris(2,4-di-tert-butylphenyl) phosphite (Irgafos®168, Ciba Specialty Chemicals Inc.), tris(nonylphenyl) phosphite,

11



The amount of phosphite and/or phosphonite can be in the range from 0 to 60 wt% (for example 5 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 35 wt%, 40 wt%, or 50 wt%), or from 0 to 50 wt% or from 5 to 60 wt% or from 10 to 50 wt%, based on the total weight of the antioxidant composition.

Thiosynergist

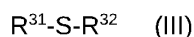
In an embodiment, the antioxidant composition of this disclosure further comprises a second thiosynergist other than the liquid compound of formula (I) of the present invention. The liquid compound of formula (I) is present as a first thiosynergist and the amount of the liquid compound of formula (I) is in the range from 50 to 100 wt% (for example 60 wt%, 70 wt%, 80 wt%, 90 wt%, or 95 wt%), preferably from 80 to 100 wt%, based on the total weight of the thiosynergist present in the antioxidant composition. The second thiosynergist can comprises thioether and/or thioester.

Thioether used according to the present disclosure includes compounds which comprise at least one thioether group, i.e. a sulfur atom which is substituted by two identical or different organic substituents. The organic substituents can each comprises 1 to 20, or 1 to 18, or 1 to 12 carbon atoms. It should be understood that the above description is not intended to limit the

scope of thioethers of the present disclosure. The present disclosure has no limitation on the thioether.

Suitable thioethers have a structure of formula (III)

5



wherein

- 10 R^{31} and R^{32} can each be, independently of one another, C_1 - C_{18} -alkyl, C_2 - C_{18} -alkyl which is interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups, C_2 - C_{18} -alkenyl, C_6 - C_{12} -aryl, C_5 - C_{12} -cycloalkyl or a five- or six-membered, oxygen-, nitrogen- and/or sulfur-comprising heterocycle, wherein the radicals mentioned are optionally substituted by hydroxy, amino, aryl, alkyl, aryloxy, alkyloxy, alkylthio, 15 alkoxycarbonyl, nitro, acyl, carbocycles, heteroatoms and/or heterocycles.

Here, R^{31} and R^{32} can each be, independently of one another, selected from a group consisting of the following groups:

- 20 methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, n-decyl, n-dodecyl, n-tetradecyl, n-hetadecyl, n-octadecyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3,3-tetramethylbutyl, benzyl, 1-phenylethyl, 2-phenylethyl, α,α -dimethylbenzyl, benzhydryl, p-tolylmethyl, 1-(p-butylphenyl)ethyl, p-chlorobenzyl, 2,4-dichlorobenzyl, p-methoxybenzyl, m-ethoxybenzyl, 2-cyanoethyl, 2-cyanopropyl, 2-methoxycarbonethyl, 2-ethoxycarbonylethyl, 2-butoxycarbonylpropyl, 1,2- 25 di(methoxycarbonyl)ethyl, 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, diethoxymethyl, diethoxyethyl, 1,3-dioxolan-2-yl, 1,3-dioxan-2-yl, 2-methyl-1,3-dioxolan-2-yl, 4-methyl-1,3-dioxolan-2-yl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, chloromethyl, 2-chloroethyl, trichloromethyl, trifluoromethyl, 1,1-dimethyl-2-chloroethyl, 2-methoxyisopropyl, butylthiomethyl, 2- 30 dodecylthioethyl, 2-phenylthioethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, 6-hydroxyhexyl, 2-aminoethyl, 2-aminopropyl, 3-aminopropyl, 4-aminobutyl, 6-aminohexyl, 2-methylaminoethyl, 2-methylaminopropyl, 3-methylaminopropyl, 4-methylaminobutyl, 6-methylaminoethyl, 2-dimethylaminoethyl, 2-dimethylaminopropyl, 3-dimethylaminopropyl, 4-dimethylaminobutyl, 6-dimethylaminoethyl, 2-hydroxy-2,2-dimethylethyl, 35 2-phenoxyethyl, 2-phenoxypropyl, 3-phenoxypropyl, 4-phenoxybutyl, 6-phenoxyhexyl, 2-methoxypropyl, 3-methoxypropyl, 4-methoxybutyl, 6-methoxyhexyl, 2-ethoxypropyl, 3-ethoxypropyl, 4-ethoxybutyl or 6-ethoxyhexyl;
- 5-hydroxy-3-oxapentyl, 8-hydroxy-3,6-dioxaoctyl, 11-hydroxy-3,6,9-trioxaundecyl, 7-hydroxy-4- 40 oxaheptyl, 11-hydroxy-4,8-dioxaundecyl, 15-hydroxy-4,8,12-trioxapentadecyl, 9-hydroxy-5-oxanonyl, 14-hydroxy-5,10-oxatetradecyl, 5-methoxy-3-oxapentyl, 8-methoxy-3,6-dioxaoctyl, 11-methoxy-3,6,9-trioxaundecyl, 7-methoxy-4-oxaheptyl, 11-methoxy-4,8-dioxaundecyl, 15-methoxy-4,8,12-trioxapentadecyl, 9-methoxy-5-oxanonyl, 14-methoxy-5,10-oxatetradecyl, 5-

ethoxy-3-oxapentyl, 8-ethoxy-3,6-dioxaoctyl, 11-ethoxy-3,6,9-trioxaundecyl, 7-ethoxy-4-oxaheptyl, 11-ethoxy-4,8-dioxaundecyl, 15-ethoxy-4,8,12-trioxapentadecyl, 9-ethoxy-5-oxanonyl or 14-ethoxy-5,10-oxatetradecyl;

- 5 vinyl, 1-propenyl, allyl, methallyl, 1,1-dimethylallyl, 2-butenyl, 2-hexenyl, octenyl, undecenyl, dodecenyl, octadecenyl, 2-phenylvinyl, 2-methoxyvinyl, 2-ethoxyvinyl, 2-methoxyallyl, 3-methoxyallyl, 2-ethoxyallyl, 3-ethoxyallyl or 1- or 2-chlorovinyl;

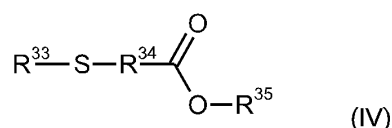
- phenyl, tolyl, xylyl, α -naphthyl, β -naphthyl, 4-diphenyl, chlorophenyl, dichlorophenyl, 10 trichlorophenyl, difluorophenyl, methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, diethylphenyl, isopropylphenyl, tert-butylphenyl, dodecylphenyl, methoxyphenyl, dimethoxyphenyl, ethoxyphenyl, hexyloxyphenyl, methylphenyl, isopropylphenyl, chloronaphthyl, ethoxynaphthyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2,6-dimethoxyphenyl, 2,6-dichlorophenyl, 4-bromophenyl, 2- or 4-nitrophenyl, 2,4- or 2,6-dinitrophenyl, 4- 15 dimethylaminophenyl, 4-acetylphenyl, methoxyethylphenyl or ethoxymethylphenyl;

- cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, methylcyclopentyl, dimethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, diethylcyclohexyl, butylcyclohexyl, methoxycyclohexyl, dimethoxycyclohexyl, diethoxycyclohexyl, butylthiocyclohexyl, chlorocyclohexyl, 20 dichlorocyclohexyl, dichlorocyclopentyl or a saturated or unsaturated bicyclic system such as norbornyl or norbornenyl; and

- furyl, thiophenyl, pyrrol, pyridyl, indolyl, benzoxazolyl, dioxolyl, dioxyl, benzimidazolyl, benzthiazolyl, dimethylpyridyl, methylquinolyl, dimethylpyrrol, methoxyfuryl, dimethoxypyridyl, 25 difluoropyridyl, methylthiophenyl, isopropylthiophenyl or tert-butylthiophenyl.

- In some embodiments, the thioether is selected from a group consisting of 2-methyl-1-propenyl tert-dodecyl thioether, cyclohexylidenemethyl n-dodecyl thioether, 3-cyclohexen-(1)-ylidenemethyl-n-octadecyl thioether, 3-cyclohexen-(1)-ylidenemethyl-n-dodecyl thioether, 3- 30 cyclohexen-(1)-ylidenemethyl n-octyl thioether, 3-cyclohexen-(1)-ylidenemethyl cyclohexyl thioether, 3-methyl-(3)-cyclohexen-(1)-ylidenemethyl n-dodecyl thioether, 3-cyclohexen-(1)-ylidenemethyl p-tolyl thioether, 3-cyclohexen-(1)-ylidenemethyl benzyl thioether and preferably 3-cyclohexen-(1)-ylidenemethyl n-dodecyl thioether and 1-hexenyl-n-dodecyl thioether.

- 35 In other embodiments, thioethers are compounds that have a structure of formula (IV)



wherein

40

R^{33} and R^{35} can each be, independently of one another, C_1 - C_{18} -alkyl, C_2 - C_{18} -alkyl, which is

interrupted by one or more oxygen and/or sulfur atoms and/or one or more substituted or unsubstituted imino groups, C₆-C₁₂-aryl or C₅-C₁₂-cycloalkyl, wherein the radicals mentioned are optionally substituted by hydroxy, amino, aryl, alkyl, aryloxy, alkyloxy, alkylthio, alkoxycarbonyl, nitro, acyl, carbocycles, heteroatoms and/or heterocycles, and

5

R³⁴ can be C₁-C₂₀-alkylene or C₃-C₁₂-cycloalkylene, wherein the radicals mentioned are optionally substituted by hydroxy, amino, aryl, alkyl, aryloxy, alkyloxy, alkylthio, alkoxycarbonyl, nitro, acyl, carbocycles, heteroatoms and/or heterocycles.

- 10 Here, R³³ and R³⁵ can each be, independently of one another, selected from a group consisting of the following groups:

15 methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, 2-ethylhexyl, 2,4,4-trimethylpentyl, n-decyl, n-dodecyl, n-tetradecyl, n-hetadecyl, n-octadecyl, 1,1-dimethylpropyl, 1,1-dimethylbutyl, 1,1,3,3-tetramethylbutyl, benzyl, 1-phenylethyl, 2-phenylethyl, α,α-dimethylbenzyl, benzhydrl, p-tolylmethyl, 1-(p-butylphenyl)ethyl, p-chlorobenzyl, 2,4-dichlorobenzyl, p-methoxybenzyl, m-ethoxybenzyl, 2-cyanoethyl, 2-cyanopropyl, 2-methoxycarbonethyl, 2-ethoxycarbonylethyl, 2-butoxycarbonylethyl, 1,2-di(methoxycarbonylethyl), 2-methoxyethyl, 2-ethoxyethyl, 2-butoxyethyl, diethoxymethyl, diethoxyethyl, 1,3-dioxolan-2-yl, 1,3-dioxan-2-yl, 2-methyl-1,3-dioxolan-2-yl, 4-methyl-1,3-dioxolan-2-yl, 2-isopropoxyethyl, 2-butoxypropyl, 2-octyloxyethyl, chloromethyl, 2-chloroethyl, trichloromethyl, trifluoromethyl, 1,1-dimethyl-2-chloroethyl, 2-methoxyisopropyl, butylthiomethyl, 2-dodecylthioethyl, 2-phenylthioethyl, 2,2,2-trifluoroethyl, 2-hydroxyethyl, 2-hydroxypropyl, 3-hydroxypropyl, 4-hydroxybutyl, 6-hydroxyhexyl, 2-aminoethyl, 2-aminopropyl, 3-aminopropyl, 4-aminobutyl, 6-aminohexyl, 2-methylaminoethyl, 2-methylaminopropyl, 3-methylaminopropyl, 4-methylaminobutyl, 6-methylaminohexyl, 2-dimethylaminoethyl, 2-dimethylaminopropyl, 3-dimethylaminopropyl, 4-dimethylaminobutyl, 6-dimethylaminohexyl, 2-hydroxy-2,2-dimethylethyl, 2-phenoxyethyl, 2-phenoxypropyl, 3-phenoxypropyl, 4-phenoxybutyl, 6-phenoxyhexyl, 2-methoxypropyl, 3-methoxypropyl, 4-methoxybutyl, 6-methoxyhexyl, 2-ethoxypropyl, 3-ethoxypropyl, 4-ethoxybutyl or 6-ethoxyhexyl;

5-hydroxy-3-oxapentyl, 8-hydroxy-3,6-dioxaoctyl, 11-hydroxy-3,6,9-trioxaundecyl, 7-hydroxy-4-oxaheptyl, 11-hydroxy-4,8-dioxaundecyl, 15-hydroxy-4,8,12-trioxapentadecyl, 9-hydroxy-5-oxanonyl, 14-hydroxy-5,10-oxatetradecyl, 5-methoxy-3-oxapentyl, 8-methoxy-3,6-dioxaoctyl, 11-methoxy-3,6,9-trioxaundecyl, 7-methoxy-4-oxaheptyl, 11-methoxy-4,8-dioxaundecyl, 15-methoxy-4,8,12-trioxapentadecyl, 9-methoxy-5-oxanonyl, 14-methoxy-5,10-oxatetradecyl, 5-ethoxy-3-oxapentyl, 8-ethoxy-3,6-dioxaoctyl, 11-ethoxy-3,6,9-trioxaundecyl, 7-ethoxy-4-oxaheptyl, 11-ethoxy-4,8-dioxaundecyl, 15-ethoxy-4,8,12-trioxapentadecyl, 9-ethoxy-5-oxanonyl or 14-ethoxy-5,10-oxatetradecyl;

40

phenyl, tolyl, xylyl, α-naphthyl, β-naphthyl, 4-diphenyl, chlorophenyl, dichlorophenyl, trichlorophenyl, difluorophenyl, methylphenyl, dimethylphenyl, trimethylphenyl, ethylphenyl, diethylphenyl, isopropylphenyl, tert-butylphenyl, dodecylphenyl, methoxyphenyl,

dimethoxyphenyl, ethoxyphenyl, hexyloxyphenyl, methylnaphthyl, isopropylnaphthyl, chloronaphthyl, ethoxynaphthyl, 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2,6-dimethoxyphenyl, 2,6-dichlorophenyl, 4-bromophenyl, 2- or 4-nitrophenyl, 2,4- or 2,6-dinitrophenyl, 4-dimethylaminophenyl, 4-acetylphenyl, methoxyethylphenyl or ethoxymethylphenyl; and

5 cyclopentyl, cyclohexyl, cyclooctyl, cyclododecyl, methylcyclopentyl, dimethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, diethylcyclohexyl, butylcyclohexyl, methoxycyclohexyl, dimethoxycyclohexyl, diethoxycyclohexyl, butylthiocyclohexyl, chlorocyclohexyl, dichlorocyclohexyl, dichlorocyclopentyl or a saturated or unsaturated bicyclic system such as
10 norbornyl or norbornenyl.

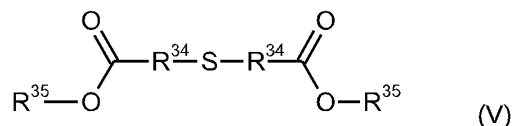
Here, R^{34} can be selected from a group consisting of the following groups:

methylene, 1,2-ethylene, 1,2- or 1,3-propylene, 1,2-, 1,3- or 1,4-butylene, 1,1-dimethyl-1,2-ethylene or 1,2-dimethyl-1,2-ethylene, 1,6-hexylene, 1,8-octylene, 1,10-decylene, 1,12-
15 dodecylene and 1,20-eicosylene, and cyclopropylene, cyclopentylene, cyclohexylene, cyclooctylene and cyclododecylene.

In some preferred embodiments, R^{33} is optionally substituted C_6 - C_{12} -aryl or C_1 - C_{18} -alkyl, preferably optionally substituted C_1 - C_{18} -alkyl, particularly preferably unsubstituted C_1 - C_{18} -alkyl;
20 R^5 is optionally substituted C_1 - C_{18} -alkyl, preferably unsubstituted C_1 - C_{18} -alkyl; and/or R^4 is methylene, 1,2-ethylene or 1,2-propylene, preferably 1,2-ethylene.

In some embodiments, especial preference is given to compounds having a structure of formula
(V)

25



wherein R^{34} and R^{35} are as defined above.

30 In preferable embodiments, the thioether is at least one selected from a group consisting of thiodipropionic esters, for example dimethyl 3,3'-thiodipropionate, didodecyl 3,3'-thiodipropionate (e.g., Irganox® PS 800 from BASF), di-lauryl-thio-di-propionate (DLTDP), ditridecyl 3,3'-thiodipropionate (DTDTP) (e.g., Songnox® DTDTP from Songwon International AG), dioctadecyl 3,3'-thiodipropionate (DSTDP), dimyristyl thiodipropionate (DMTDP) and 2,2-
35 bis[[3-(dodecylthio)-1-oxopropoxy]methyl]propane-1,3-diyl bis[3-(dodecylthio)propionate] (e.g., Seenox 412S).

Thioester can include for example dilauryl thiodipropionate, dimistryl thiodipropionate or distearyl thiodipropionate.

40

The amount of the second thiosynergist can be in the range from 0 to 90 wt% (for example 2 wt%, 4 wt%, 5 wt%, 6 wt%, 8 wt%, 10 wt%, 15 wt%, 20 wt%, 25 wt%, 30 wt%, 50 wt%, 60 wt%, 80 wt% or 85 wt%), or from 0 to 80 wt% or from 0 to 50 wt% or from 0 to 30 wt%, based on the total weight of the thiosynergist.

5

Specific embodiments of antioxidant composition

In an embodiment, the antioxidant composition comprises

liquid compound of formula (I) of the present invention;

at least one of hindered phenol, hindered amine, and combinations thereof; and

10 optionally at least one phosphite and/or phosphonite.

In an embodiment, the antioxidant composition comprises

8 to 80 wt% liquid compound of formula (I) of the present invention;

8 to 80 wt% at least one of hindered phenol, hindered amine, and combinations thereof; and

15 0 to 60 wt% optionally at least one phosphite and/or phosphonite,

in each case based on the total weight of the antioxidant composition.

In an embodiment, the antioxidant composition comprises

10 to 70 wt% liquid compound of formula (I) of the present invention;

20 10 to 70 wt% at least one of hindered phenol, hindered amine, and combinations thereof; and

0 to 50 wt% optionally at least one phosphite and/or phosphonite,

in each case based on the total weight of the antioxidant composition.

In an embodiment, the antioxidant composition comprises

25 15 to 60 wt% liquid compound of formula (I) of the present invention;

15 to 60 wt% at least one of hindered phenol, hindered amine, and combinations thereof; and

0 to 50 wt% optionally at least one phosphite and/or phosphonite,

in each case based on the total weight of the antioxidant composition.

30 In an embodiment, the antioxidant composition comprises

15 to 60 wt% liquid compound of formula (I) of the present invention;

15 to 60 wt% at least one of hindered phenol, hindered amine, and combinations thereof; and

5 to 60 wt% optionally at least one phosphite and/or phosphonite,

in each case based on the total weight of the antioxidant composition.

35

In an embodiment, the antioxidant composition comprises

15 to 60 wt% liquid compound of formula (I) of the present invention;

15 to 60 wt% at least one of hindered phenol, hindered amine, and combinations thereof; and

10 to 50 wt% optionally at least one phosphite and/or phosphonite,

40 in each case based on the total weight of the antioxidant composition.

In an embodiment, the antioxidant composition of this disclosure is present in a form of liquid, preferably emulsion.

The antioxidant composition of present disclosure can further comprise one or more additives that are commonly used in the art. Examples of suitable additives includes as protective colloid, surfactant, thickener, anti-freeze agent, anti-foaming agent, rheology modifier, preservative, and colorant.

Examples of thickener, anti-freeze agent, anti-foaming agent, rheology modifier, emulsifier, dispersant, preservative, colorant, and an inert filler suitable for present disclosure are those commonly used in the art. Skilled one in the art may select appropriate additives per specific application.

In some embodiments, the antioxidant composition of present disclosure may further comprise light stabilizer, for example, UV absorbers (like dimethyl keton benzene type, oxanilide type, benzotriazole type, triazine type), and hindered amine light stabilizers (HALS). With addition of light stabilizer, the aqueous antioxidant suspoemulsion of present disclosure can further protect polymers against photoaging.

Use and Polymer composition

One aspect of this disclosure relates to use of the antioxidant composition of the present invention for stabilizing polymer. The polymer includes but are not limited to rubber and plastic.

A further aspect of this disclosure relates to a polymer composition comprising the antioxidant composition of the present invention.

In one embodiment, the polymer in the polymer composition is in the form of aqueous suspension or emulsion, for example latex.

The polymer is preferably selected from polymers of monoolefins and diolefins (for example PP), copolymers of monoolefins and diolefins with each other or with other vinyl monomers, hydrocarbon resins and mixtures of polyalkylenes and starch, styrenics polymer, graft copolymers of vinyl aromatic monomers such as styrene or α -methylstyrene (for example ABS, rubber grafted ABS), halogen-containing polymers (for example PVC), polymers derived from α,β -unsaturated acids and derivatives thereof, polymers derived from unsaturated alcohols and amines or the acyl derivatives or acetals thereof, homopolymers and copolymers of cyclic ethers, Polyphenylene oxides and sulfides, elastomer (for example polyurethanes, styrenics), polyamides and copolyamides, polyureas, polyimides, polyamide-imides, polyetherimides, polyesterimides, polyhydantoins and polybenzimidazoles, polyesters, polycarbonates and polyester carbonates, polyketones, polysulfones, polyether sulfones and polyether ketones, crosslinked polymers derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand, drying and non-drying alkyd resins, unsaturated polyester resins, crosslinkable acrylic resins, alkyd resins, polyester resins and acrylate resins crosslinked with melamine resins, urea resins, isocyanates, isocyanurates, polyisocyanates or epoxy resins, crosslinked epoxy resins, natural

polymers and chemically modified homologous derivatives thereof, natural or synthetic rubber, aqueous dispersions of natural or synthetic rubber, linear low-density polyethylene, low-density polyethylene, high density polyethylene, ethylene-vinyl acetate copolymer, ethylene-butyl acrylate copolymer, polypropylene homopolymer and polypropylene copolymer and engineering
5 plastics.

In a preferred embodiment, the polymer can be selected from styrenics polymer, halogen-containing polymers, elastomers (for example PUR), natural or synthetic rubber, polyolefins and engineering plastics.

10 The antioxidant composition can be present in an amount of preferably 0.02 to 5 wt% (for example 0.04 wt%, 0.05 wt%, 0.08 wt%, 0.1 wt%, 0.15 wt%, 0.2 wt%, 0.25 wt%, 0.3 wt%, 0.5 wt%, 0.8 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%) or 0.04 to 4 wt%, preferably 0.1 to 3 wt% or 0.15 to 2 wt%, based on the total weight of the polymer composition.

15 The antioxidant composition according to the present invention or its individual components can be incorporated into the polymer to be stabilized by known methods, for example before or during shaping or by applying the dissolved or dispersed stabilizer to the polymer, if necessary with subsequent evaporation of the solvent.

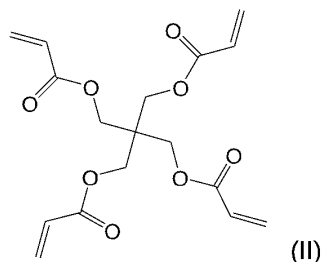
20 Examples of processing or transformation of the polymers stabilized according to the present invention are:

Injection blow molding, extrusion, blow molding, rotomolding, in mold decoration (back injection),
25 slush molding, injection molding, coinjection molding, forming, compression molding, pressing, film extrusion (cast film; blown film), fiber spinning (woven, non-woven), drawing (uniaxial, biaxial), annealing, deep drawing, calendaring, mechanical transformation, sintering, coextrusion, coating, lamination, crosslinking (radiation, peroxide, silane), vapor deposition, weld together, glue, vulcanization, thermoforming, pipe extrusion, profile extrusion, sheet extrusion; sheet cast-
30 ing, spin coating, strapping, foaming, recycling / rework, extrusion coating, visbreaking (peroxide, thermal), fiber melt blown, spun bonded, surface treatment (corona discharge, flame, plasma), sterilization (by gamma rays, electron beams), cast polymerization (R&M process, RAM extrusion), gel-coating, tape extrusion, GMT-process, SMC-process, plastisol, and dipping (PVC, latex).

35 In an embodiment, the polymer composition of the present invention can further comprise at least one additive selected from the group consisting of a surfactant, a thickener, an anti-freeze agent, anti-foaming agent, a rheology modifier, an emulsifier, a dispersant, a preservative, an antioxidant, a colorant, acid scavenger, and an inert filler.

40 Process of synthesizing the liquid compound of formula (I)
A further aspect of this disclosure relates to a process of synthesizing the liquid compound of formula (I) of the present invention, which comprises:

(i) reacting acrylic acid with pentaerythritol to obtain a liquid compound of formula (II)



(ii) reacting the compound of formula (II) with a thiol of formula (III)

R-SH (III)

5 wherein R is as defined above.

Step (i)

The reaction in step (i) can be carried out in the presence of a reducing agent for example hypo phosphorus acid. The reducing agent is added generally in an amount of 50 ppm to 5% by weight (for example 100 ppm, 500ppm, 1000 ppm, 5000 ppm, 1% by weight, 2% by weight, 3% by weight, 5% by weight), preferably 100 ppm to 4% by weight and more preferably 1000 ppm to 3% by weight, based on the amount of the pentaerythritol.

To accelerate the reaction in step (i), acidic catalysts are added additionally. Suitable catalysts are, for example, acids with a pK_a of less than 2.2; particular preference is given to strong acids.

Examples of acids with a pK_a of less than 2.2 are, for example, phosphoric acid (H_3PO_4), phosphorous acid (H_3PO_3), pyrophosphoric acid ($H_4P_2O_7$), polyphosphoric acid, hydrogensulfate (HSO_4^-), sulfuric acid (H_2SO_4), perchloric acid, hydrochloric acid, hydrobromic acid, chlorosulfonic acid, methanesulfonic acid, trichloromethanesulfonic acid, trifluoromethanesulfonic acid, benzenesulfonic acid or p-toluene sulfonic acid.

Particularly preferred inventive catalysts are sulfuric acid, phosphoric acid, polyphosphoric acid, chlorosulfonic acid, methanesulfonic acid, trichloromethanesulfonic acid, trifluoromethanesulfonic acid, benzenesulfonic acid, or p-toluenesulfonic acid.

Very particular preference is given to sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid, or p-toluenesulfonic acid.

The acid is added as a catalyst generally in an amount of 50 ppm to 15% by weight (for example 100 ppm, 500ppm, 1000 ppm, 5000 ppm, 1% by weight, 2% by weight, 5% by weight, 8% by weight, 10% by weight, 12% by weight or 14% by weight), preferably 100 ppm to 14% by weight and more preferably 1000 ppm to 12% by weight or 1 to 12% by weight, based on the amount of the pentaerythritol.

A stabilizer can be used in step (i). The stabilizer was used to prevent the polymerization of acrylate. The stabilizer can be selected from p-hydroxy anisole (MEHQ) and butylated hydroxy anisole (BHA).

- 5 The reaction can be carried out in a solvent. The solvent can be an aprotic solvent, for example toluene or benzene.

The reaction is performed typically at a temperature of 60 to 120°C, preferably 70 to 110°C, more preferably at 70 to 100°C and most preferably at 75 to 90°C.

10

The water produced can be removed in the course of the reaction from the reaction equilibrium to accelerate the reaction, for example by using molecular sieves or by dean stark assembly. The molecular sieves can be used on any pore size or morphology like 4Å, 3Å, 5Å, etc

- 15 The reaction time in step (i) can be in the range from 2 to 36 h (for example 4, 5, 8, 10, 15, 20, 25, 30 or 35 h), preferably from 5 to 30 h, more preferably from 10 to 25 h.

Step (ii)

According to the invention, the reaction of step (ii) can be carried out in the presence of a base.

- 20 The base can comprise inorganic base and organic base. Suitable inorganic base can be alkali metal hydroxides, carbonates, and bicarbonates. Specific examples of inorganic base can include Na_2CO_3 , NaHCO_3 , NaOH , K_2CO_3 , KHCO_3 , etc. Suitable organic base can comprise amine, for example primary amine, secondary amine and tertiary amine, such as triethylamine, dibutyl amine, diethyl amine, di isopropyl amine, etc. The amount of the base can be in the range from
- 25 5 to 60% weight (for example 8%, 10%, 15%, 20%, 30%, 40%, 50%, or 55% by weight), preferably from 10 to 55% by weight.

The reaction in step (ii) can be carried out in suitable solvents, such as in aprotic solvents (DMF and/or THF).

30

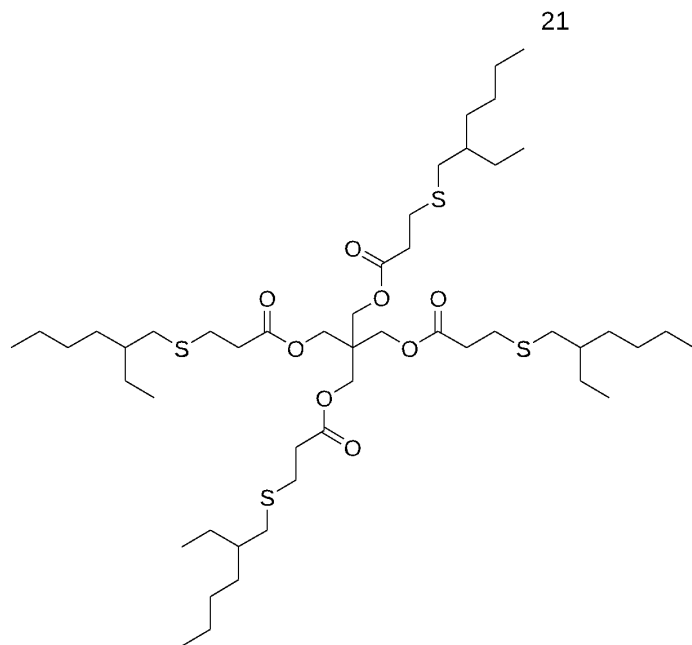
The reaction temperature in step (ii) can be between 25 to 75 °C (for example 30 °C, 40 °C, 50 °C, 60 °C or 70 °C) or preferably from 40 to 65 °C. The reaction time in step (ii) can be 3-20 h, 4-16 h, or 5-14 h.

35 EXAMPLES

Materials

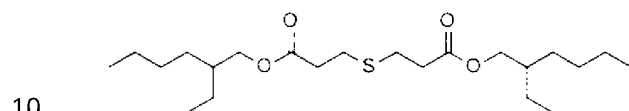
Thiosynergist:

- Liquid compound of formula (I-1) of present invention (named as "compound 408" hereinafter):



(I-1);

- Seenox 412s: tetrakis-[(3-(n-dodecylthio)propionyloxy)methyl]methan (RTM Shipro Kasei Kai-sha);
- 5 - DLTDP (Irganox PS800): didodecyl-3,3'-thiodipropionate, from BASF;
- DTDTP: ditridecyl 3,3'-thiodipropionate, from SI Group;
- DSTDP (Irganox PS802): dioctadecyl 3,3'-thiodipropionate, melting point 64-67 °C, from BASF;
- DEHTDP: bis(2-ethylhexyl) 3,3'-Thiodipropionate, from BASF.



Hindered phenol

- Wingstay L: a hindered phenol: butylated products of p-cresol and dicyclopentadiene, from BASF, melting point 115 °C;
- 15 - Irganox® 1010: pentaerythritol tetrakis[β-(3,5,-di-tert-butyl-4-hydroxyphenyl)propionate], melting point 110-125 °C.

Phosphite

- Irgafos® 168: tris(2,4-di-tert-butylphenyl) phosphite, melting point 183-186 °C.

20

Polymers

- HRG-ABS (High Rubber Grafted Acrylonitrile Butadiene Styrene): 46.5% HRG-ABS latex coagulated with H₂SO₄;
- PP: PolyPropylene (Maoming040 from Maohua Shihua, with melt flow rate of 4±2.0 g/10min according to GB/T 3682).

25

Test methods

1. Thermogravimetric Analysis (TGA): from room temperature to 600°C, heating rate 10°C/min, in air condition.

- 5 2. Oxidation induction peak time (OIT Peak time) measures the level of thermal stabilization of the material tested. OIT Peak time of samples is measured as below. In specific, the coagulated and dried stabilized sample is put in a differential scanning calorimetry (DSC) device and the sample is heated to 198°C under nitrogen atmosphere. When 198°C is reached, the sample is maintained at isothermal condition for 5 minutes, and the gas is changed from nitrogen to oxygen. The flow rate of the oxygen is maintained at 50 ml/min.
- 10

Under these conditions, the antioxidants are consumed over time. At a point, the sample starts degradation or oxidization, and thereby liberate additional heat (exotherm reaction). The time it takes for this exotherm reaction to reach peak from the time that the oxygen is introduced is reported as the OIT Peak time. The longer the OIT Peak time, the better the thermal stability of the sample.

15

3. Yellowness index (YI): Polymer plaques are tested for color development according to ASTM E-313 with a DCI SF600 spectrophotometer; large area view; spectral component included; 2 degree observer. Color is expressed as yellowness index (YI).
- 20

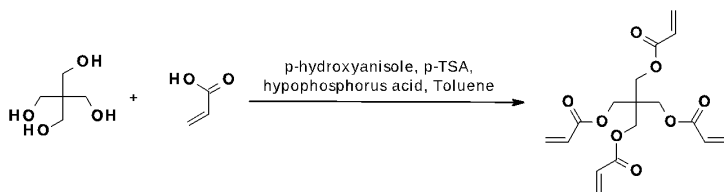
4. Melt flow index (MFI) retentions are determined for polymer samples from the zero pass and fifth pass extrudate. Melt flow index is performed according to ISO-170 on a Tinius-Olsen Extrusion Plastometer at 230°C; 2.16 kg; measured in grams of polymer that flow out of a defined orifice in 10 minutes.
- 25

5. Embrittlement: The samples (60 × 20 × 1 mm plaque) are heated at 150 °C. A clamp tool is used to clamp the specimen, when the plaque is break, record the days. The longer the embrittlement time is, the better the stabilizing effect of the antioxidant composition in the polymer.

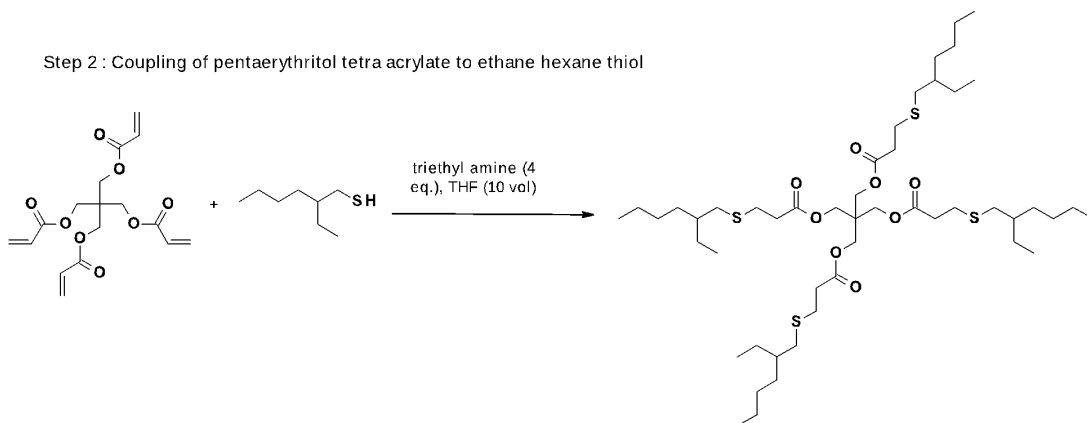
30

Example 1: synthesizing the compound 408 of the present invention

Step 1 : Synthesis of pentaerythritol tetraacrylate



Step 2 : Coupling of pentaerythritol tetra acrylate to ethane hexane thiol



Scheme 1

Step 1: Synthesis of pentaerythritol tetraacrylate:

- 5 To a 100ml 3-necked round bottom flask, 1.0g of pentaerythritol and 1.68g of acrylic acid were taken in 10.0ml of toluene, under nitrogen atmosphere. To this mixture, 0.05g of p-hydroxy anisole, 0.09g of p-toluene sulfonic acid, 0.02g of hypo phosphorus acid were added followed by 0.1g of 4Å molecular sieves to trap any water formation during reaction. The reaction mass was heated at 82°C for 18 hours and monitored by gas chromatography. After completion of the re-
- 10 action, the reaction mass was cooled to 25°C, diluted with 30.0ml toluene and 50.0ml water. The organic layer was separated and washed with 50.0ml of 1N aqueous Na₂CO₃ solution followed by 50.0ml of 1N aqueous NaOH solution. The organic layer was separated from above washings and to it 0.01g of p-hydroxy anisole was added. The organic layer was dried over anhydrous sodium sulfate and concentrated over rotavapor under high vacuum to get 0.9g crude
- 15 colorless transparent viscous monomer.
Yield: 0.9g crude (34.8% crude yield).
¹H NMR (300 MHz, Chloroform-d) δ 6.43 – 6.28 (m, 4H), 6.05 (ddd, J = 17.0, 10.4, 5.8 Hz, 4H), 5.87 – 5.73 (m, 4H), 4.34 – 4.02 (m, 8H).

- 20 Step 2: Synthesis of Thiol ester derivative of pentaerythritol tetraacrylate:

The product obtained according to the procedure in step 1 (containing 20.0g of Pentaerythritol tetraacrylate) was dissolved in 200.0ml of THF and taken in round bottom flask. To this, 8.16g of triethylamine was added. Then 33.2g of 2-ethylhexane-1-thiol was added at room temperature. Then reaction temperature was increased to 60°C within 30 minutes and stirred at this

- 25 temperature for 24 hours. After completion of the reaction, 500.0ml ethyl acetate was added to reaction mixture. This combined organic layer was washed with 500.0ml of water followed by

washing with 500.0ml saturated NaHCO₃ solution. Layers were separated and combined organic layer was collected separately. The organic layer was then dried over sodium sulphate, filtered, and evaporated to give crude compound as a colorless liquid which was taken for further purification via column chromatography.

5

The crude product thus obtained was further purified by column chromatography using silica gel as a stationary phase with heptane and EtOAc as an eluent to give the desired product as a colourless liquid. Yield: 13.8g (25.9%).

10 ¹H NMR (300 MHz, Chloroform-d) δ 4.10 (s, 8H), 2.67 (td, J = 7.1, 1.6 Hz, 8H), 2.55 (td, J = 7.1, 1.6 Hz, 8H), 2.43 (d, J = 6.0 Hz, 8H), 1.48 – 1.12 (m, 36H), 0.81 (dt, J = 9.5, 6.8 Hz, 24H).

¹³C NMR (75 MHz, Chloroform-d) δ 171.36, 62.22, 42.03, 39.16, 36.78, 34.70, 32.30, 28.82, 27.54, 25.43, 22.98, 14.11, 10.75.

15

Purity by NMR assay: 98.165% (w/w).

Example 2: TGA (Thermogravimetric Analysis)

20 The TGA results of compound 408 of the present invention and other thiosynergists were shown in table 1 below. Onset temperature denotes the temperature at which the samples start to lose weight. Temperature at 5% loss denotes the temperature at which the samples lost 5% weight. And temperature at 10% loss denotes the temperature at which the samples lost 10% weight.

Table 1-TGA results

Sample Name	Onset temperature (°C)	Temperature at different weight loss points (°C)	
		5%	10%
408	325.15	308.61	331.44
412S	286.77	281.89	296.43
1520L	278.35	265.20	279.29
1726	265.62	254.09	264.85
DEHTDP	259.29	213.33	233.18
DLTDP	261.76	236.26	252.48
DSDTDP	298.62	276.94	293.53
DTDTP	297.00	267.69	289.90

25 As can be seen, the thermal stability of compound 408 of the present invention is much higher than those of the other thiosynergists.

Example 3: Application in HRG-ABS

1) Preparation of the antioxidant dispersion

30 At 90°C, 200g antioxidants as shown in below table 2 were mixed and melted. At 70°C, 10g sodium dodecyl benzene sulfonate (SDBS) was dissolved in 290g deionized water. Then, the

molten antioxidants were dosed into SDBS solution and the mixture was homogenized with a homogenizer for 10 minutes.

2) Preparation of the polymer composition: samples 1# to 6#

5 Material: ABS latex

ABS latex has a solid content of 46%.

ABS Stabilization and Coagulation:

218g of the ABS latex was mixed with 0.94g of the aqueous antioxidant dispersion prepared according to above step. Then, 1.55g of sulfuric acid (c: 98%) was mixed with 171g of deionized water at 65°C.

At temperature of around 65°C, the stabilized ABS latex was added into the diluted solution of sulfuric acid under continuous agitation to trigger coagulation of the ABS substrates. Then, the temperature was increased to 93°C and kept this temperature for additional 3 minutes. Then, the slurry was cooled down to room temperature. The slurry was filtered and washed 3 times with deionized water. The filtrate was dried at 60°C for 20 hours to obtain dried and stabilized ABS.

20 The amount of thiosynergist was 0.25 wt% and the amount of hindered phenol was also 0.25 wt% in samples 1# to 6#, based on the total weight of the polymer composition.

The results of OIT Peak time of samples 1# to 6# were shown in table 2. Sample 1# containing compound 408 of the present invention shows longer OIT Peak time than those of the samples 2# to 6# containing other thiosynergists, which means sample 1# has better thermal stability.

Table 2

	1#	2#	3#	4#	5#	6#
thiosynergist	408	412s	DEHTDP	DLTDP	DSTDTP	DTDTP
Hindered phenol	Wingstay L	Wingstay L	Wingstay L	Wingstay L	Wingstay L	Wingstay L
OIT Peak time (min)	78	70	43	46	40	43

Example 4: Application in PP

1) Preparation of the polymer composition: samples 7# to 10#

30 Additives in amounts as shown in table 3 were blended with powder form PP free of any stabilization additives. In addition to the additives listed, all formulations were blended with 600 ppm calcium stearate. Thoroughly blended formulations were mixed in a high speed mixer at 1800rpm for 2 minutes. Then the PP blends were compounded in a twin screw extruder at 230°C to obtain the PP compounded pellets.

35

The PP compounded pellets were compressed into 60mm*2mm*1mm plaques. The embrittlement results of the resulted polymer compositions were shown in table 3. Notably, sample 9# having 0.05% 408 shows significantly improved embrittlement performance than sample 7#. Sample

10# having 0.1% 408 shows better embrittlement performance than sample 8#.

The polymer pellet compositions were extruded multiple times in a Göttfert single screw extruder model MP Ø30, at 260°C, open to air. The yellowness index and MFI of polymer compositions after multiple pass extrusion were shown in table 4 and table 5, respectively.

Table 3

	7# (comparative)	8# (comparative)	9#	10#
thiosynergist		0.1% Irganox PS802	0.05% 408	0.1% 408
hindered phenol	0.05% Irganox1010	0.05% Irganox1010	0.05% Irganox1010	0.05% Irganox1010
phosphite	0.1% Irgafos 168	0.1% Irgafos 168	0.1% Irgafos 168	0.1% Irgafos 168
calcium stearate	0.05%	0.05%	0.05%	0.05%
embrittlement (days)	9.6	48.8	42.2	50.8

All percentages in table 3 were based on the total weight of the polymer composition.

10 Table 4-YI after multiple pass extrusion

	7# (comparative)	8# (comparative)	9#	10#
YI (zero pass)	-0.04	-0.88	-0.69	-1.12
YI (first pass)	1.12	-0.14	-0.24	-0.37
YI (third pass)	2.83	1.40	0.35	0.45
YI (fifth pass)	4.42	3.47	1.44	0.88

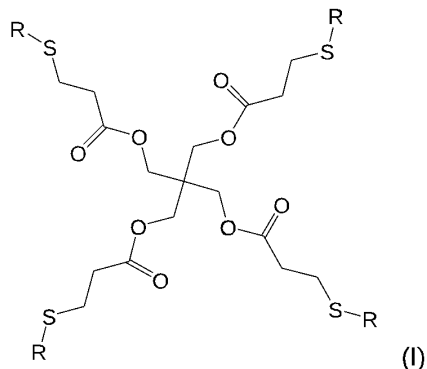
Table 5-MFI after multiple pass extrusion

	7# (comparative)	8# (comparative)	9#	10#
MFI (zero pass)	5.12	4.83	4.80	4.75
MFI (first pass)	5.71	5.42	5.33	5.25
MFI (third pass)	6.48	6.16	5.96	5.95
MFI (fifth pass)	7.51	6.93	6.69	6.69

The samples 9# and 10# according to the present invention shows much lower yellow index and MFI after multiple pass extrusion.

CLAIMS

1. A liquid compound of formula (I):



5 wherein each R is a branched C8 alkyl.

2. The liquid compound of formula (I) according to claim 1, wherein each R has one branch point.

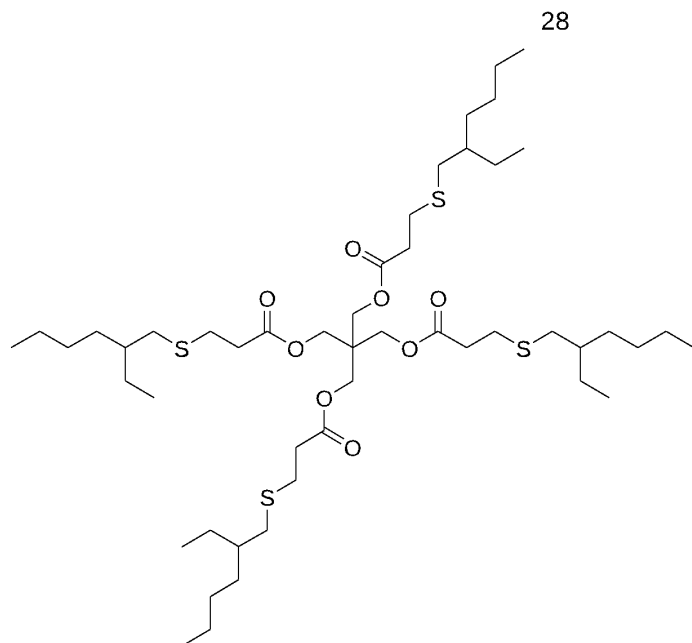
10 3. The liquid compound of formula (I) according to claim 1, wherein each R has one branch point on the second carbon atom starting from the S atom.

4. The liquid compound of formula (I) according to any of claims 1 to 3, wherein branched chain in R has 2 or 3 carbon atoms, preferably 2 carbon atoms.

15

5. The liquid compound of formula (I) according to any of claims 1 to 4, wherein each R in formula (I) is the same.

20 6. The liquid compound of formula (I) according to any of claims 1 to 5, which has the structure of formula (I-1):



7. An antioxidant composition comprising the liquid compound of formula (I) according to any of claims 1 to 6.

5

8. The antioxidant composition according to claim 7, which further comprises at least one of hindered phenol, hindered amine, and combinations thereof.

9. The antioxidant composition according to claim 8, wherein weight ratio of the liquid compound of formula (I) according to any of claims 1 to 6 to the at least one of hindered phenol, hindered amine, and combinations thereof is in the range from 10:1 to 1:10, preferably from 5:1 to 1:5.

10

10. The antioxidant composition according to any of claims 7 to 9, which further comprises at least one phosphite and/or phosphonite.

15

11. The antioxidant composition according to any of claims 7 to 10, wherein the antioxidant composition comprises a second thiosynergist which is different from the liquid compound of formula (I), and the liquid compound of formula (I) is present as a first thiosynergist and the amount of the liquid compound of formula (I) is in the range from 50 to 100 wt%, preferably from 80 to 100 wt%, based on the total weight of the thiosynergist present in the antioxidant composition.

20

12. The antioxidant composition according to any of claims 7 to 11, wherein the antioxidant composition is present in a form of liquid, preferably emulsion.

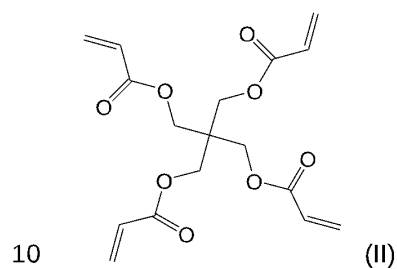
25

13. Use of the antioxidant composition according to any of claims 7 to 12 for stabilizing polymer.

14. A polymer composition comprising the antioxidant composition according to any of claims 7 to 12.

15. A process of synthesizing the liquid compound of formula (I) according to any of claims 1 to 6, which comprises:

(i) reacting acrylic acid with pentaerythritol to obtain a compound of formula (II)



(ii) reacting the compound of formula (II) with a thiol of formula (III)

R-SH (III)

wherein R is as defined in any of claims 1 to 6.