

DESCRIPTION

TITLE OF THE INVENTION: USE OF AN ANTIOXIDANT TO REDUCE AND/OR PREVENT THE TOXICITY OF A LUBRICATING COMPOSITION

TECHNICAL FIELD

[001] The present invention relates to the field of antioxidant additives used in lubricating compositions. The present invention relates in particular to the use of specific polymeric antioxidants in a lubricating composition in order to reduce and/or prevent its toxicity.

TECHNOLOGICAL BACKGROUND

[002] In a known manner, the lubricating compositions are essentially used to reduce friction between two moving elements (industrial machinery, motor vehicles, etc.). The introduction of a lubricating composition between two parts therefore allows reducing friction and therefore the negative effects resulting therefrom, such as wear, fatigue; corrosion of the parts, breakage, etc. To this end, a lubricating composition is a balanced mixture of a certain number of components generally consisting of a base oil (mineral or synthetic oil) and base additives, such as anti-wear additives, antioxidant additives, etc.

[003] They are thus used in many fields, such as in the automotive industry (for example in order to lubricate combustion engines or gearboxes), in wind power (for gears), in energy production (gas turbines or any other turbines dedicated for the energy production). Also, in the maritime, agricultural or even public works sectors, a significant amount of lubricating compositions are used as engine oil, stern oil, hydraulic fluids.

[004] However, a portion of the lubricating compositions used in the fields mentioned above, such as wind farms, the marine environment, etc., are likely to be dispersed in the environment and are a source of pollution of the seas/oceans, soils, runoff water or even groundwater.

[005] Thus, a lubricating composition must, on the one hand, meet particular technical performances allowing reducing friction between two moving elements, and, on the other hand, take into account new requirements relating to the protection of humans and their environment.

[006] In particular, the antioxidant additives are also used in a large number of applications and everyday objects, and, despite their relatively modest content in the lubricating compositions in which they are incorporated, their contribution is essential with regard to the service life and the conservation of the physicochemical properties of the latter.

[007] To date, two main categories of antioxidants are used: aromatic amines, such as diphenylamine monomers (**DPA**) and phenolic compounds. Unfortunately, recent studies show that the toxicological profile of standard antioxidants, such as those based on aromatic amines, is changing negatively, and this in a drastic and worrying manner in view of the established dangers related to humans and their environment (carcinogenic, mutagenic, or toxic character for reproduction, called "CMR" character, aquatic toxicity/ecotoxic, bioaccumulation, substance classified as Persistent, Bioaccumulative and Toxic, called "PBT"). This trend is accelerating

under the effect of international regulatory agencies pushing for increasingly accurate and intensive characterisation of chemical materials produced in very large volumes. For example, the European Chemicals Agency (ECHA) reports the obvious dangers of the main antioxidants belonging in particular to the family of diphenylamine monomers (DPA) which are massively used in the chemical industry of fluids and lubricants.

[008] In particular, the standard antioxidants and the proven toxicity(ies) thereof are listed in Table 1 below:

[Table 1]

Compound	Name	CAS No.	Toxicity (ECHA Information - 2021)
N,N-diphenylamine monomer mixture	Irganox® L57	CAS 68411-46-1	Is harmful to aquatic life with long-term effects (ecotoxic) https://echa.europa.eu/fr/substance-information/-/substanceinfo/100.063.733 Ongoing study on reprotoxicity (OECD 443)
Bis(nonylphenyl)amine	Irganox® L67	CAS 36878-20-3	Is harmful to aquatic life with long-term effects (ecotoxic) https://echa.europa.eu/fr/substance-information/-/substanceinfo/100.048.393 Assessment in 2021 for suspicion of Mutagenicity and PBT
N-phenyl-1-naphthylamine	PAN-1	CAS 90-30-2	Is very toxic to aquatic life with long-term effects (ecotoxic), is harmful if swallowed (acute toxicity), may cause damage to organs through prolonged or repeated exposure and may further cause an allergic skin reaction https://echa.europa.eu/fr/substance-information/-/substanceinfo/100.001.803
4,4'-methylene-bis-(2,6-di-tert-butylphenol)	Ethanox® 4702 or MEDBP	CAS 118-82-1	Under assessment as an endocrine disruptor and as a persistent, bioaccumulative and toxic substance (PBT substance) https://echa.europa.eu/fr/substance-information/-/substanceinfo/100.003.891

[009] The toxicity potential of certain oxidants has been confirmed in particular by recent scientific researches, such as those of Tian et al. *Science*, **2021**, 371 (6525), 185-189 or even

that of W. Huang et al. *Environ.Sci.Technol.Lett.* **2021**, 8, 381-385, which show that the main antioxidants used to date are toxic to humans and/or the environment.

[010] The publication by Tian et al. focuses on the effect of antioxidants on Pacific coho salmon (*Oncorhynchus kisutch*) (Northwestern USA). The authors found that in this salmon, the exposure to rainwater leads to an acute mortality when adult salmon migrate to urban streams to reproduce under the effect of oxidation products of antioxidants present in tire wear particles.

[011] It is known from the state of the art that the oligomers and/or polymers comprising repeating units of diphenylamine monomers have good antioxidant properties for lubricating oils containing synthetic ester-based lubricants (US 5 489 711, US 2019/127526, US 6 426 324, EP 2 217 687 and US 3 509 214).

[012] However, document WO 2019/126751, published in 2016, teaches that diphenylamine derivatives, thus including oligomers having the diphenylamine repeating units, are toxic (see start page 3).

[013] There is thus a very urgent need in the state of the art to develop alternative antioxidant additives to standard antioxidants such as those mentioned above in order to manufacture lubricant compositions which are in particular more respectful of humans and their environment, especially in the current context in which the current substances are evolving towards CMR classifications according to European regulations (REACH). The recent examples relate to antioxidants well known to lubricant formulators such as Irganox L57 and Ethanox 4702 (or also called 4,4'-Methylene-bis-(2,6-di-tert-butylphenol) (**MEDBP**) (see Table 4, entry 3), both CMR. Other assessments are ongoing under the aegis of ECHA and ANSES, such as that of Irganox L67, which in the long term risks evolving and experiencing the same evolution and the same classification as its counterpart Irganox L57. The person skilled in the art is therefore deprived of satisfactory and safe formulation solutions, that is to say non-toxic, for applications that may be general public (case for example of car engine oils) and environmentally sensitive (lost lubrication, leaks into the environment, water and oceans... manual maintenance of machines and equipment, emanation of vapours or aerosols under the effect of the heat produced within the system...).

[014] There is therefore an urgent and crucial need in the state of the art to develop alternative antioxidant additives for lubricating compositions having both a satisfactory antioxidant effect, while allowing increasing the level of safety (reduction in the danger to humans) and reducing the environmental impact of the lubricating composition in which the antioxidant is incorporated and this, in the targeted fields of application (automotive, industry, wind power, ships, energy production, agricultural and forest environments, 2T engine tools, etc.),

DISCLOSURE OF THE INVENTION

[015] In this context, the Applicant has endeavoured to develop compounds having both antioxidant properties, while allowing prevent and/or reducing the toxicity of a lubricant composition in which they are incorporated, relative to that of standard antioxidants, such as those

mentioned above belonging in particular to the family of diphenylamine (DPA) or phenolic monomers.

[016] As will be illustrated in the experimental part below, it has in particular demonstrated, surprisingly and unexpectedly, that once oligomerised and/or polymerised, the toxicity of diphenylamine monomers is drastically reduced. They thus allow forming oligomers and/or polymers comprising at least one diphenylamine repeating unit having both antioxidant properties, suitable for the various fields of use of lubricating compositions (vehicle engine, wind turbine gears, etc.), while being weakly or not at all toxic to humans and/or the environment. The present invention thus goes against the teaching of document WO 2019/126751 mentioned above which teaches that diphenylamine derivatives, thus including oligomers having the diphenylamine repeating units, are toxic.

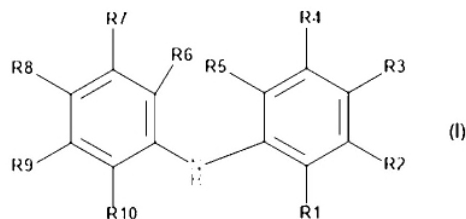
[017] However, the experimental tests below show that the antioxidants according to the invention, which were selected by the Applicant, are not arbitrary and have a different technical effect (namely they allow reducing/preventing/inhibiting the toxicity of a lubricating composition) relative to other antioxidant compounds, in particular relative to diphenylamine (DPA) monomers.

[018] As mentioned above, the antioxidant properties of some of the compounds according to the invention have for example been demonstrated in the prior art, in particular in documents FR 2 924 122, EP 0 734 432 and WO 2009/071857. Although the use of the compounds according to the invention has already been considered in the prior art as antioxidant additives, to the knowledge of the Applicant no study has allowed demonstrating their non-toxicity and consequently their interest in preventing and/or reducing, or even preventing the toxicity of a lubricating composition. The Applicant has indeed demonstrated the absence or the low toxicity of the antioxidant compounds according to the invention whether in terms of neurotoxicity, reprotoxicity, mutagenicity or even carcinogenicity, which reinforces their interest as an alternative to DPA or phenolic monomers as an antioxidant agent in the lubricating compositions.

[019] Furthermore, the Applicant considers that testing the toxicity of the antioxidants is not an obvious measure for the person skilled in the art. This is why it has developed an effective and in-depth methodology according to four models (C: carcinogenic, M: mutagenic, R: reprotoxic and N: neurotoxic) coupled with an in vivo biological measurement in order to indisputably test the toxicity of a compound in a global manner. This methodology has in particular allowed highlighting the greatly reduced toxicity of the oligomers/polymers of diphenylamines according to the invention relative to other usual antioxidant compounds. This invention constitutes a unique solution to date allowing the lubricant formulators to offer high-performance or even very high-performance and sustainable products, that is to say without the risk of seeing their classifications evolve towards CMR or otherwise toxic and/or neurotoxic categories.

SUMMARY OF THE INVENTION

[020] Thus, the present invention relates to the use of use of at least one antioxidant in a lubricating composition, said at least one antioxidant comprising at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of general formula (I):



(I)

wherein each of **R1** to **R10** is independently selected from a hydrogen atom, an alkyl group which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms and an aralkyl group which is an alkyl group as described above of which at least one of the carbon atoms is substituted by a monocyclic or polycyclic aromatic hydrocarbon aryl group comprising 5 to 14 carbon atoms, for reducing and/or preventing the toxicity of said lubricating composition.

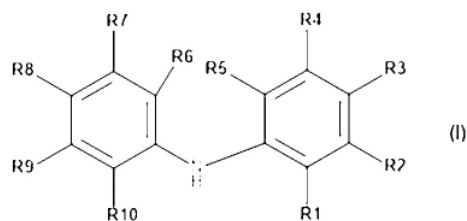
[021] Of course, the different features, variants and embodiments of the invention may be associated with each other according to various combinations to the extent that they are not incompatible or mutually exclusive.

[022] In the present invention, unless otherwise specified, the term “comprising” and the derivatives thereof should be understood as non-limiting and not excluding the presence of other components or steps. In certain particular embodiments, the term “comprising” may be understood as “consisting essentially of” or “consisting of”.

[023] Unless otherwise specified, the intervals mentioned in the present invention are understood to be inclusive.

DETAILED DESCRIPTION

[024] The present invention thus relates to the use of at least one antioxidant in a lubricating composition, said at least one antioxidant comprising at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of general formula (I):



(I)

wherein each of **R1** to **R10** is independently selected from:

a hydrogen atom,

an alkyl group which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms and

an aralkyl group which is an alkyl group as described above of which at least one of the carbon atoms is substituted by a monocyclic or polycyclic aromatic hydrocarbon aryl group comprising 5 to 14 carbon atoms,

for reducing and/or preventing the toxicity of said lubricating composition.

[025] The term “antioxidant” means specialty chemical additives which are used to interrupt the degradation process related to the oxidation in compositions in which they are integrated, in the present case lubricating compositions.

[026] According to the invention, the term “toxicity” of a substance and/or a composition, means that said substance and/or said composition has at least one, preferably at least two, in particular at least three, typically at least four, such as at least four, five, six, or even all of the following toxicities:

- the reprotoxicity which corresponds to the alteration of fertility or alteration of the mammal/living being to be born,
- the mutagenicity which is the propensity of a substance to cause genetic mutations,
- the acute toxicity which is the toxicity induced, in a short period of time (e.g. 24 hours), by the administration or contact (topical application) of a single dose (possibly massive) or of several doses acquired in this period of time of a toxic product or mixture (which is natural or chemical),
- the ecotoxicity which is all imbalances or nuisances caused by an industrial activity or the establishment of a body, of a foreign product in a natural environment generally related to human activity;
- the neurotoxicity which is the capacity of a substance or compound to induce harmful effects in the nervous system of a mammal/living being, such as humans or planarians,
- the carcinogenicity which is the propensity of a substance to cause/provoke the onset of cancer or participate in its aggravation, its onset,
- the toxicity on the synthesis, the degradation, the transport and the mode of action of hormones, as is the case with endocrine disruptors (indirect toxicity via the physiological changes they cause).

[027] A compound having a CMR character (carcinogenic, mutagenic, or toxic character for reproduction) thus has various toxicities.

[028] According to one feature of the invention, the toxicity thus comprises one or more of the following toxicities: neurotoxicity, reprotoxicity, mutagenicity, acute toxicity, carcinogenicity, toxicity on the synthesis, degradation, transport and mode of action of hormones and ecotoxicity.

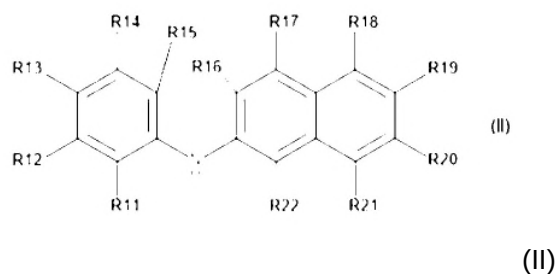
[029] The term “reducing” the toxicity of a lubricating composition means that said at least one antioxidant according to the invention (namely comprising at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of general formula (I)) is capable and/or configured to decrease the toxicity of a lubricating composition in which it is included,

namely by its presence, in particular relative to other possible standard antioxidant compounds which are generally toxic, said at least one oxidant according to the invention comprising at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of general formula (I) allows lowering/reducing the toxicity of a lubricating composition.

[030] The term “Preventing” the toxicity of a lubricating composition means that said at least one oxidant according to the invention comprising at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of general formula (I) allows preventing the lubricating composition from being considered as toxic and/or preventing the appearance of toxic symptoms in a mammal or any other living being, such as a human being or an animal that would be in contact with said lubricating composition. By way of example, neurotoxic symptoms may for example affect the central nervous system (CNS) and have the following effects: headaches, loss of appetite, drowsiness, mood and personality disorders, cognitive impairments (learning and concentration disorders), or affect the peripheral nervous system (PNS) and have the following effects: motor impairments such as weakness, tremors, incoordination, convulsions, etc. or sensory impairments, such as hearing loss, colour vision, tinnitus, loss of balance, etc.; these effects may be reversible or not depending on the degree of acute or chronic exposure of the mammal. For example, symptoms of acute toxicity may be skin irritations, an allergic skin reaction, vomiting, etc.

[031] In general, said at least one antioxidant according to the invention (namely comprising at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of general formula (I)) is capable of and/or configured to reduce and/or prevent the toxicity of a lubricating composition at the different stages of its life, namely its implementation, its use and its end of life.

[032] According to a particular embodiment, said oligomer and/or polymer also comprising at least one diphenylamine repeating unit of general formula (I) may also comprise at least one phenyl α -naphthylamine repeating unit of general formula (II):



wherein each of **R11** to **R22** is independently selected from:

a hydrogen atom and

an alkyl group which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms.

[033] The term “polymer” of at least one diphenylamine and optionally at least one phenyl α -naphthylamine means, in the present invention, a compound comprising the repetition of at least two diphenylamine units with optionally at least one phenyl α -naphthylamine unit.

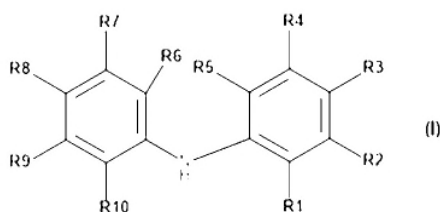
[034] The term “oligomer” of at least one diphenylamine and optionally at least one phenyl α -naphthylamine means, in the present invention, a polymer of at least one diphenylamine and optionally at least one phenyl α -naphthylamine which comprises between 2 and 15 repeating units, or a mixture of such compounds. It may in particular be a dimer, a trimer, a tetramer, a pentamer, a hexamer, a heptamer, an octamer, a nonamer, a decamer and/or any mixture of such compounds. Preferably, the oligomer contains (in relative %) at least 70%, preferably 80% and in particular 90% by mass of dimer, trimer, tetramer, pentamer or a mixture of such compounds.

[035] The term diphenylamine or phenyl α -naphthylamine “repeating unit” means the fact that, in the final structure of the oligomer or the polymer obtained according to the invention, there is at least one diphenylamine unit and at least one phenyl α -naphthylamine unit, or at least two diphenylamine units with optionally at least one phenyl α -naphthylamine unit.

[036] The diphenylamine and phenyl α -naphthylamine repeating units can be positioned in any case relative to each other in the structure of the polymer or oligomer according to the invention. Thus, the polymer or oligomer can comprise, at least over one portion of the structure thereof, a regular alternation of diphenylamine and phenyl α -naphthylamine repeating units. It can comprise, at least over one portion of the structure thereof, a random distribution of the diphenylamine and phenyl α -naphthylamine repeating units. It may finally comprise, over at least one portion of the structure thereof, a block comprising a single type of diphenylamine or phenyl α -naphthylamine repeating unit.

[037] In one embodiment, the polymer and/or oligomer according to the invention comprises in the structure thereof only diphenylamine and phenyl α -naphthylamine repeating units. In another embodiment, the polymer and/or oligomer according to the invention comprises in the structure thereof only diphenylamine repeating units.

[038] The term “diphenylamine” means a compound of formula (I):



(I)

wherein each of **R1** to **R10** is independently selected from: a hydrogen atom and an alkyl group (which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms) and an aralkyl group (which is an alkyl group as described above of which at least one of the carbon atoms is substituted by a monocyclic or polycyclic aromatic hydrocarbon aryl group comprising 5 to 14 carbon atoms).

[039] In one embodiment, the at least one diphenylamine of formula (I) is an alkylated diphenylamine, that is to say that at least one of **R1** to **R10** is an alkyl or aralkyl group. In another

embodiment, at least one of **R1** to **R5** is an alkyl or aralkyl group, and at least one of **R6** to **R10** is an alkyl or aralkyl group.

[040] In general, each of **R1** to **R10** is independently selected from: a hydrogen atom or an alkyl group which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms, preferably comprising from 1 to 15 carbon atoms, in particular 3 to 12 carbon atoms and typically 3 to 10 carbon atoms.

[041] In general, at least one, in particular at least two and typically at least three of **R1** to **R10** is an alkyl group (as defined below), the other substituents being a hydrogen atom. Generally less than nine, particularly less than six and typically less than four of the substituents from **R1** to **R10** is an alkyl group, the other substituents being a hydrogen atom. According to the invention, "at least one" includes the following numbers and all intervals between these values: 1; 2; 3; 4; 5; 6; 7; 8; 9; 10. Also, within the scope of the invention, "less than nine" includes the following numbers and all intervals between these values: 9; 8; 7; 6; 5; 4; 3; 2; 1. By way of example, one or two substituents from **R1** to **R10** is an alkyl group, the other substituents being a hydrogen atom.

[042] The term "alkyl" means in the present invention a linear, branched or cyclic saturated hydrocarbon group, comprising 1 to 24 carbon atoms. Preferably, an alkyl group comprises 1 to 12 carbon atoms. Thus, according to the invention, "an alkyl comprising 1 to 24 carbon atoms" includes the following carbon numbers and all intervals between these values: 1; 2; 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16; 17; 18; 19; 20; 21; 22; 23; 24. From the alkyl groups, there may be mentioned in particular the methyl group, the ethyl group, the n-propyl group, the iso-propyl group, the n-butyl group, the tert-butyl group, the iso-butyl group, the n-pentyl group, the iso-pentyl group, the n-hexyl group, the cyclohexyl group, the n-heptyl group, the n-octyl group, the tert-octyl group, the iso-octyl group, the n-nonyl group, the n-decyl group, the n-undecyl group, the n-dodecyl group and the iso-dodecyl group. In a particular embodiment, an alkyl group is selected from the group consisting of the tert-butyl group and the tert-octyl group, or else the n-nonyl group (nC9), and may be selected for example from the group consisting of the tert-butyl group and the tert-octyl group.

[043] In the present invention, the term "aralkyl" designates an alkyl group in which at least one of the carbon atoms is substituted by an aryl group. Among the examples of aralkyl groups, the 1-methyl-1-phenylethyl group, a styryl ($\text{C}_6\text{H}_5\text{-CH=CH-}$) or methystyryl group can be mentioned in particular.

[044] In the present invention, the term "aryl group" designates a monocyclic or polycyclic aromatic hydrocarbon group. Each aromatic or polyaromatic ring comprises 5 to 14 atoms. Among the examples of aryl groups, the phenyl group can be mentioned in particular.

[045] In one embodiment, the diphenylamine of formula (I) is selected from the group consisting of N,N-diphenylamine, N,N-di-(p-tert-butylphenyl)amine, N,N-di-(p-tert-octylphenyl)amine, N-(p-tert-butylphenyl)-N-phenylamine, N-(p-tert-octylphenyl)-N-phenylamine, N-(p-tert-butylphenyl)-N-(p-tert-octylphenyl)amine, tert-butylated and/or tert-octylated diphenylamines, nonylated diphenylamines, and any mixture thereof.

[046] In a particular embodiment, the polymer or the oligomer according to the present invention comprises only diphenylamine units. The oligomer comprising at least one diphenylamine repeating unit of general formula (I) according to the invention may thus be a dimer, a trimer, a tetramer, a pentamer of one or more of these diphenylamines of formula (I) described above, and is generally a dimer or a trimer. The oligomer may correspond, by way of example, to a dimer or a trimer of di-(p-tert-octylphenyl)amine (**DODPA**), alone or as a mixture.

[047] In particular, when the oligomer comprising at least one diphenylamine repeating unit of general formula (I) according to the invention is a dimer, the latter has at least three, generally at least four substituents from all substituents R1 to R10 of the repeating unit of formula (I) forming the dimer which are not a hydrogen atom (the other substituents are thus hydrogen atoms). According to the invention, "at least three substituents from all substituents R1 to R10 of the repeating unit of formula (I) forming the dimer" comprises the following values: 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16; 17; 18; 19; 20 and can correspond for example to three or four substituents from all substituents R1 to R10 forming the dimer. In general, said at least three substituents are preferably each an alkyl group, i.e.: a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms, preferably comprising 3 to 15 carbon atoms, in particular 5 to 12 carbon atoms and typically 6 to 9 carbon atoms. By way of example, said at least three substituents may be independently of each other a tert-butyl group or a tert-octyl group or even an n-nonyl group. Generally, said at least three substituents are independently distributed over the two diphenylamine repeating units of formula (I) of the dimer. Typically, each repeating unit comprises at least one of said three substituents. By way of example, a repeating unit of the dimer comprises at least one substituent from R1 to R10 which is not a hydrogen atom (and is preferably an alkyl group as defined above) and the other unit of the dimer comprises at least two substituents from R1 to R10 which is not a hydrogen atom (and is preferably an alkyl group as defined above).

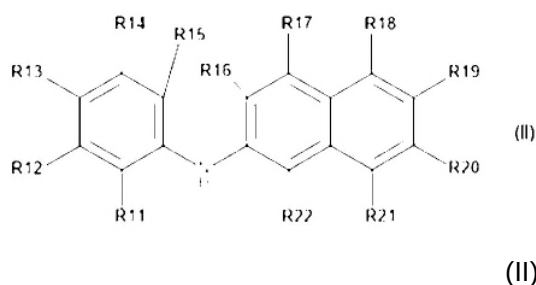
[048] In general, when the oligomer comprising at least one diphenylamine repeating unit of general formula (I) according to the invention is a trimer, the latter has at least one, preferably at least two substituents from all substituents R1 to R10 of the repeating unit of formula (I) forming the trimer, which is not a hydrogen atom (the other substituents are thus hydrogen atoms). According to the invention, "at least one substituent from all substituents R1 to R10 of the repeating unit of formula (I) forming the trimer" comprises the following values: 1, 2, 3; 4; 5; 6; 7; 8; 9; 10; 11; 12; 13; 14; 15; 16; 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30 and may correspond for example to five or six substituents from all substituents R1 to R10 forming the trimer. In particular, said at least one, preferably five, or even six substituents are generally each an alkyl group, i.e.: linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms, preferably comprising 3 to 15 carbon atoms, in particular 5 to 12 carbon atoms and typically 6 to 9 carbon atoms. By way of example, said substituent(s) may be, independently of each other, a tert-butyl group or a tert-octyl group or an n-nonyl group and is typically a tert-octyl group. Generally, said at least one, preferably five, or even six substituents is/are independently distributed over the three diphenylamine repeating units of formula (I) forming the trimer. Typically,

each repeating unit of the trimer comprises at least one or even two substituents from R1 to R10 which is an alkyl group as defined above (the other substituents being hydrogen atoms). Generally, said alkyl substituent(s) are independently distributed over the three diphenylamine repeating units of formula (I) of the trimer. Typically, each repeating unit of the trimer comprises at least one or even two alkyl substituents (the other substituents being hydrogen atoms).

[049] The diphenylamines according to the invention may be isolated, or mixed together. For example, they may be in the form of a mixture of N,N-diphenylamine, N,N-di-(p-tert-butylphenyl)amine, N,N-di-(p-tert-octylphenyl)amine, N-(p-tert-butylphenyl)-N-phenylamine, N-(p-tert-octylphenyl)-N-phenylamine and N-(p-tert-butylphenyl)-N-(p-tert-octylphenyl)amine, tert-butylated and/or tert-octylated diphenylamines, nonylated diphenylamines.

[050] The oligomers and/or polymers comprising at least one diphenylamine repeating unit of general formula (I) may correspond to the compounds exemplified below.

[051] According to the present invention, the phenyl α -naphthylamine designated a compound of formula (II):



wherein each of **R11** to **R22** is independently selected from:

a hydrogen atom and

an alkyl group which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms.

[052] In one embodiment, at least one of **R11** to **R22** is an alkyl group. In one embodiment, only one of **R11** to **R22** is an alkyl group, in particular a tert-octyl group.

[053] In a particular embodiment, phenyl α -naphthylamine is N-(4-tert-octylphenyl)-1-naphthylamine, with CAS number 4572-51-4 (**OPAN**).

[054] In one embodiment of the invention, the at least one diphenylamine is in the form of a mixture of N,N-diphenylamine, N,N-di-(p-tert-butylphenyl)amine, N,N-di-(p-tert-octylphenyl)amine, N-(p-tert-butylphenyl)-N-phenylamine, N-(p-tert-octylphenyl)-N-phenylamine and N-(p-tert-butylphenyl)-N-(p-tert-octylphenyl)amine, and the at least one phenyl α -naphthylamine is N-(4-tert-octylphenyl)-1-naphthylamine (**OPAN**).

[055] In another embodiment of the invention, the at least one diphenylamine is di-(p-tert-octylphenyl)amine (**DODPA**) and the at least one phenyl α -naphthylamine is N-phenyl 1,1,3,3-tetramethylbutyl-naphthalen 1-amine (**OPAN**). The oligomer forming the antioxidant according to the invention can thus correspond to a **2DODPA/1OPAN**, **1DODPA/2OPAN**, **3DODPA** trimer. According to one embodiment, said at least one oligomer can correspond to a

mixture of trimers, such as a mixture of **2DODPA/1OPAN**, **1DODPA/2OPAN** and **3DODPA**. In particular, within this mixture, the **2DODPA/1OPAN** oligomer constitutes the major part. In general, said at least one oligomer comprises a mixture of trimers (such as **2DODPA/1OPAN**, **1DODPA/2OPAN**, **3DODPA**), tetramers, pentamers and hexamers.

[056] The relative proportions by mass of the two types of diphenylamine and phenyl α -naphthylamine units within the polymer or oligomer can vary to a large extent from 0/100 to 100/0. Preferably, the relative proportion by mass of diphenylamine/phenyl α -naphthylamine is comprised between 100/0 and 10/90, in particular comprised between 100/0 and 30/70 (such as 50/50 or 80/20), in particular comprised between 100/0 and 90/10 and typically comprised between 100/0 and 95/5.

[057] The polymer or oligomer according to the present invention forming said at least one antioxidant according to the invention can in particular be prepared according to the method described in the patent application FR 2010199 filed by the Applicant company, namely in a continuous reactor. The person skilled in the art is able to adjust the amounts of diphenylamine and phenyl α -naphthylamine to be introduced into the reactor depending in particular on the desired structure of the oligomer or polymer to be synthesised and the desired thermal characteristics. The polymer or oligomer according to the present invention forming said at least one antioxidant according to the invention can in particular also be prepared according to the method described in document WO 2008/022028.

[058] For the present invention, the Applicant has demonstrated the non-toxicity of said at least one antioxidant comprising at least one oligomer and/or one polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) according to the invention by QSAR modelling tests for neurotoxicity, for reprotoxicity, for mutagenicity and carcinogenicity.

[059] In particular, the oligomer and/or polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) has a QSAR value for measuring each of the following toxicities: neurotoxicity (neurotoxic QSAR), reprotoxicity (reprotoxic QSAR), mutagenicity (mutagenic QSAR) and carcinogenicity (carcinogenic QSAR), corresponding to a statistical threshold value (%) subtracted from a delta of at least 30%, said statistical threshold value being determined, for each of said toxicities, by QSAR (Quantitative Structure-Activity Relationship) modelling (quantitative structure-activity relationship) according to the method described below in the experimental part.

[060] According to the invention, "a delta of at least 30%" for QSAR modelling includes the following values and all intervals between these values: 30; 31; 32; 33; 34; 35; 36; 37; 38; 39; 40; 41; 42; 43; 44; 45; 46; 47; 48; 49; 50; 51; 52; 55; 60; 65; 70; 75; 80; 85; 90; 91; 92; 93; 94; 95; 96; 97; 98; 99; 100 (this range of at least 30% is to be adapted for each of the toxicities).

[061] According to one embodiment, the statistical threshold value (neurotoxic QSAR) in percentage is typically 55%.

[062] Preferably, the delta for the measurement of the neurotoxic QSAR is at least 45%, advantageously at least 55% and typically at least 53%.

[063] In general, the oligomer and/or the polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) has a percentage (%) value by QSAR modelling which is less than or equal to 10%, preferably less than or equal to 5% and typically less than or equal to 2% for the measurement of neurotoxicity (neurotoxic QSAR).

[064] According to the invention, a value which is less than or equal to 10% for the neurotoxic QSAR modelling includes the following values and all intervals between these values: 10; 9; 8; 7; 6; 5; 4; 3; 2; 1; 0.9; 0.8; 0.70; 0.69; 0.68; 0.67; 0.66; 0.65; 0.64; 0.63; 0.62; 0.61; 0.60; 0.59; 0.58; 0.57; 0.56; 0.55; 0.54; 0.53; 0.52; 0.51; 0.50; 0.49; 0.48; 0.47; 0.46; 0.45; 0.44; 0.42; 0.40; 0.38; 0.36; 0.34; 0.32; 0.30; 0.28; 0.26; 0.24; 0.22; 0.20; 0.18; 0.16; 0.14; 0.12; 0.10; 0.09; 0.08; 0.07; 0.06; 0.005; 0.04; 0.03; 0.02; 0.01; 0.00.

[065] According to another embodiment, the statistical threshold value (reprotoxic QSAR) in percentage is typically 90%.

[066] Preferably, the delta for the measurement of the reprotoxic QSAR is at least 41%, advantageously at least 43% and typically at least 46%.

[067] In general, the oligomer and/or polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) has a percentage (%) value by QSAR modelling which is less than or equal to 65%, preferably less than or equal to 50% and typically less than or equal to 45% for the measurement of reprotoxicity (reprotoxic QSAR).

[068] According to the invention, a value which is less than or equal to 65% for the reprotoxic QSAR modelling includes the following values and all intervals between these values: 65; 64; 63; 62; 61; 60; 59; 58; 57; 56; 55; 54; 53; 52; 51; 50; 49; 48; 47; 46; 45; 44; 43; 42; 41; 40; 39; 38; 37; 36; 35; 34; 33; 32; 31; 30; 29; 28; 27; 26; 25; 24; 23; 22; 21; 20; 15; 10; 5; 3; 1; 0.50; ; 0.49; 0.48; 0.47; 0.46; 0.45; 0.44; 0.42; 0.40; 0.38; 0.36; 0.34; 0.32; 0.30; 0.28; 0.26; 0.24; 0.22; 0.20; 0.18; 0.16; 0.14; 0.12; 0.10; 0.09; 0.08; 0.07; 0.06; 0.005; 0.04; 0.03; 0.02; 0.01; 0.00.

[069] According to another embodiment, the statistical threshold value (mutagenic QSAR) in percentage is typically 58%.

[070] Preferably, the delta for the measurement of the mutagenic QSAR is at least 48%, advantageously at least 53% and typically at least 56%.

[071] Generally, the oligomer and/or the polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) has a percentage (%) value by QSAR modelling which is less than or equal to 10%, preferably less than or equal to 5% and typically less than or equal to 2% for the measurement of mutagenicity (mutagenic QSAR).

[072] According to the invention, a value which is less than or equal to 10% for the mutagenic QSAR modelling includes the following values and all intervals between these values: 10; 9; 8; 7; 6; 5; 4; 3; 2; 1; 0.9; 0.8; 0.70; 0.69; 0.68; 0.67; 0.66; 0.65; 0.64; 0.63; 0.62; 0.61; 0.60; 0.59; 0.58; 0.57; 0.56; 0.55; 0.54; 0.53; 0.52; 0.51; 0.50; 0.49; 0.48; 0.47; 0.46; 0.45; 0.44; 0.42;

0.40; 0.38; 0.36; 0.34; 0.32; 0.30; 0.28; 0.26; 0.24; 0.22; 0.20; 0.18; 0.16; 0.14; 0.12; 0.10; 0.09; 0.08; 0.07; 0.06; 0.005; 0.04; 0.03; 0.02; 0.01; 0.00.

[073] According to another embodiment, the statistical threshold value (carcinogenic QSAR) in percentage is typically 85%.

[074] Preferably, the delta for the measurement of the carcinogenic QSAR is at least 77%, advantageously at least 82% and typically at least 85%.

[075] In general, the oligomer and/or polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) has a percentage (%) value by QSAR modelling which is less than or equal to 10%, preferably less than or equal to 5% and typically less than or equal to 2% for the measurement of the carcinogenic character (carcinogenic QSAR).

[076] According to the invention, a value which is less than or equal to 10% for the carcinogenic QSAR modelling includes the following values and all intervals between these values: 10; 9; 8; 7; 6; 5; 4; 3; 2; 1; 0.9; 0.8; 0.70; 0.69; 0.68; 0.67; 0.66; 0.65; 0.64; 0.63; 0.62; 0.61; 0.60; 0.59; 0.58; 0.57; 0.56; 0.55; 0.54; 0.53; 0.52; 0.51; 0.50; 0.49; 0.48; 0.47; 0.46; 0.45; 0.44; 0.42; 0.40; 0.38; 0.36; 0.34; 0.32; 0.30; 0.28; 0.26; 0.24; 0.22; 0.20; 0.18; 0.16; 0.14; 0.12; 0.10; 0.09; 0.08; 0.07; 0.06; 0.005; 0.04; 0.03; 0.02; 0.01; 0.00.

[077] The term "lubricating composition" designates a composition capable of reducing friction, and where appropriate heating, between two parts during the operation phase, but also during machining.

[078] In general, the lubricating composition according to the invention comprises a lubricating base and at least one additive including at least the antioxidant according to the invention as described above.

[079] Preferably, the lubricating base is well known to the person skilled in the art and may comprise at least one mineral base oil and/or one synthetic base oil.

[080] A mineral base oil may be a paraffinic or naphthenic base oil.

[081] A synthetic base oil may correspond to an oil based on synthetic esters, polyalphaolefins (PAO), or Poly alkyl glycol (PAG (PAG)).

[082] For example, the base oil based on synthetic esters may be produced from mono-hydroxylated alcohols and mono-carboxylic acids, or from mono-hydroxylated alcohols and dicarboxylic acids. Such esters are well known to the person skilled in the art. They are described for example in US Patent No. US 3,432,433. The alcohols and acids which are used to prepare the esters may contain one to six functional groups, which allows the production of mono-, di-, tri- and tetra-, penta- and hexa-esters. Included are esters of alcohols, diols, triols and pentaerythritols, said alcohols or polyols having from 2 to 20 carbon atoms, and mono- and dicarboxylic acids having 2 to 20 carbon atoms, preferably 4 to 12 carbon atoms. Polyols include trimethylolpropane, pentaerythritol, dipentaerythritol, neopentyl glycol, tripentaerythritol, di-TMP and mixtures thereof.

[083] The esters which are likely be contained in a lubricating composition according to the invention include monoesters originating from the reaction of linear or branched

monocarboxylic acids with a chain length of 2 to 24 carbons, such as, for example, monoesters of octyl acetate, decyl acetate, octadecyl acetate, ethyl-2-hexyl caprylate/caproate, methyl myristate, butyl stearate, methyl oleate, as well as polyesters of dibutyl phthalate, dioctyl adipate, di-2-ethylhexyl azelate and ethylhexyl sebacate, polyesters, reaction of polyols with linear and/or branched monocarboxylic acids of 2 to 24 carbons and polycarboxylic acids of 2 to 40 carbons or polyesters, reaction of polycarboxylic acids of 2 to 40 carbons with monoalcohols of 1 to 24 carbons and polyols. The polyol ester type base oil may be an oil prepared from dipentaerythritol or technical pentaerythritol or trimethylol propane and a mixture of linear and/or branched carboxylic acids having 4 to 24 carbon atoms. Technical pentaerythritol is a mixture which comprises about 85% to 92% by weight of monopentaerythritol and 8% to 15% by weight of dipentaerythritol. A conventional commercial technical pentaerythritol contains about 88% by weight of monopentaerythritol and about 12% by weight of dipentaerythritol, relative to the total weight of said ester type base oil. Technical pentaerythritol may also contain a certain amount of tri- and tetra-pentaerythritol which are usually formed as by-products during the production of technical pentaerythritol.

[084] The lubricating composition generally comprises other additives, other than said at least one antioxidant according to the invention.

[085] These other additives may be selected from detergent agents, dispersing agents, anti-foaming agents, anti-corrosion agents, anti-wear agents, additives suitable for extreme pressures, stabilising agents against hydrolysis, friction modifiers or else viscosity modifying agents. Such additives are well known to the person skilled in the art and commonly commercially available.

[086] Generally, said lubricating composition and/or said at least one antioxidant additive does not substantially comprise, preferably does not comprise, diphenylamine (DPA) monomers, phenolic monomers and/or any other standard (toxic and/or ecotoxic) antioxidant such as those mentioned above in the description of the prior art. In certain embodiments, the lubricating composition used according to the invention or the antioxidant agent used according to the invention does not substantially comprise, preferably does not comprise, any antioxidant additive other than the oligomer and/or the polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) according to the invention.

[087] In general, the antioxidant additive according to the invention represents, by mass, relative to the total mass of the antioxidant agents present in the lubricating composition, 50% to 100%, preferably 80% to 100%, and in particular 90% to 100% and typically 100%. According to the invention, the term "50% to 100%" means the following values or any interval between these values: 50; 55; 60; 65; 70; 75; 80; 85; 90; 95; 100.

[088] Said at least one antioxidant agent and generally said at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) is present in the lubricating composition used in the present invention in an amount such as those conventionally used in the art. For

example, they may be used in an amount of 0.1 to 10% by weight, preferably 0.5 to 5% by weight, typically 1 to 4% relative to the total weight of said lubricating composition.

[089] According to the invention, the term “0.1% to 10%” meant the following values or any interval comprised between these values: 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7; 0.8; 0.9; 1; 1.5; 2; 2.5; 3; 3.5; 4; 4.5; 5; 5.5; 6; 6.5; 7; 7.5; 8; 8.5; 9; 9.5; 10.

[090] By way of example, the lubricating composition according to the invention comprises, by mass, relative to the total mass thereof:

- at least 90% (a) of said lubricating base;
- 1 to 5% of at least one antioxidant comprising at least said at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II);
- 1 to 5% of at least one anti-wear agent;
- 0 to 3% of pour point improvement additive and
- 0.01 to 0.3% of at least one metal corrosion inhibitor.

[091] The present invention can also be applied to a method for preserving the physicochemical and mechanical properties of a lubricating composition comprising:

- preparing said lubricating composition, which preferably does not comprise diphenylamine monomers (**DPA**) or phenolic monomers,
- incorporating into said lubricating composition an effective amount of at least one antioxidant comprising an oligomer and/or polymer comprising at least one diphenylamine repeating unit of formula (I) as defined above and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) as defined above,

said at least one antioxidant being capable of reducing and/or preventing the toxicity of said lubricating composition.

[092] According to the invention, unless otherwise specified, the percentages indicated in the present application are percentages by mass.

[093] In the present invention, the term “about” a V value designates an interval comprised between 0.9xV and 1.1xV. In certain embodiments, it designates an interval comprised between 0.95xV and 1.05xV, in particular an interval comprised between 0.99xV and 1.01xV.

EXAMPLES

Example 1: QSAR toxicity study

[094] The oligomers and/or polymers comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) according to the invention were studied and compared to other standard antioxidant compounds, in terms of QSAR modelling for neurotoxicity, reprotoxicity, mutagenicity and carcinogenicity.

QSAR modeling protocol

[095] The degrees of toxicity of different compounds used according to the invention and other standard antioxidants were assessed by QSAR (quantitative structure-activity relationship) modelling.

Selection of training and validation sets

[096] A set of test molecules was defined with chemical structures compiled from several publicly available sources such as: HSBD (Hazardous Substances Data Bank), EPA (U.S. Environmental Protection Agency), ECHA (European Chemicals Agency) and NTP (National Toxicology Program). About 34,000 molecules were selected for this project, including: 3,245 compounds classified as neurotoxic compounds, 12,609 compounds classified as reprotoxic compounds, 4,084 compounds classified as mutagenic compounds, 12,158 compounds classified as carcinogenic compounds and 1,953 compounds, called non-toxic compounds, classified as neither neurotoxic, nor reprotoxic, nor mutagenic, nor carcinogenic.

[097] From this set of test molecules, two sets of molecules were defined: a training set and a validation set. To do this, the “leave one out” method was used. The set of test molecules was divided into two sets, one containing 90% of the test molecules and forming the training set; and the other, containing the remaining 10% of the test molecules, and forming the validation set.

QSAR model performance

[098] A generalised linear model (GLM) method was chosen to carry out a quantitative structure-activity relationship (QSAR) approach. From the training set, GLM models were trained separately to discriminate chemical structures between (i) neurotoxic and non-neurotoxic compounds, (ii) between reprotoxic and non-reprotoxic compounds, (iii) between mutagenic and non-mutagenic compounds, and (iv) between carcinogenic and non-carcinogenic compounds. This approach resulted in four GLM models with **respectively 328, 313, 327, and 330** significant descriptors within the neurotoxic, reprotoxic, mutagenic, and carcinogenic training sets. During training, the performance of the QSAR models was measured by ROC (Receiver Operator Characteristic) curves and resulted in area under the curve (AUC) values of **0.8831** for the prediction of neurotoxicity, **0.7967** for the prediction of reprotoxicity, **0.8444** for the prediction of mutagenicity, and **0.8333** for the prediction of carcinogenicity.

[099] In order to validate the robustness of the QSAR models, they were then used to predict (i) the neurotoxicity categories of the compounds in the validation set (that is to say the neurotoxic/non-neurotoxic categorisation), (ii) the reprotoxicity categories of the compounds in the validation set (i.e., reprotoxic/non-reprotoxic categorisation), (iii) the mutagenicity categories of the compounds in the validation set (that is to say the mutagenic and non-mutagenic categorisation), and (iv) the carcinogenicity categories of the compounds in the validation set (that is to say the carcinogenic and non-carcinogenic categorisation). During validation, the performance of the QSAR models was measured by area under the curve (AUC) values and has provided significant values of **0.76** and above for the prediction of neurotoxicity, mutagenicity and carcinogenicity and has provided significant values of **0.70** and above for the prediction of reprotoxicity.

[0100] The GLM-based QSAR models were then used to study the compounds according to the invention.

Interpretation of the results

[0101] Once the model is built on the training set, then validated with the validation set, it mathematically determines, on a statistical basis, a statistical threshold value in percentage.

[0102] The statistical QSAR threshold values for the different tested toxicities are illustrated in Table 2 below:

[Table 2]

	Non-toxic and moderately toxic molecules (%)	Toxic molecules (%)
Neurotoxic QSAR	< 55%	≥ 55 %
Reprotoxic QSAR	< 90%	≥ 90 %
Mutagenic QSAR	< 58 %	≥ 58 %
Carcinogenic QSAR	< 85 %	≥ 85 %

[0103] This statistical threshold is a first draft allowing distinguishing non-toxic, moderately toxic and toxic molecules. However, it does not allow the total exclusion of toxic molecules from non-toxic molecules (margin of error on the probability of the risk of toxicity). The Applicant has thus refined its research and determined that a reduction in the statistical threshold of a delta of 30% for each model (neurotoxic QSAR, reprotoxic QSAR, etc.) allowed reliably guaranteeing the toxicity or not of the tested molecules. Indeed, this new threshold (statistical threshold -30%), allows indisputably excluding moderately toxic and toxic residual molecules from non-toxic molecules. Also, an intermediate fringe (non-zero probability of toxicity) including moderately toxic and/or toxic residual molecules was established in order to establish a more accurate classification.

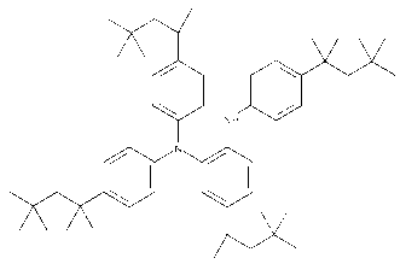
[0104] The classification refined by the Applicant is illustrated in Table 3 below.

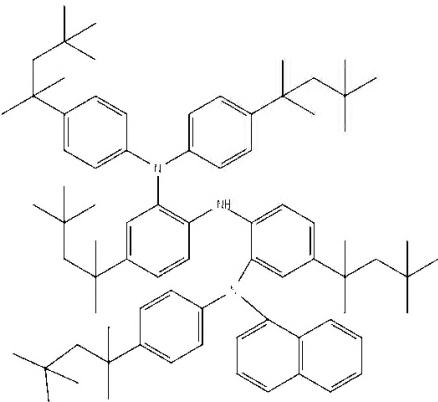
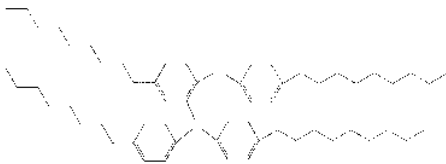
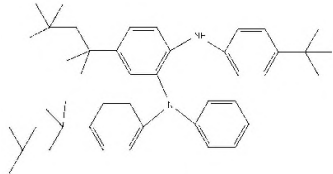
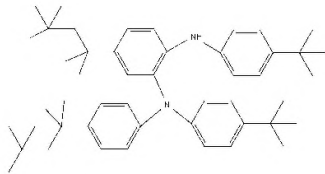
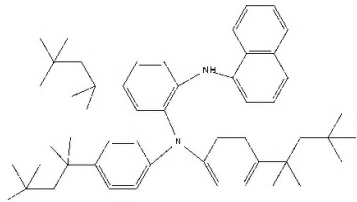
[Table 3]

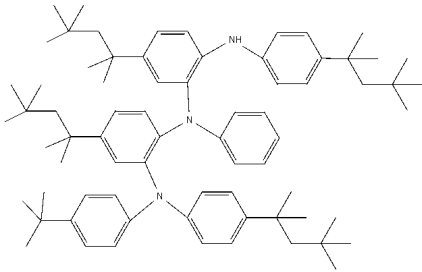
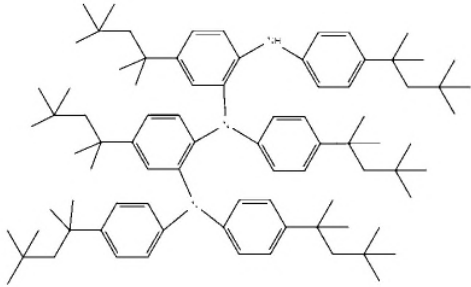
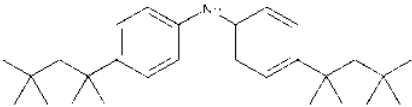
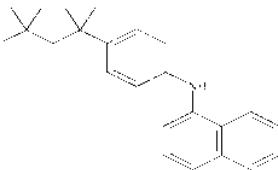
	Low toxicity (%)	Moderately toxic (intermediate fringe) (%)	Highly Toxic (%)
Neurotoxic QSAR	< 25	25 ≤ QSAR < 55	55 ≤ QSAR ≤ 100
Reprotoxic QSAR	< 60	60 ≤ QSAR < 90	90 ≤ QSAR ≤ 100
Mutagenic QSAR	< 28	28 ≤ QSAR < 58	58 ≤ QSAR ≤ 100
Carcinogenic QSAR	< 55	55 ≤ QSAR < 85	85 ≤ QSAR ≤ 100

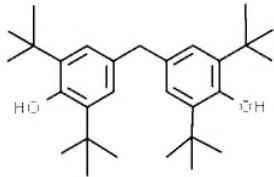
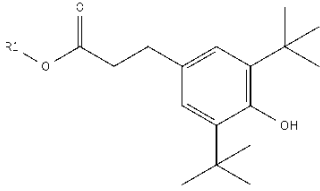
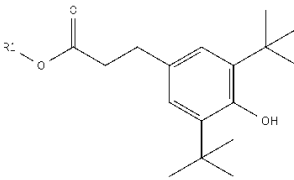
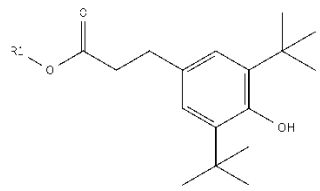
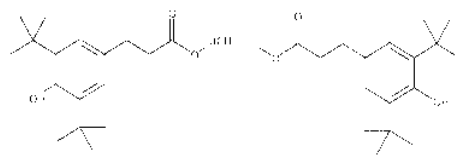
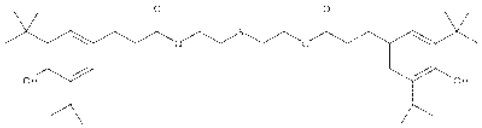
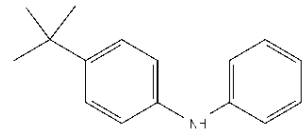
[0105] The tested compounds are numbered as follows (Table 4 below):

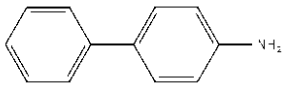
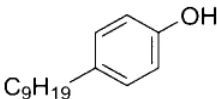
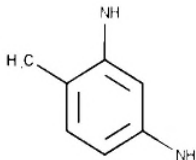
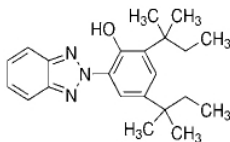
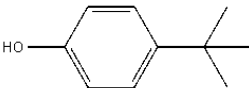
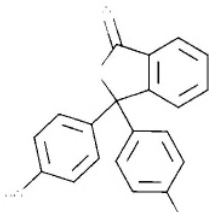
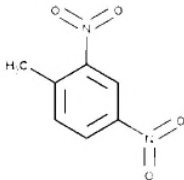
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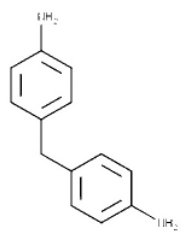
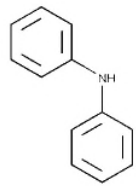
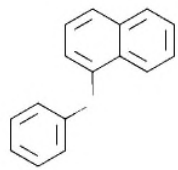
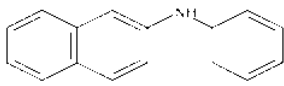
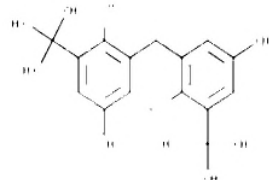
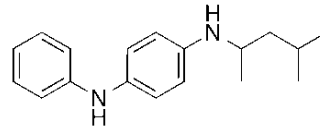
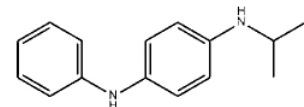
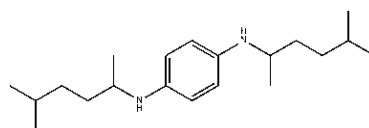
Ex.	Chemical name	CAS No.	Developed formula
A	p,p'-Diocylldiphenylamine dimer or DODPA dimer	35972-72-6	

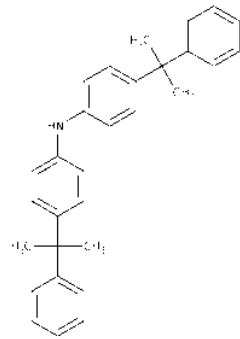
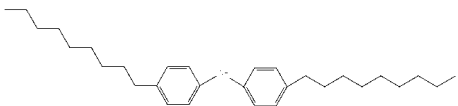
Ex.	Chemical name	CAS No.	Developed formula
B	Trimer: 2DODPA / 1 OPAN	-	
C	4-Nonyl-n-(4-nonylphenyl)aniline dimer or [di(nC9)DPA] ₂	-	
D	(H,isoC8 DPA)(isoC4,isoC8 DPA)	-	
E	(isoC4,isoC8 DPA) ₂	-	
F	(DODPA)(OPAN)	-	

Ex.	Chemical name	CAS No.	Developed formula
G	(H,isoC8 DPA)(isoC4,isoC8 DPA)(di-isoC8 DPA)	-	
H	(DODPA) ₃	-	
1	p,p'-dioctyldiphenylamine (DODPA)	15721-78-5	
2	N-(4-tert-octylphenyl)-1-naphthylamine (OPAN)	4572-51-4	

Ex.	Chemical name	CAS No.	Developed formula
3	4,4'-Methylene-bis-(2,6-di-tert-butylphenol) (MEDBP)	118-82-1	
4	Octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate Irganox® L107	2082-79-3	 R1 = nC ₁₈ H ₃₇
5	Octyl 3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)phenyl]propanoate	125643-61-0	 R1 = nC ₈ H ₁₇
6	2-ethylhexyl 3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)phenyl]propanoate Irganox® L145	144429-84-5	 R1 = 2Ethylhexyl
7	1,6-Hexanediyl bis{3-[4-hydroxy-3,5-bis(2-methyl-2-propanyl)phenyl]propanoate} Irganox® L109	35074-77-2	
8	2-[(2-[[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoyl]oxy]ethyl)sulfanyl]ethyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propanoate Irganox® L115	41484-35-9	
9	4-tert-butyl diphenylamine as a component of Irganox® L57 (68411-46-1)	4496-49-5	

Ex.	Chemical name	CAS No.	Developed formula
10	Biphenyl-4-ylamine	92-67-1	
11	Nonylphenol	25154-52-3	mixture of positional isomers 
12	4-methylbenzene-1,3-diamine	95-80-7	
13	2-(2H-benzotriazol-2-yl)-4,6-ditertpentylphenol	25973-55-1	
14	4-tert-butylphenol	98-54-4	
15	3,3-bis(4-hydroxyphenyl)-1,3-dihydro-2-benzofuran-1-one	77-09-8	
16	2,4-dinitrotoluene	121-14-2	

Ex.	Chemical name	CAS No.	Developed formula
17	4-[(4-aminophenyl)methyl]aniline (MDA)	101-77-9	
18	N-phenylaniline ("Diphenylamine" DPA)	122-39-4	
19	N-phenylnaphthalene-1-amine (PAN (alpha))	90-30-2	
20	N-phenylnaphthalene-2-amine (PAN (beta))	135-88-6	
21	2-tert-butyl-6-[(3-tert-butyl-2-hydroxy-5-methylphenyl)methyl]-4-methylphenol	119-47-1	
22	N-(1,3-Dimethylbutyl)-N'-phenyl-p-phenylenediamine (6PPD)	793-24-8	
23	N-Isopropyl-N'-phenyl-p-phenylenediamine (IPPD)	101-72-4	
24	N,N'-Bis(1,4-dimethylpentyl)-P-phenylenediamine (77PD)	3081-14-9	

Ex.	Chemical name	CAS No.	Developed formula
25	Bis[4-(2-phenyl-2-propyl)phenyl]amine (NAUGARD® 445)	10081-67-1	
26	4-Nonyl-n-(4-nonylphenyl)aniline	24925-59-5	

[0106] Thus, the examples named **A to H** are according to the invention and the examples named **1 to 26** are comparative examples (standard antioxidants and anti-ozonants).

[0107] The results of the QSAR modelling are illustrated in Table 5 below:

[Table 5]

Ex.	Carcinogenic QSAR	Mutagenic QSAR	Reprotoxic QSAR	Neurotoxic QSAR
A	0.0	0.0	32.4	0.5
B	0.4	0.1	44.6	0.0
C	0.2	0.0	6.9	0.2
D	11.7	0.0	53.6	0.0
E	4.0	0.0	32.7	0.0
F	6.6	0.0	37.5	0.0
G	0.1	0.0	1.3	0.0
H	0.2	0.0	0.0	NA
1	64.1	8.0	60.0	0.4
2	86.0	31.6	83.5	6.0
3	72.9	0.2	60.0	2.4
4	84.2	3.1	74.9	0.5
5	83.3	5.5	76.4	2.9
6	85.6	3.5	76.7	5.4
7	74.7	0.3	67.3	0.0
8	69.5	0.3	76.4	0.0
9	78.0	19.4	84.1	30.0
10	93.1	84.7	94.0	83.3

Ex.	Carcinogenic QSAR	Mutagenic QSAR	Reprotoxic QSAR	Neurotoxic QSAR
11	91.8	28.5	93.2	37.2
12	99.6	96.7	99.4	93.0
13	96.0	40.1	85.9	8.1
14	95.5	71.4	89.0	73.2
15	86.2	13.9	83.3	3.3
16	99.1	93.6	94.0	43.9
17	98.7	93.5	98.5	70.1
18	95.5	79.7	95.5	95.7
19	92.4	73.3	88.1	70.8
20	90.6	78.2	88.5	59.9
21	85.8	5.0	76.4	9.1
22	77.3	21.1	78.8	8.8
23	87.3	40.4	88.2	11.2
24	90.2	38.2	91.0	17.2
25	63.6	55.6	83.5	11.0
26	34.8	4.1	72.8	8.7

[0108] As shown in Table 5 above, the antioxidants comprising an oligomer and/or polymer comprising at least one diphenylamine repeating unit and optionally at least one phenyl α -naphthylamine repeating unit according to the invention have both very low neurotoxicity, reprotoxicity, mutagenicity, and low carcinogenicity. On the contrary, the compounds composing the standard anti-ozonant antioxidants are generally highly toxic, whether in terms of neurotoxicity, reprotoxicity, mutagenicity and/or carcinogenicity. For example, 4-tert-butyl diphenylamine (component of Irganox® L57, line 9 of the table) is assessed as particularly carcinogenic, neurotoxic and reprotoxic and thus confirms the importance of the ongoing assessment on the reprotoxicity (OECD 443) of this molecule commissioned by the ECHA. It consequently appears essential to replace it with a weakly, or even non-toxic compound such as proposed by the invention. By way of additional examples, alpha and beta PANs (examples 19 and 20) both have on the 4 QSAR models (C, M, R and N) very high levels of probability relative to the toxicity, which consequently make them potentially particularly compounds of concern.

[0109] This QSAR modelling test therefore demonstrates that the oligomers and/or polymers comprising at least one diphenylamine repeating unit and optionally at least one phenyl α -naphthylamine repeating unit according to the invention allow preventing and/or reducing the toxicity of a rubber-based composition.

Example 2: Protocol for assessing the toxicity by in vivo tests on non-vertebrate organisms

[0110] In order to complement the QSAR modelling tests, the Applicant has conducted *in vivo* tests on models called planarians, invertebrate microorganisms living in water having a cephalic sphere and an apparent neuronal system, used in the literature to assess the neurotoxicity, neurodevelopment and reprotoxicity of compounds of concern such as pesticides

and other toxic organophosphorus compounds (Poirier et al. Médecine/Sciences (Paris) 2019; 35 (6-7):544-8 “La planaire, un modèle animal original pour la toxicologie”; D. Hagstrom et al. Archives of toxicology, 2017 91(8), 2837–2847; Zhang et al. TOXICOLOGICAL SCIENCES, 2018, 1–19; Ireland et al. Chemosphere, 2020, 253, 126718).

[0111] The tests are performed under conditions close to those reported in the mentioned publication (Zhang et al. TOXICOLOGICAL SCIENCES, 2018, 1–19).

[0112] The used operating conditions are as follows:

- Number of test concentrations per chemical: 5
- Concentration ranges: 0.22 mg/L - 22 mg/L in semi-logarithmic increments
- Studied organism: Whole adult planarians
- Test duration: 12 days with an assessment of the control points at 7 and 12 days
- Control points: lethality, adherence (production of sticky mucus by the skin leading the planarian to be stuck to a wall rather than floating), movement speed, rest (pro rata of resting time relative to time spent moving), phototaxis and “scrunching” (specific mode of movement nominally used by the planarian in case of danger, here excessive heat).

- Number of replicates: 3

[0113] The methodology used is as follows

All compounds are supplied in powder form. An appropriate volume of 100% DMSO (Sigma) was added, as indicated on the tubes, to obtain a stock solution at 4.4 mg/ml (i.e. 200 times more concentrated than the maximum test concentration).

Each replicate was prepared using a 48-well multi-screen culture tray following the same procedure as described in Zhang et al., Neurotoxicology and Teratology, 2019.

[Table 6]

Ex.	Concentration from which behavioral disorders potentially related to cognitive disorders of the planarian are observed**	Concentration from which a significant planarian mortality is observed according to Zhang et al., Neurotoxicology and Teratology, 2019
A + B*	> 22 mg/L	> 22 mg/L
19	2,2 -3.9 mg/L	6.9 mg/L
22	1.5 mg/L	4.8 mg/L

*Oligomers containing mainly A and B: amino oligomeric mixture based on **DODPA** and **OPAN** (i.e.: including 0-5% monomers, 25-30% A dimers, 20-25% B trimers, 15-20% tetramers) obtained according to the method described in patent applications FR 2 924 122.

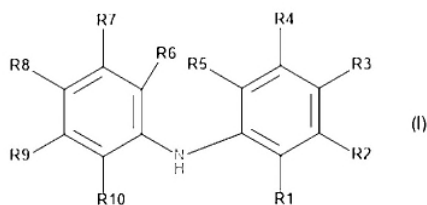
** Recorded behavioural disorders: adhesion (production of sticky mucus by the skin leading the planarian to be stuck to a wall rather than floating), movement speed, rest (pro rata of resting time relative to time spent moving), phototaxis and “scrunching” (specific mode of movement nominally used by the planarian in case of danger, here excessive heat).

[0114] This test shows that the antioxidants according to the invention (mixture of the compounds A and B) have a low toxicity in vivo, in particular in comparison with the comparative antioxidants PAN alpha and 6PPD.

[0115] Of course, various other modifications can be made to the invention within the scope of the appended claims.

CLAIMS

1. A use of at least one antioxidant in a lubricating composition, said at least one antioxidant comprising at least one oligomer and/or polymer comprising at least one diphenylamine repeating unit of general formula (I)



(I)

wherein each of **R1** to **R10** is independently selected from
a hydrogen atom,

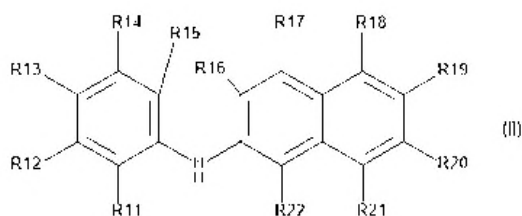
an alkyl group which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms and

an aralkyl group which is an alkyl group as described above of which at least one of the carbon atoms is substituted by a monocyclic or polycyclic aromatic hydrocarbon aryl group comprising 5 to 14 carbon atoms,

for reducing and/or preventing the toxicity of said lubricating composition.

2. The use according to claim 1, wherein the toxicity comprises one or more of the following toxicities: neurotoxicity, reprotoxicity, mutagenicity, acute toxicity, carcinogenicity, toxicity on the synthesis, degradation, transport and mode of action of hormones and ecotoxicity.

3. The use according to claim 1 or 2, wherein said oligomer and/or polymer also comprises at least one phenyl α -naphthylamine repeating unit of general formula (II):



(II)

wherein each of **R11** to **R22** is independently selected from a hydrogen atom and an alkyl group which is a linear or branched saturated hydrocarbon group comprising 1 to 24 carbon atoms.

4. The use according to any one of the preceding claims, wherein the at least one diphenylamine of formula (I) is an alkylated diphenylamine wherein at least one, preferably two, of **R1** to **R10** is an alkyl or aralkyl group, such as a tert-butyl group or a tert-octyl group or else an n-nonyl group.

5. The use according to any one of the preceding claims 1 to 4, wherein the at least one diphenylamine of formula (I) is an alkylated diphenylamine wherein at least one, preferably two, of **R1** to **R5** is an alkyl or aralkyl group, such as a tert-butyl group or a tert-octyl group and at least one, preferably two, of **R6** to **R10** is an alkyl or aralkyl group, such as a tert-butyl group or a tert-octyl group.

6. The use according to any one of the preceding claims, wherein the diphenylamine of formula (I) is selected from the group consisting of N,N-diphenylamine, N,N-di-(p-tert-butylphenyl)amine, N,N-di-(p-tert-octylphenyl)amine, N-(p-tert-butylphenyl)-N-phenylamine, N-(p-tert-octylphenyl)-N-phenylamine, N-(p-tert-butylphenyl)-N-(p-tert-octylphenyl)amine, tert-butylated and/or tert-octylated diphenylamines, nonylated diphenylamines, and any mixture thereof.

7. The use according to any one of the preceding claims 3 to 6, wherein said oligomer and/or polymer comprising at least one diphenylamine repeating unit is selected from one or more of the following compounds: a dimer of di-tert-octyl-diphenylamine, a trimer of di-tert-octyl-diphenylamine, a trimer comprising two di-tert-octyl-diphenylamine units and an N-(4-tert-octylphenyl)-1-naphthylamine unit, and the oligomer of the N,N-diphenylamine, N,N-di-(p-tert-butylphenyl)amine, N,N-di-(p-tert-octylphenyl)amine, N-(p-tert-butylphenyl)-N-phenylamine, N-(p-tert-octylphenyl)-N-phenylamine, N-(p-tert-butylphenyl)-N-(p-tert-octylphenyl)amine mixture.

8. The use according to any one of claims 3 to 7, wherein the phenyl α -naphthylamine is N-(4-tert-octylphenyl)-1-naphthylamine.

9. The use according to any one of the preceding claims 3 to 8, wherein the polymer and/or oligomer comprises, in the structure thereof, only diphenylamine repeating units and optionally phenyl α -naphthylamine repeating units.

10. The use according to one of the preceding claims 3 to 9, wherein the oligomer and/or the polymer comprising at least one diphenylamine repeating unit of formula (I) and optionally at least one phenyl α -naphthylamine repeating unit of formula (II) has a QSAR value for measuring each of the following toxicities: neurotoxicity (neurotoxic QSAR), reprotoxicity (reprotoxic QSAR), mutagenicity (mutagenic QSAR) and carcinogenicity (carcinogenic QSAR), corresponding to a statistical threshold value (%) subtracted from a delta of at least 30%, said statistical threshold value being determined, for each of said toxicities, by QSAR modelling according to the method described below in the experimental part.

11. The use according to any one of claims 1 to 10, for reducing and/or preventing the toxicity of a lubricating composition in an engine of a combustion vehicle.