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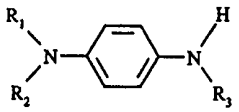
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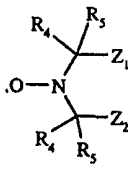
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(54) Title: STABILISED COMPOSITIONS COMPRISING OLEFINS



(I)



(II)

(57) Abstract

Subject of the invention is a composition stabilized against premature polymerization comprising a) a light olefin monomer, and an effective polymerization inhibiting amount of b) at least one phenylenediamine of formula (I) wherein R_1, R_2, and R_3 are the same or different and are hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, straight or branched chain alkyl of 1 to 20 carbon atoms which is substituted by one to three aryl groups, aryl of 1 to 12 carbon atoms, or aryl of 1 to 12 carbon atoms which is substituted by one to three alkyl groups of 1 to 6 carbon atoms; and c) at least one nitroxide of formula (II) wherein R_4 and R_5 are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene; and Z_1 and Z_2 are each methyl or Z_1 and Z_2 together form a linking moiety which may or may not contain heteroatoms or carbonyl groups and which additionally may be substituted by hydroxy, cyanohydrin, amino, alkoxy, amido, ketal, carboxy, hydantoin, carbamate, or a urethane group. A further subject of the invention is a method for inhibiting the premature polymerization of reactive light olefins and the use of a phenylendiamine together with at least one nitroxide to prevent polymerization of reactive light olefins.

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STABILISED COMPOSITIONS COMPRISING OLEFINS

The present invention pertains to novel methods and compositions for inhibiting polymerization in industrial plant streams which contain reactive light olefins, thereby preventing fouling of processing equipment and of product in storage tanks. Particularly, the invention pertains to the use of a combination of phenylenediamines and nitroxides to prevent undesired polymerization in reactive light olefins.

Industrial plant streams and processes which contain reactive light olefins are plagued with fouling problems due to unwanted polymerization. Examples of such plant streams and processes are hydrocarbon cracking processes in which light olefins are generated, industrial distillation processes of light olefin monomers, hydrogenation of light olefins and acetylenic compounds, and the like. Particular examples of such plant streams are depropanizer and debutanizer bottoms, light olefins typically generated in ethylene crackers. Such processes employ elevated temperatures which results in unwanted polymerization of the light olefin monomers. This unwanted polymerization results in the formation of deposits, or fouling, in distillation columns and other equipment such as heat transfer surfaces, reactor beds, reboilers, process lines, compressors, etc.

Fouling of the equipment or product during the stages of handling, processing, purification, and storage results in significant economic loss. Formation of deposits on heat transfer surfaces reduces process efficiency, and the unwanted polymerization also results in a loss of the desired product. Eventually the process must be stopped to clean the affected equipment.

To minimize fouling, commercial antifoulants are often added at 1-100 ppm levels at some point in the industrial process. Many classes of antifoulants are known, including phenylenediamines, hydroxylamines, nitroxides, and hindered phenols. However, fouling problems in reactive light olefin plant streams are not completely solved and industry continues to search for better solutions as well as for more cost effective ways to attack this problem.

Unexpectedly, the combination of phenylenediamines with nitroxides is found to be synergistic in its ability to prevent fouling in reactive light olefin streams. The activity of this

combination exceeds that of state-of-the-art antifoulants. The state-of-the-art is described in the patents below, the relevant parts of which are incorporated herein by reference.

U.S. Pat. No. 4,670,131 discusses the use of any stable free radical to prevent polymerization in unsaturated organic feed streams. Specifically claimed is the prevention of fouling in olefinic feed streams by incorporation of a nitroxide at less than 700 ppb.

U.S. Pat. No. 5,282,957 discloses the use of hydroxyalkylhydroxylamine compounds to inhibit polymerization of hydrocarbon fluids containing dissolved oxygen.

U.S. Pat. No. 5,396,005 discloses the combination of a methoxyphenol, either eugenol or 2-t-butytl-4-hydroxyanisole, with a phenylenediamine to prevent polymerization of ethylenically unsaturated monomers.

U.S. Pat. No. 5,416,258 discusses the method of inhibiting polymerization of a butadiene-containing stream by the addition of a combination of a phenylenediamine and a hydroxytoluene compound.

The following patents teach the use of nitroxides as inhibitors in combination with coadditives to prevent polymerization in various systems. The coadditives include phenylenediamines.

JP 93/320217 discloses the use of nitroxides with coadditives in methacrylic acid. The coadditives are phenothiazines, aromatic amines, and phenols.

DE 19609312 A1 and related WO 97/32833 disclose the use of nitroxides as inhibitors for monomers in which the vinyl group is attached to a heteroatom. The compositions may additionally contain one or more costabilizers of the group of phenothiazines, quinones, hydroquinones and their ethers, hydroxylamines or phenylenediamines.

U.S. Patent No. 5,711,767 discloses the use of nitroxides to prevent oxidative degradation and gum or deposit formation in gasoline. A costabilizer may also be employed which is selected from the group consisting of an aromatic amine, a phenolic antioxidant or a mixture of an aromatic amine and a phenolic antioxidant.

The synergistic activity of the combination of phenylenediamines with nitroxides towards preventing fouling in reactive light olefins is unknown. The superior performance of this particular combination to prevent premature polymerization in light olefins is not disclosed or suggested in the prior art.

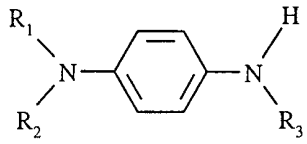
The present invention pertains to novel methods and compositions for preventing premature polymerization in industrial plant streams and processes containing reactive light olefins. The use of these novel methods and compositions prevents fouling of equipment and product during handling, processing, purification, and storage.

The novel compositions of this invention, stabilized against premature polymerization, comprise

a) a light olefin monomer, and

an effective polymerization inhibiting amount of

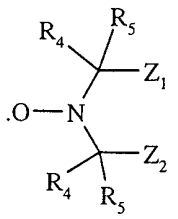
b) at least one phenylenediamine of the formula I



I

wherein R_1, R_2, and R_3 are the same or different and are hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, straight or branched chain alkyl of 1 to 20 carbon atoms which is substituted by one to three aryl groups, aryl of 6 to 12 carbon atoms, or aryl of 6 to 12 carbon atoms which is substituted by one to three alkyl groups of 1 to 6 carbon atoms; and

c) at least one nitroxide of the formula II



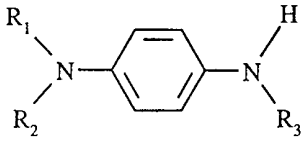
II

wherein R_4 and R_5 are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene; and Z_1 and Z_2 are each methyl or Z_1 and Z_2 together form a linking moiety which may or may not contain heteroatoms or carbonyl groups and which additionally may be substituted by hydroxy, cyanohydrin, amino, alkoxy, amido, ketal, carboxy, hydantoin, carbamate, or a urethane group.

The novel method of this invention comprises

adding to a reactive light olefin an effective polymerization inhibiting amount of

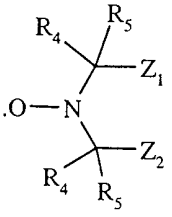
b) at least one phenylenediamine of the formula I



I

wherein R_1, R_2, and R_3 are as defined previously; and

c) at least one nitroxide of the formula II



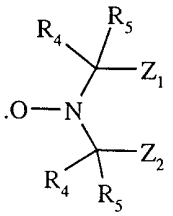
II

wherein R_4, R_5, Z_1, and Z_2 are as defined previously.

The phenylenediamines of this invention have at least one N-H group. Preferred examples of phenylenediamines of this invention include N-phenyl-N'-methyl-1,4-phenylediamine,
N-phenyl-N'-ethyl-1,4-phenylediamine, N-phenyl-N'-n-propyl-1,4-phenylediamine, N-phenyl-N'-isopropyl-1,4-phenylediamine, N-phenyl-N'-n-butyl-1,4-phenylediamine, N-phenyl-N'-iso-butyl-1,4-phenylediamine, N-phenyl-N'-sec-butyl-1,4-phenylediamine, N-phenyl-N'-t-butyl-1,4-phenylediamine, N-phenyl-N'-n-pentyl-1,4-phenylediamine, N-phenyl-N'-n-hexyl-1,4-phenylediamine, N-phenyl-N'-(1-methylhexyl)-1,4-phenylediamine, N-phenyl-N'-(1,3-dimethylbutyl)-1,4-phenylediamine, N-phenyl-N'-(1,4-dimethylpentyl)-1,4-phenylediamine, N-phenyl-N',N'-dimethyl-1,4-phenylenediamine, N-phenyl-N',N'-diethyl-1,4-phenylenediamine, N-phenyl-N',N'-di-n-butyl-1,4-phenylenediamine, N-phenyl-N',N'-di-sec-butyl-1,4-phenylenediamine, N-phenyl-N'-methyl-N'-ethyl-1,4-phenylenediamine, N,N'-dimethyl-1,4-phenylenediamine, N,N'-diethyl-1,4-phenylenediamine, N,N'-di-isopropyl-1,4-phenylenediamine, N,N'-di-iso-butyl-1,4-phenylenediamine, N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-1,4-phenylenediamine, N,N'-bis(1,3-dimethylbutyl)-1,4-phenylenediamine, N,N'-diphenyl-1,4-phenylenediamine, N,N,N'-trimethyl-1,4-phenylenediamine, and N,N,N'-triethyl-1,4-phenylenediamine.

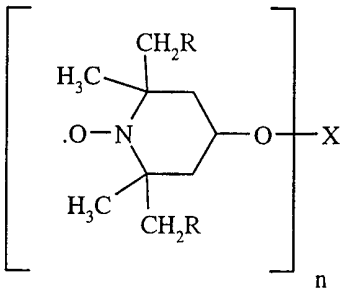
Particularly preferred examples of phenylenediamines of this invention include N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-1,4-phenylenediamine, N,N'-di-iso-butyl-1,4-phenylenediamine, N,N'-bis(1,3-dimethylbutyl)-1,4-phenylenediamine, N-phenyl-N'-(1,4-dimethylpentyl)-1,4-phenylenediamine, N-phenyl-N'-(1,3-dimethylbutyl)-1,4-phenylenediamine, N-phenyl-N'-iso-butyl-1,4-phenylenediamine, and N-phenyl-N'-sec-butyl-1,4-phenylenediamine.

Nitroxides of this invention have the general formula

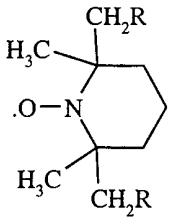


wherein R_4, R_5, Z_1, and Z_2 are as defined previously.

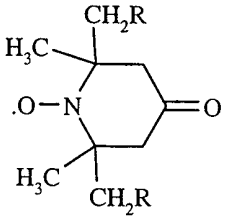
Preferably, the nitroxides of this invention have the formulae III, IV, V, VI, VII, VIII, and/or IX



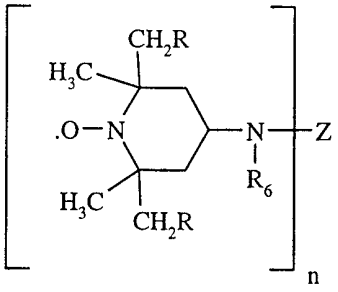
III



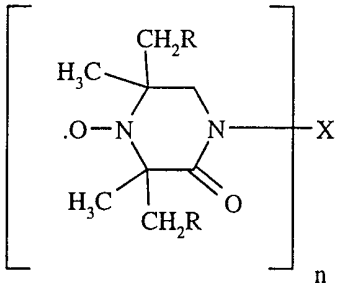
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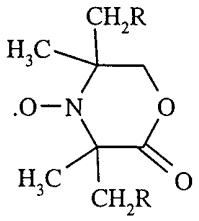
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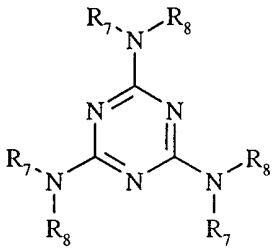
VI



VII



VIII



IX

wherein

R is hydrogen or methyl,

n is 1 or 2 in compounds of formula III, VI, and VII,
when n is 1 in compounds of formulae III and VII,

X is hydrogen; alkyl of 1 to 18 carbon atoms; alkanoyl of 2 to 18 carbon atoms; propargyl; glycidyl; benzoyl; phenyl; alkyl or alkanoyl of 2 to 50 carbon atoms interrupted by one to twenty -C=C-, -O-, -CO- and/or -COO- groups; alkyl of 1 to 50 carbon atoms or alkanoyl of 2 to 50 carbon atoms substituted by one to ten -OH and/or -COOY groups; alkyl or alkanoyl of 2 to 50 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups; cycloalkyl of 5 to 12 carbon atoms; cycloalkanoyl of 6 to 13 carbon atoms; or said cycloalkyl or cycloalkanoyl interrupted by one to six -C=C-, -O-,
-CO- and/or -COO- groups; or said cycloalkyl or cycloalkanoyl substituted by one to six -OH and/or -COOY groups; or said cycloalkyl or cycloalkanoyl both interrupted by said -C=C-, -O-,
-CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups,

Y is hydrogen, alkyl of 1 to 4 carbon atoms, or phenyl,

when n is 2 in compounds of formulae III and VII,

X is alkylene of 1 to 12 carbon atoms; alkylenoyl of 2 to 12 carbon atoms; alkylen-di-oyl of 2 to 12 carbon atoms; phenylene; phthaloyl; isophthaloyl; terephthaloyl; alkylene, alkylenoyl or alkylen-di-oyl of 2 to 50 carbon atoms interrupted by one to twenty -C=C-, -O-, -CO- and/or
-COO- groups; alkylene of 1 to 50 carbon atoms, alkylenoyl of 2 to 50 carbon atoms or alkylen-di-oyl of 3 to 50 carbon atoms substituted by one to ten -OH and/or -COOY groups; alkylene or alkylenoyl of 2 to 50 carbon atoms, or alkylen-di-oyl of 3 to 50 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups; cycloalkylene of 5 to 12 carbon atoms; cycloalkylenoyl of 6 to 13 carbon atoms; cycloalkylen-di-oyl of 7 to 14 carbon atoms; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl interrupted by one to six -C=C-, -O-, -CO- and/or -COO- groups; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl substituted by

one to six -OH and/or -COOY groups; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl both interrupted by said -C=C-, -O-,
-CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups,
wherein Y has the same definition as above,

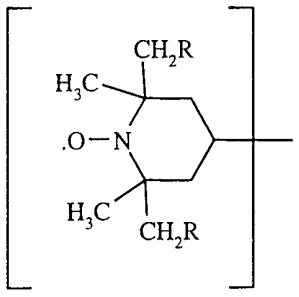
in compounds of formula VI, R_6 is hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, alkanoyl of 2 to 18 carbon atoms, alkenoyl of 3 to 18 carbon atoms or benzoyl,

Z has the same meaning as for X above for when n is 1 or 2, or Z and R_6 together may form a cycloalkyl of 5 to 12 carbon atoms; cycloalkyl of 5 to 12 carbon atoms interrupted by one to six -C=C-, -O-, -CO- and/or -COO- groups; cycloalkyl of 5 to 12 carbon atoms substituted by one to six alkyl of 1 to 20 carbon atoms, alkenyl of 1 to 20 carbon atoms, -OH, and/or -COOY groups; or cycloalkyl of 5 to 12 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or
-COO- groups and substituted by said alkyl, alkenyl, -OH, and/or -COOY groups,

Y has the same meaning as above,

in compounds of formula IX, each R_7 is independently hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, or cycloalkyl of 5 to 12 carbon atoms,

each R_8 is independently hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, or a radical of the formula XI,



XI

where R is as defined previously and with the proviso that at least one of the R_8 groups is of formula XI.

The alkyl radicals in the various substituents may be linear or branched. Examples of alkyl containing 1 to 18 carbon atoms are methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, 2-pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, t-octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, hexadecyl and octadecyl.

Examples for hydroxy substituted alkyl are hydroxy propyl, hydroxy butyl or hydroxy hexyl.

C_2-C_{18}alkyl interrupted by at least one O atom is for example -CH_2-CH_2-O-CH_2-CH_3, -CH_2-CH_2-O-CH_3- or -CH_2-CH_2-O-CH_2-CH_2-CH_2-O-CH_2-CH_3-. It is preferably derived from polyethlene glycol. A general description is -$((CH_2)_a$-$O)_b$-H/CH_3, wherein a is a number from 1 to 6 and b is a number from 2 to 10.

C_5-C_{12}cycloalkyl is typically cyclopentyl, methylcyclopentyl, dimethylcyclopentyl, cyclohexyl, methylcyclohexyl or trimethylcyclohexyl.

C_6-C_{10} aryl is for example phenyl or naphthyl, but also comprised are C_1-C_4alkyl substituted phenyl, C_1-C_4alkoxy substituted phenyl, hydroxy, halogen or nitro substituted phenyl. Examples for alkyl substituted phenyl are ethylbenzene, toluene, xylene and its isomers, mesitylene or isopropylbenzene. Halogen substituted phenyl is for example dichlorobenzene or bromotoluene.

Examples of C_2-C_{12}alkylene bridges are ethylene, propylene, butylene, pentylene, hexylene and dodecylene.

Examples for alkanoyl or cycloalkanoyl derived from a monovalent radical of a carboxylic acid are acetyl, caproyl, stearoyl, acryloyl, methacryloyl or cyclohexylcarboxyloyl.

Further examples are derived from propionic acid, laurinic acid or methyl ethyl acetic acid or the other isomers of valeric acid.

Typical unsaturated carboxylic acids are acrylic acid, methacrylic acid or crotonic acid.

Particularly preferred examples of nitroxides of this invention include bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, 1-oxyl-2,2,6,6-

tetramethylpiperidin-4-yl acetate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 2-ethylhexanoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-t-butyl-benzoate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)n-butylmalonate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)phthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) isophthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) terephthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) hexahydroterephthalate, N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipamide, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) caprolactam, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) dodecylsuccinimide, 2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-s-triazine, and 4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one).

The light olefins of this invention include hydrocarbon monomers generally having 2-6 carbon atoms. Examples are ethylene, propylene, butadiene, and isoprene.

The industrial plant streams are essentially the light olefins of this invention or they may additionally contain acetylenic compounds and/or saturated hydrocarbons. Examples of such streams are depropanizer and debutanizer bottoms which are generated in ethylene cracking processes.

The compositions of this invention are comprised of b) at least one phenylenediamine and c) at least one nitroxide, each as described supra. The inhibitor mixture may be added neat or it may be added as a solution in an appropriate hydrocarbon solvent. The components may be added separately or together as a mixture.

The ratio of b) to c) employed is in the range of 1:10 to 10:1.

The amount of components b) and c) necessary to prevent unwanted polymerization will depend on the temperature and duration of the particular process and may each be between 0.1 and 10,000 parts per million (ppm) based on the olefin. Preferably the amount used is between 0.1 and 100 ppm each on the olefin.

The industrial processes of this invention include any process in which a light olefin is handled or manipulated other than the intentional polymerization of the olefin. Such processes include but are not limited to hydrocarbon cracking processes, preheating, distillation, hydrogenation, extraction, etc.

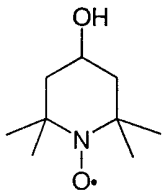
The compositions and methods of this invention may also be used with other additives known to prevent fouling such as antioxidants, metal deactivators, corrosion inhibitors and the like. The stabilizer combination of this invention may be applied at any point in an industrial plant stream or process where it is effective.

A further subject of the invention is the use of a phenylenediamine of formula I and a nitroxide of formula II, according to claim 1 for inhibiting the premature polymerization of reactive light olefins.

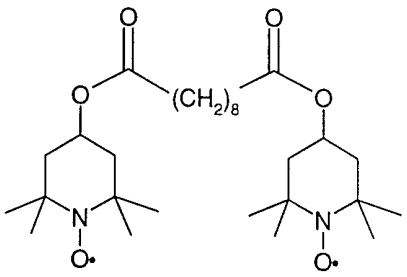
All definitions and preferences given for the composition above apply also for the other subjects of the invention.

Although specific embodiments of the present invention have been described in the detailed description above, the description is not intended to limit the invention to the particular forms or embodiments disclosed therein since they are to be recognized as illustrative rather than restrictive and it will be obvious to those skilled in the art that the invention is not so limited. Thus, the invention is declared to cover all changes and modifications of the specific examples of the invention herein disclosed for purposes of illustration which do not constitute departure from the spirit and scope of the invention. The embodiments of the invention in which a specific property or privilege is claimed are defined as follows.

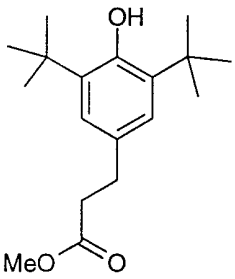
The inhibitors used in the following Examples are:



NO1

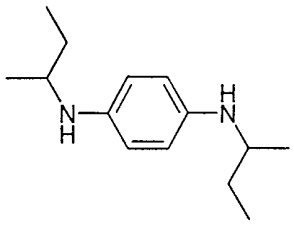


NO2



IRGANOX® 1300

(HP)



N,N'-Di-sec-butyl-1,4-phenylenediamine

(DBPDA)

Example 1

Heat Induced Gum Test

The heat induced gum test utilizes heat under a nitrogen atmosphere to induce low molecular weight polymer formation (gum). The method is an adaptation of ASTM D 381, "Standard Test Method for Existent Gum in Fuels by Jet Evaporation," and D 873, "Standard Test Method for Oxidation Stability of Aviation Fuels (Potential Residue Method)."

Commercial isoprene is distilled in an inert atmosphere to obtain inhibitor-free isoprene which is stored under nitrogen below 0°C until used. The diluent is ACS reagent grade toluene which is purged with nitrogen for 30 minutes prior to use. Nitrogen, not less than 99.6 %, is used as the overpressure gas in the heat aging bomb and as the evaporation gas for gum determination. Inhibitor concentrations are reported in parts per million (ppm) by weight based on total hydrocarbons.

Table 1

Heat Induced Gum Content

Trial	Isoprene (vol %)	Inhibitor	Conc. wt -ppm	Temp. (^{O}F)	Time (hours)	Gum Content (mg/100mL) Insoluble	Soluble
a)	50	none	--	212	4	na*	470
b)	50	NO1	8	212	4	0	0
c)	50	NO2	8	212	4	1	176
d)	50	DBPDA	9	212	4	na*	220
e)	50	HP	8	212	4	0	395
f)	50	NO1 HP	4 4	212	4	3	212
g)	50	NO2 HP	4 4	212	4	1	298
h)	50	NO1 DBPDA	2.7 1.3	212	4	0	0
i)	50	NO1	4	212	4	2	212

*na = not available

It is seen from Table 1 that the combined use of the nitroxides and the phenylenediamines of the present invention provides a synergistic method for inhibiting polymerization of isoprene at elevated temperatures. Nitroxides and phenylenediamines each have an inhibiting effect, comparing b), c), d), and i) to the blank trial a). However trial h), in which a combination of a nitroxide with a phenylenediamine at a total level of 4 ppm was used had no gum formation. This was as good as double the amount of the nitroxide NO1 alone and far better than the use of 4 ppm of NO1 alone (trial i)) as well as far better than the use of more than double the amount of the phenylenediamine alone (trial d)). No such synergy is found with the combination of the nitroxides with other inhibitors of the prior art such as hindered phenols. The combinations of nitroxides with the hindered phenol IRGANOX® 1300 (HP) are not as good at inhibiting isoprene polymerization as the nitroxides alone (comparing trials f) and g) to b) and c)).

Table 2

Heat Induced Gum Content

Trial	Isoprene (vol %)	Inhibitor	Conc. wt -ppm	Temp. (^{O}F)	Time (hours)	Gum Content (mg/100mL) Insoluble	Soluble
j)	50	NO1 DBPDA	5.3 2.7	248	4	1	893
k)	50	NO1 DBPDA	2.7 5.3	248	4	2	858
l)	50	NO1	15	248	4	2	961
m)	50	NO2	15	248	4	2	1258

n)	50	NO1 NO2	7.5 7.5	248	4	0	1410
o)	50	NO1 DBPDA	5 10	248	4	0	352

Table 2 illustrates the synergistic polymerization inhibiting ability of the combination of nitroxides and phenylenediamines at 248° F. Note trials j) and k) perform better than l) at about one half the total loading of inhibitor. At equal total loading the performance of the combination of this invention is superior (trial o)).

Table 3

Heat Induced Gum Content

Trial	Isoprene (vol %)	Inhibitor	Conc. wt -ppm	Temp. (°F)	Time (hours)	Gum Content (mg/100mL) Insoluble	Soluble
p)	25	NO1	3	248	2.5	6	264
q)	25	NO1 DBPDA	2 1	248	2.5	5	68

Table 3 illustrates the effectiveness of the use of low levels (3 ppm on total hydrocarbons) of inhibitor on dilute solutions of isoprene. The combined use of a nitroxide with a phenylenediamine as directed by this invention is superior at inhibiting polymer formation under these conditions.

Example 2

Heat Induced Gum Test

The Heat Induced Gum Test is performed as in Example 1 replacing isoprene with 1,3-butadiene. The combined use of the nitroxides and phenylenediamines of the present invention provides a synergistic method for inhibiting polymerization of 1,3-butadiene at elevated temperatures.

Tables 1 through 3 illustrate the synergistic activity of a combination of a nitroxide and a phenylenediamine towards inhibiting polymerization of light olefins. This combination is superior to state of the art inhibitors. This provides for a more cost-effective method to prevent fouling in industrial plant streams and processes that involve the handling, storage, processing, and purification of reactive light olefins.

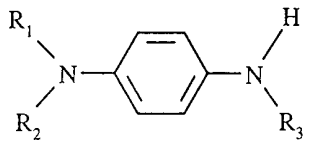
What is Claimed is:

1. A composition stabilized against premature polymerization comprising

a) a light olefin monomer, and

an effective polymerization inhibiting amount of

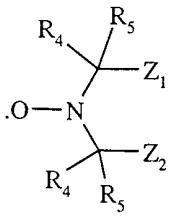
b) at least one phenylenediamine of the formula I



I

wherein R_1, R_2, and R_3 are the same or different and are hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, straight or branched chain alkyl of 1 to 20 carbon atoms which is substituted by one to three aryl groups, aryl of 1 to 12 carbon atoms, or aryl of 1 to 12 carbon atoms which is substituted by one to three alkyl groups of 1 to 6 carbon atoms; and

c) at least one nitroxide of the formula II



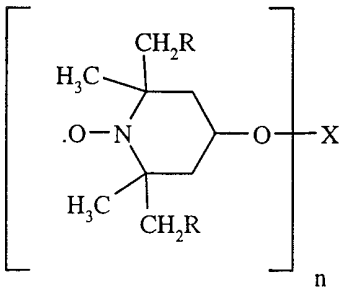
II

wherein R_4 and R_5 are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene; and Z_1 and Z_2 are each methyl or Z_1 and Z_2 together form a linking moiety which may or may not contain heteroatoms or carbonyl groups and which additionally may be substituted by hydroxy, cyanohydrin, amino, alkoxy, amido, ketal, carboxy, hydantoin, carbamate, or a urethane group.

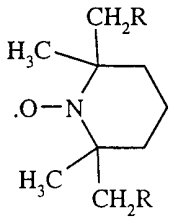
2. A composition according to claim 1 in which component b) is at least one phenylenediamine selected from N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-1,4-phenylenediamine, N,N'-di-iso-butyl-1,4-phenylenediamine, N,N'-bis(1,3-

dimethylbutyl)-1,4-phenylenediamine, N-phenyl-N'-(1,4-dimethylpentyl)-1,4-phenylenediamine, N-phenyl-N'-(1,3-dimethylbutyl)-1,4-phenylenediamine, N-phenyl-N'-iso-butyl-1,4-phenylenediamine, and N-phenyl-N'-sec-butyl-1,4-phenylenediamine.

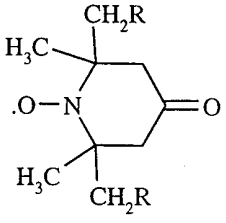
3. A composition according to claim 1 in which component c) is at least one nitroxide of the formulae III, IV, V, VI, VII, VIII, or IX



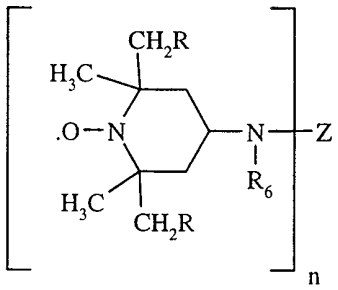
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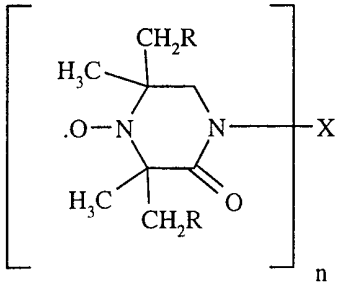
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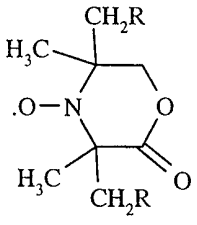
V



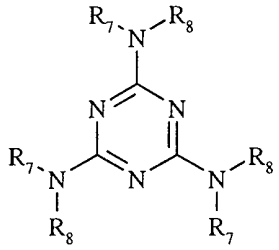
VI



VII



VIII



IX

wherein

R is hydrogen or methyl,

n is 1 or 2 in compounds of formula III, VI, and VII,

when n is 1 in compounds of formulae III and VII,

X is hydrogen; alkyl of 1 to 18 carbon atoms; alkanoyl of 2 to 18 carbon atoms; propargyl; glycidyl; benzoyl; phenyl; alkyl or alkanoyl of 2 to 50 carbon atoms interrupted by one to twenty -C=C-, -O-, -CO- and/or -COO- groups; alkyl of 1 to 50 carbon atoms or alkanoyl of 2 to 50 carbon atoms substituted by one to ten -OH and/or -COOY groups; alkyl or alkanoyl of 2 to 50 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups; cycloalkyl of 5 to 12 carbon atoms; cycloalkanoyl of 6 to 13 carbon atoms; or said cycloalkyl or cycloalkanoyl interrupted by one to six -C=C-, -O-,
-CO- and/or -COO- groups; or said cycloalkyl or cycloalkanoyl substituted by one to six -OH and/or -COOY groups; or said cycloalkyl or cycloalkanoyl both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups,

Y is hydrogen, alkyl of 1 to 4 carbon atoms, or phenyl,

when n is 2 in compounds of formulae III and VII,

X is alkylene of 1 to 12 carbon atoms; alkylenoyl of 2 to 12 carbon atoms; alkylen-di-oyl of 2 to 12 carbon atoms; phenylene; phthaloyl; isophthaloyl; terephthaloyl; alkylene, alkylenoyl or alkylen-di-oyl of 2 to 50 carbon atoms interrupted by one to twenty -C=C-, -O-, -CO- and/or -COO- groups; alkylene of 1 to 50 carbon atoms, alkylenoyl of 2 to 50 carbon atoms or alkylen-di-oyl of 3 to 50 carbon atoms substituted by one to ten -OH and/or -COOY groups; alkylene or alkylenoyl of 2 to 50 carbon atoms, or alkylen-di-oyl of 3 to 50 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups; cycloalkylene of 5 to 12 carbon atoms; cycloalkylenoyl of 6 to 13 carbon atoms; cycloalkylen-di-oyl of 7 to 14 carbon atoms; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl interrupted by one to six -C=C-, -O-, -CO- and/or -COO- groups; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl substituted by one to six -OH and/or -COOY groups; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups,

wherein Y has the same definition as above,

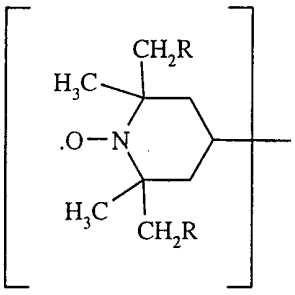
in compounds of formula VI, R_6 is hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, alkanoyl of 2 to 18 carbon atoms, alkenoyl of 3 to 18 carbon atoms or benzoyl,

Z has the same meaning as for X above for when n is 1 or 2, or Z and R_6 together may form a cycloalkyl of 5 to 12 carbon atoms; cycloalkyl of 5 to 12 carbon atoms interrupted by one to six -C=C-, -O-, -CO- and/or -COO- groups; cycloalkyl of 5 to 12 carbon atoms substituted by one to six alkyl of 1 to 20 carbon atoms, alkenyl of 1 to 20 carbon atoms, -OH, and/or -COOY groups; or cycloalkyl of 5 to 12 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said alkyl, alkenyl, -OH, and/or -COOY groups,

Y has the same meaning as above,

in compounds of formula IX, each R_7 is independently hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, or cycloalkyl of 5 to 12 carbon atoms,

each R_8 is independently hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, or a radical of the formula XI,



XI

where R is as defined previously and with the proviso that at least one of the R_8 groups is of formula XI.

4. A composition according to claim 1 in which component c) is at least one nitroxide selected from bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 4-hydroxy-1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl acetate, 1-oxyl-2,2,6,6-

tetramethylpiperidin-4-yl 2-ethylhexanoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl stearate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl benzoate, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl 4-t-butyl-benzoate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)-n-butylmalonate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) phthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) isophthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) terephthalate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) hexahydroterephthalate, N,N'-bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) adipamide, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) caprolactam, N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl) dodecylsuccinimide, 2,4,6-tris-[N-butyl-N-(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)]-s-triazine, and 4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one).

5. A composition according to claim 1 which further contains acetylenic compounds and/or one or more saturated hydrocarbons.

6. A composition according to claim 1 in which the ratio of components b) to c) is in the range of 1:10 to 10:1.

7. A composition according to claim 1 in which components b) and c) are each present in the range of from about 0.1 parts per million to about 10,000 parts per million of component a).

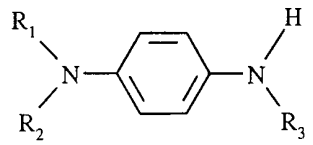
8. A composition according to claim 1 in which component a) has 2 to 6 carbon atoms.

9. A composition according to claim 1 in which component a) is ethylene, propylene, butadiene, or isoprene.

10. A method for inhibiting the premature polymerization of reactive light olefins comprising

adding to said olefins an effective polymerization inhibiting amount of

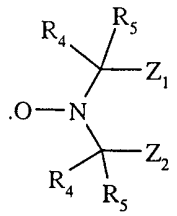
b) at least one phenylenediamine of the formula I



I

wherein R_1, R_2, and R_3 are the same or different and are hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, straight or branched chain alkyl of 1 to 20 carbon atoms which is substituted by one to three aryl groups, aryl of 1 to 12 carbon atoms, or aryl of 1 to 12 carbon atoms which is substituted by one to three alkyl groups of 1 to 6 carbon atoms; and

c) at least one nitroxide of the formula II

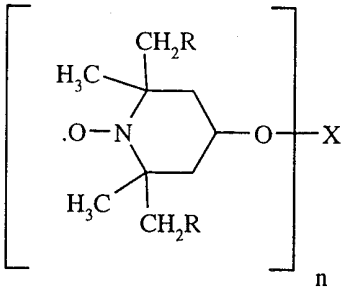


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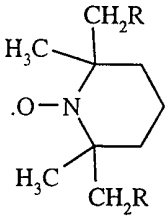
wherein R_4 and R_5 are independently alkyl of 1 to 4 carbon atoms or are together pentamethylene; and Z_1 and Z_2 are each methyl or Z_1 and Z_2 together form a linking moiety which may or may not contain heteroatoms or carbonyl groups and which additionally may be substituted by hydroxy, cyanohydrin, amino, alkoxy, amido, ketal, carboxy, hydantoin, carbamate, or a urethane group.

11. A method according to claim 10 in which component b) is at least one phenylenediamine selected from N,N'-di-sec-butyl-1,4-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-1,4-phenylenediamine, N,N'-di-iso-butyl-1,4-phenylenediamine, N,N'-bis(1,3-dimethylbutyl)-1,4-phenylenediamine, N-phenyl-N'-(1,4-dimethylpentyl)-1,4-phenylenediamine, N-phenyl-N'-(1,3-dimethylbutyl)-1,4-phenylenediamine, N-phenyl-N'-iso-butyl-1,4-phenylenediamine, and N-phenyl-N'-sec-butyl-1,4-phenylenediamine.

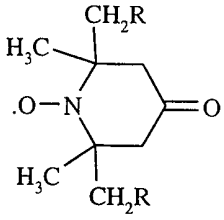
12. A method according to claim 10 in which component c) is at least one nitroxide of the formulae III, IV, V, VI, VII, VIII, or IX



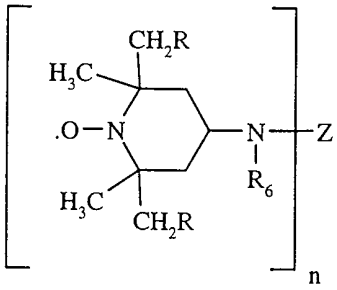
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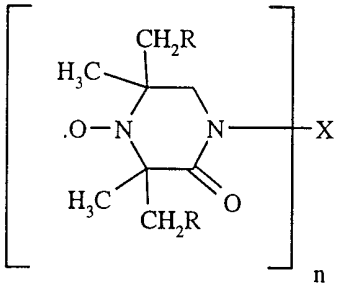
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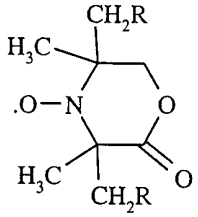
V



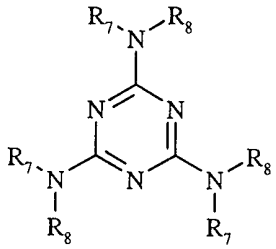
VI



VII



VIII



IX

wherein

R is hydrogen or methyl,

n is 1 or 2 in compounds of formula III, VI, and VII,

when n is 1 in compounds of formulae III and VII,

X is hydrogen; alkyl of 1 to 18 carbon atoms; alkanoyl of 2 to 18 carbon atoms; propargyl; glycidyl; benzoyl; phenyl; alkyl or alkanoyl of 2 to 50 carbon atoms interrupted by one to twenty -C=C-, -O-, -CO- and/or -COO- groups; alkyl of 1 to 50 carbon atoms or

alkanoyl of 2 to 50 carbon atoms substituted by one to ten -OH and/or -COOY groups; alkyl or alkanoyl of 2 to 50 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups; cycloalkyl of 5 to 12 carbon atoms; cycloalkanoyl of 6 to 13 carbon atoms; or said cycloalkyl or cycloalkanoyl interrupted by one to six -C=C-, -O-, -CO- and/or -COO- groups; or said cycloalkyl or cycloalkanoyl substituted by one to six -OH and/or -COOY groups; or said cycloalkyl or cycloalkanoyl both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups,

Y is hydrogen, alkyl of 1 to 4 carbon atoms, or phenyl,

when n is 2 in compounds of formulae III and VII,

X is alkylene of 1 to 12 carbon atoms; alkylenoyl of 2 to 12 carbon atoms; alkylen-di-oyl of 2 to 12 carbon atoms; phenylene; phthaloyl; isophthaloyl; terephthaloyl; alkylene, alkylenoyl or alkylen-di-oyl of 2 to 50 carbon atoms interrupted by one to twenty -C=C-, -O-, -CO- and/or -COO- groups; alkylene of 1 to 50 carbon atoms, alkylenoyl of 2 to 50 carbon atoms or alkylen-di-oyl of 3 to 50 carbon atoms substituted by one to ten -OH and/or -COOY groups; alkylene or alkylenoyl of 2 to 50 carbon atoms, or alkylen-di-oyl of 3 to 50 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups; cycloalkylene of 5 to 12 carbon atoms; cycloalkylenoyl of 6 to 13 carbon atoms; cycloalkylen-di-oyl of 7 to 14 carbon atoms; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl interrupted by one to six -C=C-, -O-, -CO- and/or -COO- groups; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl substituted by one to six -OH and/or -COOY groups; or said cycloalkylene, cycloalkylenoyl or cycloalkylen-di-oyl both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said -OH and/or -COOY groups,

wherein Y has the same definition as above,

in compounds of formula VI, R_6 is hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, aralkyl of 7 to 15 carbon atoms, alkanoyl of 2 to 18 carbon atoms, alkenoyl of 3 to 18 carbon atoms or benzoyl,

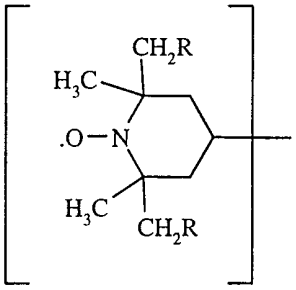
Z has the same meaning as for X above for when n is 1 or 2, or Z and R_6 together may form a cycloalkyl of 5 to 12 carbon atoms; cycloalkyl of 5 to 12 carbon atoms interrupted by

one to six -C=C-, -O-, -CO- and/or -COO- groups; cycloalkyl of 5 to 12 carbon atoms substituted by one to six alkyl of 1 to 20 carbon atoms, alkenyl of 1 to 20 carbon atoms, -OH, and/or -COOY groups; or cycloalkyl of 5 to 12 carbon atoms both interrupted by said -C=C-, -O-, -CO- and/or -COO- groups and substituted by said alkyl, alkenyl, -OH, and/or -COOY groups,

Y has the same meaning as above,

in compounds of formula IX, each R_7 is independently hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, or cycloalkyl of 5 to 12 carbon atoms,

each R_8 is independently hydrogen, straight or branched chain alkyl of 1 to 20 carbon atoms, cycloalkyl of 5 to 12 carbon atoms, or a radical of the formula XI,



XI

where R is as defined previously and with the proviso that at least one of the R_8 groups is of formula XI.

13. Use of a phenylenediamine of formula I and a nitroxide of formula II, according to claim 1 for inhibiting the premature polymerization of reactive light olefins.

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/EP 99/08676

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C7/20

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 02400 A (A H MARKS AND COMPANY LIMITED) 22 January 1998 (1998-01-22) claims page 3	1-13
A	DE 19 44 233 A (BP CHEMICALS) 9 April 1970 (1970-04-09) claims	1
A	US 5 416 258 A (ARHANCET GRACIELA B ET AL) 16 May 1995 (1995-05-16) cited in the application claims	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 March 2000	17/03/2000

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern al Application No
PCT/EP 99/08676

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