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(71) Applicant *(for all designated States except US)*: **CHEMTURA CORPORATION** [US/US]; Benson Road, Middlebury, CT 06749 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **KOSOVER, Vilen** [US/US]; 202 Curve Hill Road, Cheshire, CT 06410 (US). **FABIAN, Jesus, R.** [PE/US]; Apt. #1, 91 Folly Brook Blvd., Wethersfield, CT 06109 (US). **LIPPAI, Istvan** [—/US]; 206 Spring Street, Apt. #16, Naugatuck, CT 06770 (US). **BENAGE, Brigitte** [US/US]; 79 Richard Avenue, Wolcott, CT 06716 (US). **ABRUSCATO, Gerald, J.** [US/US]; 144 Cascade Ridge, Southington, CT 06489 (US).

(74) Agent: **DILWORTH, Michael, P.**; Chemtura Corporation, Benson Road, Middlebury, CT 06749 (US).

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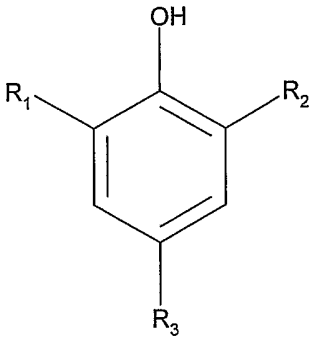
(54) **Title:** SULFONATED PHENOLS WITH NITROPHENOLS AS POLYMERIZATION INHIBITORS



(I)

(57) **Abstract:** Disclosed herein is a method for inhibiting the premature polymerization and the polymer growth of ethylenically unsaturated monomers comprising adding to said monomers an effective amount of a combination of (A) at least one inhibitor that is a sulfonated phenol of the formula (I): wherein (1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and (2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H; (B) at least one inhibitor that is a nitrophenol; and, optionally, (C) an inhibitor selected from the group consisting of nitroxyl compounds and nitrosoanilines; and (D) an amine.

WO 2006/036274 A1

0234-PA

SULFONATED PHENOLS WITH NITROPHENOLS AS POLYMERIZATION INHIBITORS

We claim the benefit under Title 35, United States Code, § 120 of U.S. of Provisional Application Number 60/614,378, filed September 28, 2004 entitled "Sulfonated Phenol Polymerization Inhibitors"and Provisional Application Number 60/631,241, filed November 29, 2004, entitled "Sulfonated Phenols with Nitrophenols as Polymerization Inhibitors".

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention is directed to the inhibition of the polymerization of ethylenically unsaturated monomers by means of the addition thereto of the combination of a sulfonated phenol and a nitrophenol.

2. Description of Related Art

Many ethylenically unsaturated monomers undesirably polymerize at various stages of their manufacture, processing, handling, storage, and use. Polymerization, such as thermal polymerization, during their purification results in the loss of the monomer, i.e., a lower yield, and an increase in the viscosity of any tars that may be produced. The processing and handling of the higher viscosity tars then requires higher temperature and work (energy cost) to remove residual monomer.

Polymerization can also result in equipment fouling, especially in the case of production of acrylic monomers. Such polymerization causes loss in production efficiency owing to the deposition of polymer in or on the equipment being used. These deposits must be removed from time to time, leading to additional loss in production of the monomer.

0234-PA

A wide variety of compounds has been proposed and used for inhibiting uncontrolled and undesired polymerization of ethylenically unsaturated monomers. However, many of these compounds have not been fully satisfactory.

U.S. Patent No. 2,867,672 discloses that the polymerization of uninhibited styrene condensing in liquid form on the surfaces containing the vapor space above the liquid level of the main body of styrene in a tank may be minimized by spraying the surfaces enclosing the vapor space with a styrene polymerization inhibitor.

U.S. Patent No. 4,086,147 discloses a process for the distillation of readily polymerizable vinyl aromatic compounds comprising subjecting a vinyl aromatic compound to elevated temperatures in a distillation system in the presence of a polymerization inhibitor comprising m-nitro-p-cresol.

U.S. Patent No. 4,468,343 discloses a compound and a process for utilizing the compound to prevent the polymerization of vinyl aromatic compounds, such as styrene, during heating. The composition includes effective amounts of 2,6-dinitro-p-cresol and either a phenylenediamine or 4-tert-butylcatechol respectively, to act as a polymerization co-inhibitor system in the presence of oxygen.

U.S. Patent No. 4,670,131 discloses controlling the fouling of equipment used for processing of organic feed streams containing olefinic compounds by inhibiting polymerization of the olefinic compounds by carrying out the processing in the presence of from about 20 ppb to less than 1000 ppb of a stable free radical, such as a nitroxide.

0234-PA

U.S. Patent No. 5,254,760 discloses the inhibition of the polymerization of a vinyl aromatic compound, such as styrene, during distillation or purification by the presence of at least one stable nitroxyl compound together with at least one aromatic nitro compound.

U.S. Patent No. 5,290,888 discloses a process for stabilizing an ethylenically unsaturated monomer or oligomer from premature polymerization whereby a stabilizing amount of an N-hydroxy substituted hindered amine is added to said polymerizable monomer or oligomer. The ethylenically unsaturated monomer or oligomer encompasses vinyl monomers or oligomers bearing at least one polymerizable moiety. The N-hydroxy substituted hindered amine is said to inhibit premature polymerization in the liquid and/or vapor phase.

U.S. Patent No. 5,446,220 discloses methods for inhibiting the polymerization of vinyl aromatic monomers in oxygen-free processing systems. These methods comprise adding from 1 to about 10,000 parts per million parts monomer of a combination of a dinitrophenol compound, a hydroxylamine compound and a phenylenediamine compound. Preferably, 2-sec-butyl-4,6-dinitrophenol or 4,6-dinitro-o-cresol are used in combination with bis-(hydroxypropyl)hydroxylamine and N,N' -di-sec-butyl-p-phenylenediamine.

U.S. Patent No. 5,545,786 discloses that nitroxyl inhibitors in combination with some oxygen reduce the premature polymerization of vinyl aromatic monomers during the manufacturing processes for such monomers. It is also disclosed that even small quantities of air used in combination with the nitroxyl inhibitors result in vastly prolonged inhibition times for said monomers.

0234-PA

U.S. Patent No. 5,932,735 discloses that selected derivatives of 1-oxyl-2,2,6,6-tetramethyl-4-hydroxypiperidine are effective as inhibitors to prevent the premature polymerization of acrylic and methacrylic acids, their esters, their amides, vinyl acetate and acrylonitrile in the presence of water.

U.S. Patent No. 6,143,205 discloses a mixture for inhibiting the premature polymerization of monomers that contains (A) vinyl-containing monomers, and (B) an effective amount of a mixture of (i) from 0.05 to 4.5% by weight, based on the total mixture (B), of at least one N-oxyl compound of a secondary amine which carries no hydrogen atoms on the α-carbon atoms and (ii) from 99.95 to 95.5% by weight, based on the total mixture (B), of at least one nitro compound.

Russian patents 1,027,150; 1,139,722; and 1,558,888 disclose decreased polymer formation during normal operating conditions (true inhibitors), but do not protect the system in emergency feed shut off situations, i.e., there is no retarder effect.

The foregoing are incorporated herein by reference in their entirety.

SUMMARY OF THE INVENTION

In accordance with the present invention, inhibiting systems comprising sulfonated phenols have been found to be excellent inhibitors and retarders to prevent polymerization of ethylenically unsaturated monomers, especially vinyl aromatic compounds, when used with nitrophenols, such as 2,4-dinitro-o-sec-butylphenol (DNBP). Optionally, this inhibitor system can be used in combination with nitroxyl radical type compounds or nitrosoanilines and amines.

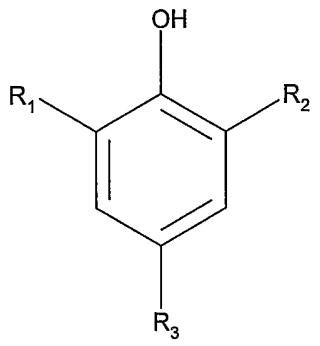
0234-PA

It is an advantage of the present invention that the sulfonated phenols can be produced in the DNBP manufacturing process. Since DNBP is a preferred second component of the claimed inhibitor blend, both components can be manufactured in the same process. Accordingly, manufacturing can be simplified by producing both components in the same process at the same location. This provides the economic advantage that the material can be produced in an already existing process at low cost without capital investment. From a customer point of view, an economic advantage is realized owing to the low manufacturing cost (low price) and the superior performance of the claimed inhibitor blend. The latter results in low inhibitor usage and low polymer make.

It is thus an object of the present invention to develop a highly efficient and inexpensive polymerization inhibitor blend with superb true inhibitor and retarder capabilities.

This and other objects are obtained by the present invention, which is directed to a method for inhibiting the premature polymerization and the polymer growth of ethylenically unsaturated monomers comprising adding to said monomers an effective amount of a combination of

(A) at least one inhibitor that is a sulfonated phenol of the formula:



0234-PA

wherein

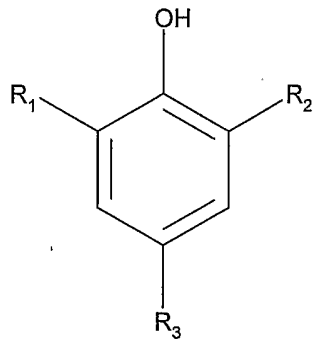
(1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and

(2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H; and

(B) at least one inhibitor that is a nitrophenol.

In a preferred embodiment, the present invention is directed to a method for inhibiting the premature polymerization and the polymer growth of ethylenically unsaturated monomers comprising adding to said monomers an effective amount of a combination of

(A) at least one inhibitor that is a sulfonated phenol of the formula:



wherein

(1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and

(2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H;

(B) at least one inhibitor that is a nitrophenol;

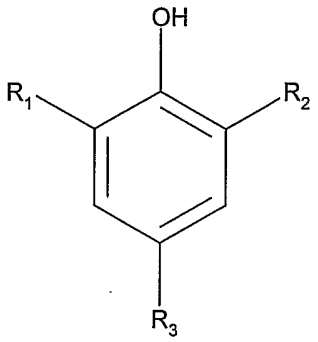
0234-PA

(C) at least one inhibitor selected from the group consisting of nitroxyl compounds and nitrosoanilines; and

(D) at least one amine.

In another aspect, the present invention is directed to a composition comprising a combination of

(A) at least one inhibitor that is a sulfonated phenol of the formula:



wherein

(1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and

(2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H;

(B) at least one inhibitor that is a nitrophenol;

(C) at least one inhibitor selected from the group consisting of nitroxyl compounds and nitrosoanilines; and

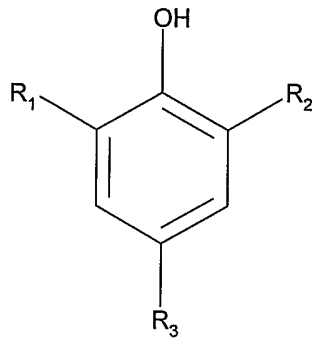
(D) at least one amine.

0234-PA

DESCRIPTION OF THE PREFERRED EMBODIMENTS

As stated above, the present invention is directed to inhibiting systems comprising a combination of

(A) at least one inhibitor that is a sulfonated phenol of the formula:



wherein

(1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and

(2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H; and

(B) at least one inhibitor that is a nitrophenol.

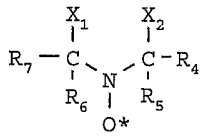
In a preferred embodiment the inhibiting system further comprises at least one amine and at least one additional inhibitor selected from the group consisting of nitroxyl compounds and nitrosoanilines.

Where R_2 is hydrocarbyl, it is preferably a straight chain or branched chain alkyl or alkenyl group of from 1 to to 50 carbon atoms, more preferably of from 1 to 18 carbon atoms including, but not limited to, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, 2-ethyl

hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, oleyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, triacontyl, isomers of the foregoing (such as, for example, isopropyl, sec-butyl, neopentyl, etc.), and the like; or cyclic alkyl groups, such as cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and cyclododecyl.

Nitrophenols that can be employed in the practice of the present invention include, but are not limited to, 2,6-dinitro-4-methylphenol, 2-nitro-4-methylphenol, 2,4-dinitro-1-naphthol, 2,4,6-trinitrophenol (picric acid), 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol, 2,4-dinitro-6-sec-butylphenol, 4-cyano-2-nitrophenol, 3-iodo-4-cyano-5-nitrophenol, *m*-nitro-*p*-cresol, 2,6-dinitro-*p*-cresol, and the like. 2,4-Dinitro-6-sec-butylphenol is preferred.

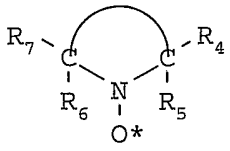
Where the inhibiting system of the present invention comprises an additional inhibitor that is a nitroxyl compound, the nitroxyl compound is preferably a stable hindered nitroxyl compound having the structural formula:



wherein R_4 and R_7 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl and R_5 and R_6 are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl; and X_1 and X_2 (1) are independently selected from the group consisting of halogen, cyano, $COOR_7$, -S-COR_7, -$OCOR_7$, (wherein R_7 is alkyl or aryl), amido, -S-C_6H_5, carbonyl, alkenyl, or alkyl of 1 to 15 carbon atoms, or (2) taken together, form a ring structure with the nitrogen.

0234-PA

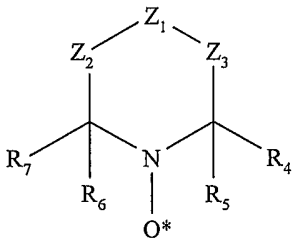
In a particularly preferred embodiment, the stable hindered nitroxyl compound has the structural formula:



wherein R_4 and R_7 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl and R_5 and R_6 are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl, and the

portion represents the atoms necessary to form a five-, six-, or seven-membered heterocyclic ring.

Accordingly, one of the several classes of cyclic nitroxides that can be employed in the practice of the present invention can be represented by the following structural formula:

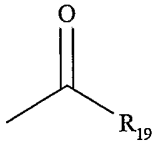


wherein Z_1, Z_2, and Z_3 are independently selected from the group consisting of oxygen, sulfur, secondary amines, tertiary amines, phosphorus of various oxidation states, and substituted or unsubstituted carbon atoms, such as $>CH_2$, $>CHCH_3$, $>C=O$, $>C(CH_3)_2$,

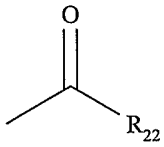
>CHBr, >CHCl, >CHI, >CHF, >CHOH, >CHCN, >C(OH)CN, >CHCOOH, >CHCOOCH$_3$, >CHCOOC$_2$H$_5$, >C(OH)COOC$_2$H$_5$, >C(OH)COOCH$_3$, >C(OH)CHOHC$_2$H$_5$, >CR$_8$OR$_9$, >CHNR$_8$R$_9$, >CCONR$_8$R$_9$, >C=NOH, >C=CH-C$_6$H$_5$, >CF$_2$, >CCl$_2$, >CBr$_2$, >CI$_2$, >CR$_8$PR$_{13}$R$_{14}$R$_{15}$, and the like, where R$_8$ and R$_9$ are independently selected from the group consisting of hydrogen, alkyl, aryl, and acyl and R$_{13}$, R$_{14}$, and R$_{15}$ are independently selected from the group consisting of unshared electrons, alkyl, aryl, =O, OR$_{16}$, and NR$_{17}$R$_{18}$, where R$_{16}$, R$_{17}$, and R$_{18}$ are independently selected from the group consisting of hydrogen, alkyl, and aryl . Where R$_8$ and/or R$_9$ are alkyl, it is preferred that they be a lower alkyl (i.e., one having one to five carbon atoms, e.g., methyl, ethyl, propyl, butyl, pentyl, and isomers thereof).

Where R$_8$ and/or R$_9$ are aryl, it is preferred that they be aryl of from 6 to 10 carbon atoms, e.g., phenyl or naphthyl, which, in addition, may be substituted with non-interfering substituents, e.g., lower alkyl groups, halogens, and the like.

Where R$_8$ and/or R$_9$ are acyl, it is preferred that they be acyl of the structure

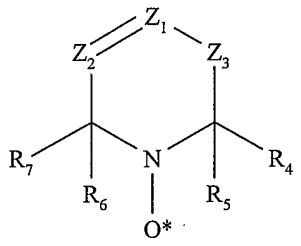


where R$_{19}$ is alkyl, aryl, OR$_{20}$, or NR$_{20}$R$_{21}$ and where R$_{20}$ and R$_{21}$ are alkyl, aryl, or



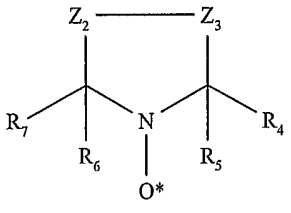
where R_{22} is alkyl or aryl. Where R_{19}, R_{20}, R_{21}, or R_{22} are alkyl, they are preferably alkyl of from 1 to 15 carbon atoms, more preferably lower alkyl of from 1 to 5 carbon atoms, as described above. Where R_{19}, R_{20}, R_{21}, or R_{22} are aryl, they are preferably aryl of from 6 to 10 carbon atoms, as described above.

Another of the several classes of cyclic nitroxides that can be employed in the practice of the present invention can be represented by the following structural formula:



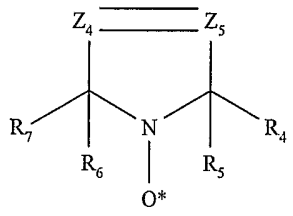
wherein Z_1 and Z_2, which may be the same or different, are nitrogen or substituted or unsubstituted carbon atoms, such as =C(H)-, =C(CH_3)-, =C(COOH)-, =C($COOCH_3$)-, =C($COOC_2H_5$)-, =C(OH)-, =C(CN)-, =C(NR_8R_9)-, =C($CONR_8R_9$)-, and the like, and where Z_3, R_8, and R_9 are as described above.

The cyclic nitroxides employed in the practice of the present invention can also be derived from five-membered rings. These compounds are of the structure:



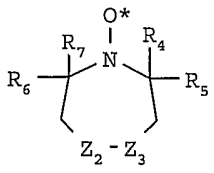
wherein Z_2 and Z_3, which may be the same or different, are sulfur, oxygen, secondary amines, tertiary amines, phosphorus of various oxidation states, or substituted or unsubstituted carbon atoms, such as, $>CH_2$, $>CHCH_3$, $>C=O$, $>C(CH_3)_2$, $>CHBr$, $>CHCl$, $>CHI$, $>CHF$, $>CHOH$, $>CHCN$, $>C(OH)CN$, $>CHCOOH$, $>CHCOOCH_3$, $>CHCOOC_2H_5$, $>C(OH)COOC_2H_5$, $>C(OH)COOCH_3$, $>C(OH)CHOHC_2H_5$, $>CR_8OR_9$, $>CHNR_8R_9$, $>CCONR_8R_9$, $>C=NOH$, $>C=CH\text{-}C_6H_5$, CF_2, CCl_2, CBr_2, CI_2, $>CR_8PR_{13}R_{14}R_{15}$, and the like, wherein the several R groups are as described above.

The cyclic nitroxides employed in the practice of the present invention can also have the structure:



wherein Z_4 and Z_5, which can be the same or different, can be nitrogen or a substituted or unsubstituted carbon atom, such as $=C(H)\text{-}$, $=C(CH_3)\text{-}$, $=C(COOH)\text{-}$, $=C(COOCH_3)\text{-}$, $=C(COOC_2H_5)\text{-}$, $=C(OH)\text{-}$, $=C(CN)\text{-}$, $=C(NR_8R_9)\text{-}$, $=C(CONR_8R_9)\text{-}$, and the like, where R_8 and R_9 are as described above.

Another class of cyclic nitroxides that can be employed in the practice of the present invention is of the structure:



wherein Z_2 and Z_3, which may be the same or different, are sulfur, oxygen, secondary amines, tertiary amines, or substituted or unsubstituted carbon atoms, such as, $>CH_2$, $>CHCH_3$, >C=O, $>C(CH_3)_2$, >CHBr, >CHCl, >CHI, >CHF, >CHOH, >CHCN, >C(OH)CN, >CHCOOH, $>CHCOOCH_3$, $>CHCOOC_2H_5$, $>C(OH)COOC_2H_5$, $>C(OH)COOCH_3$, $>C(OH)CHOHC_2H_5$, $>CHNR_8R_9$, $>CCONR_8R_9$, $>CR_8OR_9$, >C=NOH, $>C=CH\text{-}C_6H_5$, CF_2, CCl_2, CBr_2, CI_2, $>CR_8PR_{13}R_{14}R_{15}$, and the like, where the several R groups are as described above.

Further, two or more nitroxyl groups can be present in the same molecule, for example, by being linked through one or more of the Z-type moieties by a linking group E, as disclosed in U.S. Patent Number 5,254,760, which is incorporated herein by reference.

As stated above, for all the nitroxyl structures above, R_4 and R_7 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl and R_5 and R_6 are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl. The alkyl (or heteroatom-substituted alkyl) groups R_4 through R_7 can be the same or different and preferably contain 1 to 15 carbon atoms, e.g., methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, and the like, and isomers thereof, e.g., t-butyl, 2-ethylhexyl, and the like. It is more preferred that R_4 through R_7 be independently selected lower alkyl (or heteroatom-substituted lower alkyl) of one to five carbon atoms (e.g., methyl, ethyl, propyl, butyl, pentyl, and isomers thereof). Where heteroatom substituents are present, they can, for example, include halogen, oxygen, sulfur, nitrogen, and the like. It is most preferred that all of R_4 through R_7 be methyl.

0234-PA

Examples of suitable nitroxide free radical compounds that can be used in combination with the hydrogen donor or electron acceptor in the practice of the present invention, include, but are not limited to:

N,N-di-*tert*-butylnitroxide;

N,N-di-*tert*-amylnitroxide;

N-*tert*-butyl-2-methyl-1-phenyl-propylnitroxide;

N-*tert*-butyl-1-diethylphosphono-2,2-dimethylpropylnitroxide;

2,2,6,6-tetramethyl-piperidinyloxy;

4-amino-2,2,6,6-tetramethyl-piperidinyloxy;

4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-oxo-2,2,6,6-tetramethyl-piperidinyloxy;

4-dimethylamino-2,2,6,6-tetramethyl-piperidinyloxy;

4-ethanoyloxy-2,2,6,6-tetramethyl-piperidinyloxy;

2,2,5,5-tetramethylpyrrolidinyloxy;

3-amino-2,2,5,5-tetramethylpyrrolidinyloxy;

2,2,4,4-tetramethyl-1-oxa-3-azacyclopentyl-3-oxy;

2,2,4,4-tetramethyl-1-oxa-3-pyrrolinyl-1-oxy-3-carboxylic acid;

2,2,3,3,5,5,6,6-octamethyl-1,4-diazacyclohexyl-1,4-dioxy;

4-bromo-2,2,6,6-tetramethyl-piperidinyloxy;

4-chloro-2,2,6,6-tetramethyl-piperidinyloxy;

4-iodo-2,2,6,6-tetramethyl-piperidinyloxy;

4-fluoro-2,2,6,6-tetramethyl-piperidinyloxy;

0234-PA

4-cyano-2,2,6,6-tetramethyl-piperidinyloxy;

4-carboxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-carbomethoxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-carbethoxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-cyano-4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-methyl-2,2,6,6-tetramethyl-piperidinyloxy;

4-carbethoxy-4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy;

4-hydroxy-4-(1-hydroxypropyl)-2,2,6,6-tetramethyl-piperidinyloxy;

4-methyl-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

4-carboxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

4-carbomethoxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

4-carbethoxy-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

4-amino-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

4-amido-2,2,6,6-tetramethyl-1,2,5,6-tetrahydropyridine -1-oxyl;

3,4-diketo-2,2,5,5-tetramethylpyrrolidinyloxy;

3-keto-4-oximino-2,2,5,5-tetramethylpyrrolidinyloxy;

3-keto-4-benzylidine-2,2,5,5-tetramethylpyrrolidinyloxy;

3-keto-4,4-dibromo-2,2,5,5-tetramethylpyrrolidinyloxy;

2,2,3,3,5,5-hexamethylpyrrolidinyloxy;

3-carboximido-2,2,5,5-tetramethylpyrrolidinyloxy;

3-oximino-2,2,5,5-tetramethylpyrrolidinyloxy;

3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

0234-PA

3-cyano-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

3-carbomethoxy-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

3-carbethoxy-3-hydroxy-2,2,5,5-tetramethylpyrrolidinyloxy;

2,2,5,5-tetramethyl-3-carboxamido-2,5-dihydropyrrole-1-oxyl;

2,2,5,5-tetramethyl-3-amino-2,5-dihydropyrrole-1-oxyl;

2,2,5,5-tetramethyl-3-carbethoxy-2,5-dihydropyrrole-1-oxyl;

2,2,5,5-tetramethyl-3-cyano-2,5-dihydropyrrole-1-oxyl;

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)sebacate;

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;

4,4'-ethylenebis(1-oxyl-2,2,6,6-tetramethylpiperazin-3-one); and the like.

0234-PA

As used herein, the abbreviation TEMPO stands for 2,2,6,6-tetramethyl-1-piperidinyloxy. Thus, 4-amino-TEMPO is 4-amino-2,2,6,6-tetramethyl-1-piperidinyloxy; 4-hydroxy-TEMPO is 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (also known in the art as HTEMPO); 4-oxo-TEMPO is 4-oxo-2,2,6,6-tetramethyl-1-piperidinyloxy; and so on.

It is preferred that one member of the combination employed in the practice of the present invention be 4-amino-TEMPO, 4-oxo-TEMPO, 4-hydroxy-TEMPO, or TEMPO.

Blends of two or more of the foregoing, e.g., 4-amino-TEMPO and 4-oxo-TEMPO, can also be employed.

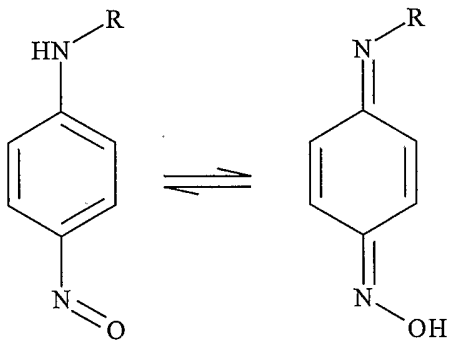
Such stable nitroxide free radical compounds can be prepared by known methods. (See, for example, U.S. Patent Numbers 3,163,677; 3,334,103; 3,372,182; 3,422,144; 3,494,930; 3,502,692; 3,873,564; 3,966,711; and 4,665,185; which are incorporated herein by reference.) They are suitable for use over a wide range of temperatures, but distillation temperatures employed with the ethylenically unsaturated monomers that are stabilized by the process of the present invention typically range from about 60°C to about 180°C, preferably from about 70°C to about 165°C, and, more preferably, from about 80°C to about 150°C. Such distillations are generally performed at an absolute pressure in the range of about 10 to about 1,200 mm of Hg.

Where the inhibiting system of the present invention comprises an additional inhibitor that is a nitrosoaniline, it can be an N-nitrosoaniline or a C-nitrosoaniline. Preferably, the nitrosoaniline compound is a C-nitrosoaniline.

0234-PA

C-nitrosoaniline compounds can be prepared by C-nitrosation of the corresponding anilines in any typical manner used for the C-nitrosation of aromatic amines. For example, reaction of the amine with cold nitrous acid produces an N-nitroso compound that rearranges to a para-nitrosoaniline under the influence of an excess of hydrochloric acid. In some cases, it is more convenient to effect the nitrosation and rearrangement in one step by conducting the reaction in methanol solution in the presence of an excess of hydrogen chloride under anhydrous conditions. This procedure is described in U.S. Patent Number 2,046,356.

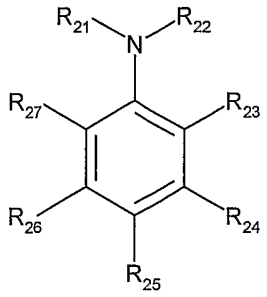
Those skilled in the art will be aware that nitrosoaniline derivatives are understood to tautomerize to quinone imine oxime derivatives, i.e.,



See, for example, Sidgwick, N.V., *The Organic Chemistry of Nitrogen,* Third Edition, Clarendon Press, Oxford, 1966. Thus, both forms can be present, especially in solution at elevated temperatures, and can be expected to contribute to the inhibiting activity of these compounds.

The nitrosoanilines that can be employed in the practice of the present invention are preferably of the structure:

0234-PA



wherein

R_{21} and R_{22} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, hydroxyl, alkoxy, nitroso, and sulfonyl, or R_{21} and R_{22} can form a cyclic ring that is aryl, cycloalkyl, polyaryl, or heterocyclic;

R_{23} through R_{27} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, hydroxyl, alkoxy, acyloxy, $NR_{28}(R_{29})$, nitro, nitroso, halogen, and sulfonyl, or any two adjacent R's can form a cyclic ring that is aryl, cycloalkyl, polyaryl, or heterocyclic, provided that at least one of R_{23} through R_{27} must be a nitroso group; and

R_{28} and R_{29} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, and nitroso. Preferably R_{28} is hydrogen and R_{29} is alkyl.

Where the inhibiting system of the present invention comprises an additional inhibitor that is an amine, the amine can be a primary, secondary, or tertiary amine, and can comprise alkyl groups, aryl groups, or combinations thereof. Such amines include, but are not limited to, α-naphthylamine, thiodiarylamines, *p*-phenylenediamine, *o*-phenylenediamine, 2,4-diamino diphenylamine, cyclohexyl naphthyl amine, polybutyl amines, methyl aniline, diphenyl-*p*-phenylene diamine, phenyl-β-naphthylamine, isopropoxydiphenylamine, aldol-α-naphthyl amine, symmetrical di-β-naphthyl-*p*-phenylenediamine, trimethyl dihydroquinoline,

ditolylamines, phenyl-α-naphthylamine, phenyl-β-naphthylamine, diaminophenol, 4-cyclohexylaminophenol, *p*-aminophenol, *o*-aminophenol, 5-amino-2-hydroxytoluene, and the like.

The ethylenically unsaturated monomer, the premature polymerization and polymer growth of which is an object of the present invention, can be any such monomer for which unintended polymerization and/or polymer growth during its manufacture, storage, and/or distribution is a problem. Among those monomers that will benefit from the practice of the present invention are: styrene, α-methylstyrene, styrene sulfonic acid, vinyltoluene, divinylbenzenes, polyvinylbenzenes, alkylated styrene, 2-vinylpyridine, acrylonitrile, methacrylonitrile, methyl acrylate, ethyl acrylate, methyl methacrylate, ethyl methacrylate, acrylic acid, methacrylic acid, butadiene, chloroprene, isoprene, and the like.

The ethylenically unsaturated monomers will not necessarily be stabilized indefinitely by the presence of the inhibitor(s), especially when the monomers are heated as in distillation, but they can be considered to be stabilized as long as A) there is a measurable increase in the time for which they can be heated before the onset of polymerization and/or polymer growth in a static system, B) the amount of polymer made at a constant temperature remains constant over time in a dynamic system, and/or C) the rate of polymer growth is significantly slower than when the growth inhibiting system is not present.

Those skilled in the art will understand that, if desired, free radical scavengers can also be included in the practice of the present invention. For example, air or O_2, as disclosed in U.S. Patent Numbers 5,545,782 and 5,545,786, can be added, as can the aromatic nitro compounds disclosed in U.S. Patent Number 5,254,760, the dihetero-substituted benzene

compounds having at least one transferable hydrogen, e.g., a quinone derivative such as the mono-methyl-ether of hydroquinone disclosed in European Patent Application 0 765 856 A1, the iron compounds disclosed in WO 98/25872, and other inhibitors, e.g., phenolics and certain inorganic salts, well-known to those skilled in the art.

The polymerization inhibitors can be introduced into the monomer to be protected by any conventional method. They can, for example, be added as a concentrated solution in suitable solvents just upstream from the point of desired application by any suitable means. In addition, individual inhibiting components can be injected separately into the distillation train along with the incoming feed and/or through separate and multiple entry points, provided there is an efficient distribution of the inhibiting composition. Since the inhibitors are gradually depleted during the distillation operation, it is generally advantageous to maintain the appropriate amount of them in the distillation apparatus by adding them during the course of the distillation process. Adding inhibitors can be done either on a generally continuous basis or intermittently, in order to maintain the inhibitor concentration above the minimum required level.

The total inhibitor concentration should be from about 1 to about 2000 ppm versus the monomer being inhibited; preferably from about 5 to about 1000 ppm, depending on the conditions of use.

The ratio of the first component (A) to the second component (B), based on the total of both components is from about 1 to 100 wt % A : about 99 to 0 wt % B; preferably, about 25-75 wt % A : about 75-25 wt% B; more preferably about 50-75 wt % A : about 50-25 wt % B.

The advantages and the important features of the present invention will be more apparent from the following examples.

EXAMPLES

Example 1

Concentrated H_2SO_4 (280 grams, 2.8 moles) was placed in a one liter flask equipped with a mechanical stirrer, thermocouple, heating mantle, condenser, and plastic tube. The acid was preheated to 40°C and 300 grams of o-sec-butylphenol (OSBP) (2 moles) was loaded through the plastic tube fast enough to heat the system to 82°C. The initial temperature of 40°C reached 82°C after 40 minutes. After that, the reaction mixture had to be heated to maintain the temperature at 82°C. The addition took 1 hour and 45 minutes. The product, sulfonated OSBP (SOSBP), was used for inhibitor performance tests in the presence of DNBP.

Example 2

The styrene inhibitor and retarder properties of this material were tested in a Continuous Dynamic Reboiler Test monitoring the polymer formation with UV spectrophotometry. According to this test, the inhibitor is added to styrene monomer from which *tert*-butylcatechol (TBC) is previously removed by distillation. This styrene (180 grams) is loaded into a flask, which is immersed into an oil bath. The temperature of styrene is usually 116°C. During the test, a fresh feed is charged into the flask at the rate of three grams/minute and, at the same time, the material from flask is discharged at the same rate. The steady stage is continued until equilibrium. For feed shut off stage, the charging and discharging are discontinued. Samples are taken every hour at the steady stage and every 5-

10 minutes at feed shut off.

After 5 hours of steady stage, at 50 ppm/100 ppm SOSBP/DNBP concentration, 0.0007 % polymer was measured while 1.5 hour feed shut off resulted in 0.024 % polymer.

Example 3

Continuous Dynamic Reboiler Test of SOSBP/NMP/DNBP at a concentration of 250 ppm/285 ppm/250 ppm resulted in 0.0039 polymer in steady stage and 0.25% polymer after two hours feed shut off. NMP (1-methyl-2-pyrrolidinone) was added to neutralize the acidic SOSBP.

Example 4

Continuous Dynamic Reboiler Test of SOSBP/DNBP at a concentration of 250 ppm/250 ppm resulted in 0.0004 % polymer in 5 hours steady stage and 0.025 % polymer after 2 hours feed shut off.

Example 5

Continuous Dynamic Reboiler Test of N,N-diethyl-4-nitrosoaniline/SOSBP/NMP/DNBP at a concentration of 100 ppm/250 ppm/170 ppm/250 ppm resulted in 0.0038 % polymer in 5 hours steady stage and 0.315 % polymer after 2 hours feed shut off.

Example 6

Continuous Dynamic Reboiler Test of 4-oxo-TEMPO/SOSBP/NMP/DNBP at a concentration of 100 ppm/250 ppm/187 ppm/250 ppm resulted in 0.0004 % polymer in 5 hours steady stage and 0.016 % polymer after 2 hours feed shut off.

0234-PA

Example 7

Continuous Dynamic Reboiler Test of DNBP alone at 500 ppm concentration revealed 0.11 % of polymer in steady stage and 1.18 % of polymer after 2 hours feed shut off.

In view of the many changes and modifications that can be made without departing from principles underlying the invention, reference should be made to the appended claims for an understanding of the scope of the protection to be afforded the invention.

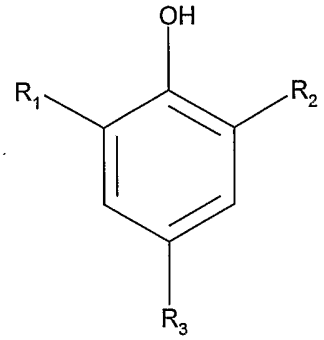
0234-PA

CLAIMS

What is claimed is:

1. A method for inhibiting the premature polymerization and the polymer growth of ethylenically unsaturated monomers comprising adding to said monomers an effective amount of a combination of

(A) at least one inhibitor that is a sulfonated phenol of the formula:



wherein

(1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and

(2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H; and

(B) at least one inhibitor that is a nitrophenol.

2. The method of claim 1 wherein R_2 is a straight chain or branched chain alkyl or alkenyl group of from 1 to 50 carbon atoms.

0234-PA

3. The method of claim 2 wherein R_2 is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, 2-ethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, oleyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, triacontyl, isomers of the foregoing, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and cyclododecyl.

4. The method of claim 3 wherein R_2 is *sec*-butyl.

5. The method of claim 1 wherein the nitrophenol is selected from the group consisting of 2,6-dinitro-4-methylphenol, 2-nitro-4-methylphenol, 2,4-dinitro-1-naphthol, 2,4,6-trinitrophenol (picric acid), 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol, 2,4-dinitro-6-sec-butylphenol, 4-cyano-2-nitrophenol, 3-iodo-4-cyano-5-nitrophenol, *m*-nitro-*p*-cresol, and 2,6-dinitro-*p*-cresol

6. A method for inhibiting the premature polymerization and the polymer growth of ethylenically unsaturated monomers comprising adding to said monomers an effective amount of a combination of

(A) at least one inhibitor that is a sulfonated phenol of the formula:

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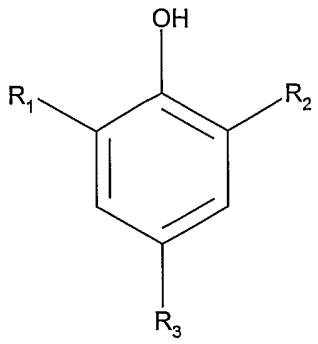


wherein

(1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and

(2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H;

(B) at least one inhibitor that is a nitrophenol;

(C) at least one inhibitor selected from the group consisting of nitroxyl compounds and nitrosoanilines; and

(D) at least one amine.

7. The method of claim 6 wherein R_2 is a straight chain or branched chain alkyl or alkenyl group of from 1 to 50 carbon atoms.

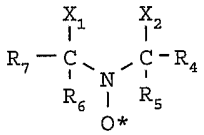
8. The method of claim 7 wherein R_2 is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, 2-ethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, oleyl, nonadecyl,

eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, triacontyl, isomers of the foregoing, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and cyclododecyl.

9. The method of claim 8 wherein R_2 is *sec*-butyl.

10. The method of claim 6 wherein the nitrophenol is selected from the group consisting of 2,6-dinitro-4-methylphenol, 2-nitro-4-methylphenol, 2,4-dinitro-1-naphthol, 2,4,6-trinitrophenol (picric acid), 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol, 2,4-dinitro-6-sec-butylphenol, 4-cyano-2-nitrophenol, 3-iodo-4-cyano-5-nitrophenol, *m*-nitro-*p*-cresol, and 2,6-dinitro-*p*-cresol

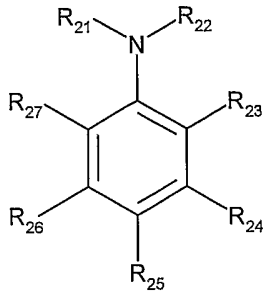
11. The method of claim 6 wherein (C) is a stable hindered nitroxyl compound having the structural formula:



wherein R_4 and R_7 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl and R_5 and R_6 are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl; and X_1 and X_2 (1) are independently selected from the group consisting of halogen, cyano, $COOR_7$, -S-COR_7, -$OCOR_7$, (wherein R_7 is alkyl or aryl), amido, -S-C_6H_5, carbonyl, alkenyl, or alkyl of 1 to 15 carbon atoms, or (2) taken together, form a ring structure with the nitrogen.

0234-PA

12. The method of claim 6 wherein (C) is a nitrosoaniline of the structure:



wherein

R_{21} and R_{22} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, hydroxyl, alkoxy, nitroso, and sulfonyl, or R_{21} and R_{22} can form a cyclic ring that is aryl, cycloalkyl, polyaryl, or heterocyclic;

R_{23} through R_{27} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, hydroxyl, alkoxy, acyloxy, $NR_{28}(R_{29})$, nitro, nitroso, halogen, and sulfonyl, or any two adjacent R's can form a cyclic ring that is aryl, cycloalkyl, polyaryl, or heterocyclic, provided that at least one of R_{23} through R_{27} must be a nitroso group; and

R_{28} and R_{29} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, and nitroso.

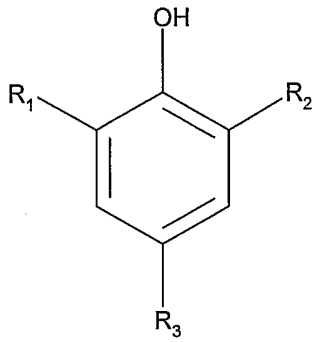
13. The method of claim 6 wherein (D) is selected from the group consisting of α-naphthylamine, thiodiarylamines, *p*-phenylenediamine, *o*-phenylenediamine, 2,4-diamino diphenylamine, cyclohexyl naphthyl amine, polybutyl amines, methyl aniline, diphenyl-*p*-phenylene diamine, phenyl-β-naphthylamine, isopropoxydiphenylamine, aldol-α-naphthyl amine, symmetrical di-β-naphthyl-*p*-phenylenediamine, trimethyl dihydroquinoline,

0234-PA

ditolylamines, phenyl-α-naphthylamine, phenyl-β-naphthylamine, diaminophenol, 4-cyclohexylaminophenol, *p*-aminophenol, *o*-aminophenol, and 5-amino-2-hydroxytoluene.

14. A composition comprising a combination of

(A) at least one inhibitor that is a sulfonated phenol of the formula:



wherein

(1) R_2 is selected from the group consisting of hydrogen and hydrocarbyl; and

(2) R_1 and R_3 are independently selected from the group consisting of hydrogen and SO_3H, provided that at least one of R_1 and R_3 is SO_3H;

(B) at least one inhibitor that is a nitrophenol;

(C) an inhibitor selected from the group consisting of nitroxyl compounds and nitrosoanilines; and

(D) an amine.

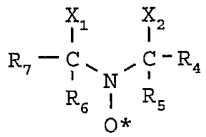
0234-PA

15. The composition of claim 14 wherein R_2 is a straight chain or branched chain alkyl or alkenyl group of from 1 to 50 carbon atoms.

16. The composition of claim 15 wherein R_2 is selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, 2-ethyl hexyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, oleyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, triacontyl, isomers of the foregoing, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, and cyclododecyl.

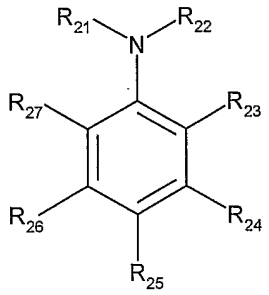
17. The composition of claim 14 wherein the nitrophenol is selected from the group consisting of 2,6-dinitro-4-methylphenol, 2-nitro-4-methylphenol, 2,4-dinitro-1-naphthol, 2,4,6-trinitrophenol (picric acid), 2,4-dinitro-6-methylphenol, 2,4-dinitrophenol, 2,4-dinitro-6-sec-butylphenol, 4-cyano-2-nitrophenol, 3-iodo-4-cyano-5-nitrophenol, *m*-nitro-*p*-cresol, and 2,6-dinitro-*p*-cresol

18. The composition of claim 14 wherein (C) is a stable hindered nitroxyl compound having the structural formula:



wherein R_4 and R_7 are independently selected from the group consisting of hydrogen, alkyl, and heteroatom-substituted alkyl and R_5 and R_6 are independently selected from the group consisting of alkyl and heteroatom-substituted alkyl; and X_1 and X_2 (1) are independently selected from the group consisting of halogen, cyano, $COOR_7$, -S-COR_7, -$OCOR_7$, (wherein R_7 is alkyl or aryl), amido, -S-C_6H_5, carbonyl, alkenyl, or alkyl of 1 to 15 carbon atoms, or (2) taken together, form a ring structure with the nitrogen.

19. The composition of claim 14 wherein (C) is a nitrosoaniline of the structure:



wherein

R_{21} and R_{22} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, hydroxyl, alkoxy, nitroso, and sulfonyl, or R_{21} and R_{22} can form a cyclic ring that is aryl, cycloalkyl, polyaryl, or heterocyclic;

R_{23} through R_{27} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, hydroxyl, alkoxy, acyloxy, $NR_{28}(R_{29})$, nitro, nitroso, halogen, and sulfonyl, or any two adjacent R's can form a cyclic ring that is aryl, cycloalkyl, polyaryl, or heterocyclic, provided that at least one of R_{23} through R_{27} must be a nitroso group; and

R_{28} and R_{29} are independently selected from the group consisting of hydrogen, alkyl, aryl, acyl, and nitroso.

20. The composition of claim 14 wherein (D) is selected from the group consisting of α-naphthylamine, thiodiarylamines, *p*-phenylenediamine, *o*-phenylenediamine, 2,4-diamino diphenylamine, cyclohexyl naphthyl amine, polybutyl amines, methyl aniline, diphenyl-*p*-phenylene diamine, phenyl-β-naphthylamine, isopropoxydiphenylamine, aldol-α-naphthyl amine, symmetrical di-β-naphthyl-*p*-phenylenediamine, trimethyl dihydroquinoline, ditolylamines, phenyl-α-naphthylamine, phenyl-β-naphthylamine, diaminophenol, 4-cyclohexylaminophenol, *p*-aminophenol, *o*-aminophenol, and 5-amino-2-hydroxytoluene.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/026016

A. CLASSIFICATION OF SUBJECT MATTER
C07C7/20 C07C309/42

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 532 240 A (NALCO CHEMICAL COMPANY) 17 March 1993 (1993-03-17) column 1, lines 1-5 column 1, line 55 - column 2, line 14 column 2, line 33 - line 58 claims figure 4	1-20
Y	PATENT ABSTRACTS OF JAPAN vol. 018, no. 615 (C-1277), 24 November 1994 (1994-11-24) & JP 06 234700 A (DAINIPPON INK & CHEM INC), 23 August 1994 (1994-08-23) abstract	1-20
Y	US 4 086 147 A (WATSON ET AL) 25 April 1978 (1978-04-25) claim 1	1-20

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[X] Further documents are listed in the continuation of box C.

[X] 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

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 November 2005	12/12/2005

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	O'Sullivan, P

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/026016

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 4 664 845 A (JANCIS ET AL) 12 May 1987 (1987-05-12) claims	1-20
Y	WO 02/33026 A (UNIROYAL CHEMICAL COMPANY, INC; BENAGE, BRIGITTE) 25 April 2002 (2002-04-25) claims	1-20
Y	WO 03/070687 A (CROMPTON CORPORATION) 28 August 2003 (2003-08-28) page 6, line 15 - page 7, line 21 claim 1	1-20

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