compositions comprising quinone methides.

Later, two classes of inhibitors were used, these being; dialkylhydroxylamines (including hydroxypropylhydroxylamine (HPHA)) and stable nitroxide free radicals. Other inhibitors have been used since then. Examples are N,N'-dialkylphenylenediamines, N,N'-diarylphenylenediamines N-aryl-N'-alkylphenylenediamines. Quinone diimide compounds are also another class of inhibitors. The use of quinone diimides is taught in US Patent 4,774,374, US Patent 5,562,863, US Patent 6,184,276, US Patent 6,447,649 and US Patent 6,592,722.

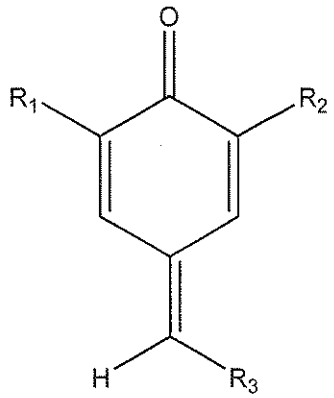
To ensure safety in the event of a plant malfunction, inhibitors are typically not to be used alone but are often combined with retarders.

The art described in this section is not intended to constitute an admission that any patent, publication or other information referred to herein is "prior art" with respect to this invention, unless specifically designated as such. In addition, this section should not be construed to mean that a search has been made or that no other pertinent information as defined in 37 C.F.R. § 1.56(a) exists. Any and all patents, patent applications, and other references cited by this application are hereby incorporated by reference in their entirety.

Brief Summary ~~**of the Invention**~~

At least one embodiment of the present disclosure~~invention~~ is directed towards a method for inhibiting the polymerization of vinyl monomers in a liquid comprising adding to said monomers a composition comprising Compound A and Compound B wherein:

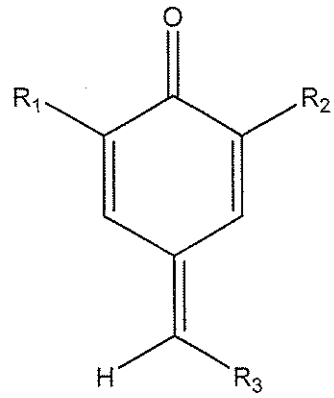
Compound A is a quinone methide compound with the formula:



wherein R_1 and R_2 are independently H, C_4 to C_{18} alkyl; C_5 to C_{12} cycloalkyl; C_7 to C_{15} phenylalkyl, and any combination thereof. Preferably, R_1 and R_2 are *tert*-butyl, *tert*-amyl, *tert*-octyl, cyclohexyl, α-methylbenzyl or α,α-dimethylbenzyl; with *tert*-butyl, *tert*-amyl or *tert*-octyl most preferred, and, R_3 is preferably aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino and carboxy, and R_3 is also preferably nitrile, methoxy, 4-hydroxy-3,5-di-*tert*-butylphenyl, an acetylenic group, or phenyl-substituted acetyleno preferably substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino and carboxy.

In an aspect, there is provided a method of inhibiting polymerization of vinyl monomers in a liquid, comprising adding to said liquid a composition comprising Compound A and Compound B, wherein:

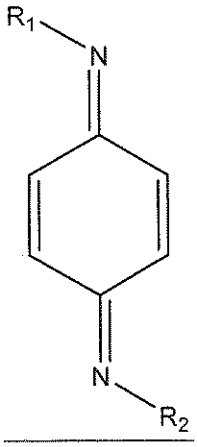
Compound A is a quinone methide compound with the formula:



wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of H, C_4 to C_{18} alkyl, C_5 to C_{12} cycloalkyl, C_7 to C_{15} phenylalkyl, and any combination

thereof, and R_3 is an aryl, an aryl substituted with C_1 to C_6 alkyl, an alkoxy, a nitro, an amino, a carboxy, a nitrile, a methoxy, 4-hydroxy-3,5-di-tert-butylphenyl, an acetylenic group, a phenyl-substituted acetyleno, a phenyl-substituted acetyleno substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino, carboxy, and any combination thereof;

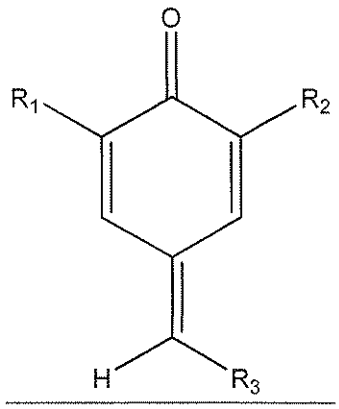
Compound B is a quinone diimide compound of the formula:



wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of an alkyl, an aryl, an alkaryl, and an aralkyl; wherein the weight ratio of Compound A to Compound B is from about 9:1 to about 1:9, and the polymerization is inhibited within an anaerobic environment.

In another aspect, there is provided a method of inhibiting polymerization of vinyl monomers in a liquid comprising adding to said liquid a composition comprising Compound A and Compound B, wherein:

Compound A is a quinone methide compound with the formula:

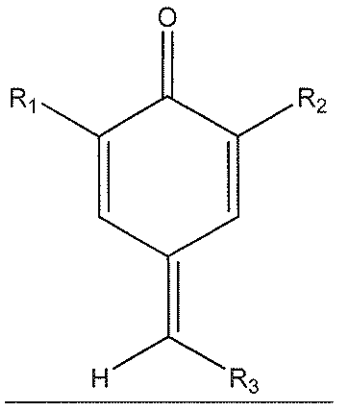


wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of H, C_4 to C_{18} alkyl, C_5 to C_{12} cycloalkyl, C_7 to C_{15} phenylalkyl, and any combination thereof, and, R_3 is aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino and carboxy, nitrile, methoxy, 4-hydroxy-3,5-di-tert-butylphenyl, an acetylenic group, or phenyl-substituted acetyleno, phenyl-substituted acetyleno substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino, carboxy, and any combination thereof;

Compound B is a quinone diimide compound selected from the group consisting of: a N,N'-dialkyl-p-benzoquinonediimide, a N-phenyl-N'-alkyl-p-benzoquinonediimide, and combinations thereof; wherein the weight ratio of Compound A to Compound B is from about 9:1 to about 1:9, and the polymerization is inhibited within an anaerobic environment.

In another aspect, there is provided a method of inhibiting polymerization of vinyl monomers in a liquid comprising adding to said liquid a composition comprising Compound A and Compound B, wherein:

Compound A is a quinone methide compound with the formula:



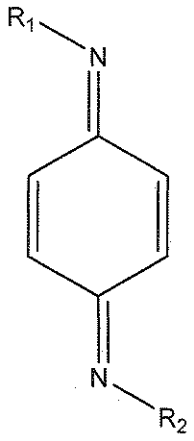
wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of H, C_4 to C_{18} alkyl, C_5 to C_{12} cycloalkyl, C_7 to C_{15} phenylalkyl, and any combination thereof, and R_3 is aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino and carboxy, nitrile, methoxy, 4-hydroxy-3,5-di-tert-butylphenyl, an acetylenic group, or phenyl-substituted acetyleno, phenyl-substituted acetyleno substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino, carboxy, and any combination thereof;

Compound B is a quinone diimide compound selected from the group consisting of: N,N′-di-sec-butyl-p-benzoquinonediimide, N-phenyl-N′-methyl-p-benzoquinonediimide, N-phenyl-N′-ethyl-p-benzoquinonediimide, N-phenyl-N′-propyl-p-benzoquinonediimide, N-phenyl-N′-n-butyl-p-benzoquinonediimide, N-phenyl-N′-iso-butyl-p-benzoquinonediimide, N-phenyl-N′-sec-butyl-p-benzoquinonediimide, N-phenyl-N′-tert-butyl-p-benzoquinonediimide, N-phenyl-N′-n-pentyl-p-benzoquinonediimide, N-phenyl-N′-(1-methylhexyl)-p-benzoquinonediimide, N-phenyl-N′-(1,3-dimethylhexyl)-p-benzoquinonediimide, N,N′-bis(1,4-dimethylpentyl)-p-benzoquinonediimide, N-phenyl-N′-(1,4-dimethylpentyl)-p-benzoquinonediimide and N-phenyl-N′-(1,4-dimethylbutyl)-p-benzoquinonediimide, and combinations thereof; wherein the weight

ratio of Compound A to Compound B is from about 9:1 to about 1:9, and the polymerization is inhibited within an anaerobic environment.

At least one embodiment of the present disclosure~~invention~~ is directed towards a composition comprising Compound A and Compound B wherein:

Compound B is a quinone diimide compound of the formula:

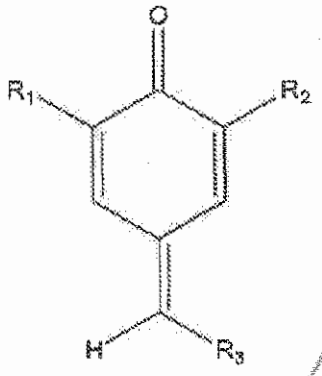


in which substituents R_1 and R_2 are the same or different and are alkyl, aryl, alkaryl, aralkyl

Claims

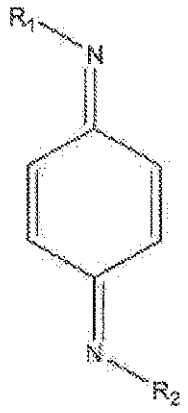
1. A method for inhibiting the polymerization of vinyl monomers in a liquid comprising adding to said monomers a composition comprising Compound A and Compound B, wherein: m

Compound A is a quinone methide compound with the formula:



wherein R_1 and R_2 are independently one selected from the list consisting of H, C_4 to C_{18} alkyl, C_5 to C_{12} cycloalkyl, C_7 to C_{15} phenylalkyl, and any combination thereof, having an arrangement which is selected from the list consisting of alkyl, *tert*-butyl, *tert*-amyl, *tert*-octyl, cyclohexyl, α-methylbenzyl, α,α-dimethylbenzyl, and any combination thereof, and, R_3 is aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino and carboxy, nitrile, methoxy, 4-hydroxy-3,5-di-*tert*-butylphenyl, an acetylenic group, or phenyl-substituted acetyleno, phenyl-substituted acetyleno substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino, carboxy, and any combination thereof;

Compound B is a quinone diimide compound of the formula:



in which R_1 and R_2 are the same or different and are alkyl, aryl, alkaryl, or aralkyl groups wherein the weight ratio of Compound A to Compound B is about 9:1 to about 1:9.

2. The method of claim 1 in which Compound A is preferably a stable quinone methide selected form the list consisting of: 7-cyano quinone methide (2-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)acetonitrile, a 7-substituted-quinone methide also called 2,6-di-*tert*-butyl-7-cyano quinone methide), 4-Benzylidene-2,6-di-*tert*-butyl-cyclohexa-2,5-dienone also called 7-phenyl quinone methide, 2,6-di-*tert*-butyl-4-(methoxymethylene)cyclohexa-2,5-dienone also called 7-methoxy quinone methide, 2,6-di-*tert*-butyl-4-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)cyclohexa-2,5-dienone also called 7-(4-hydroxy-3,5-di-*tert*-butylphenyl) quinone methide, and any combination thereof.

3. The method of claim 1 in which Compound B is a quinone diimide.

4. The method of claim 3 in which Compound B is benzoquinonediimide compound N,N'-(cyclohexa-2,5-diene-1,4-diylidene)dibutan-1-amine.

5. The method of claim 3 in which Compound B is benzoquinonediimide compound (E)-N-((E)-4-(4-methylpentan-2-ylimino)cyclohexa-2,5-dienylidene)aniline.

6. The method of claim 1 in which the monomer is a vinylic monomer.

7. The method of claim 1 in which amount of said composition added to the monomer varies

from 1 to 10,000 parts per million of said monomer.

8. The method of claim 1 in which the weight proportion of Compound A to Compound B is between about 9:1 and about 1:9 to about 1:1.

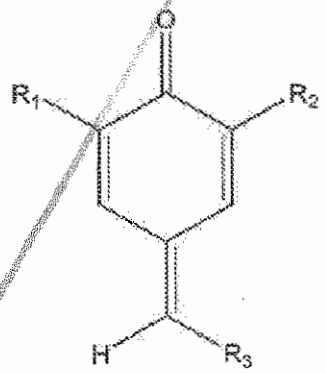
9. The method of claim 1 in which the weight proportion of Compound A to to quinone diimide ranges from 4:6 to 6:4.

10. The method of claim 1 in which the polymerization is substantially inhibited.

11. The method of claim 1 in which the polymerization is inhibited within an anaerobic environment.

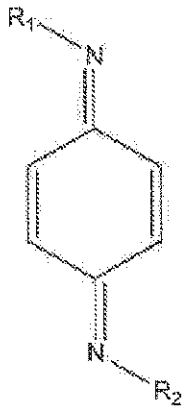
12. The method of claim 1 in which the inhibition is more effective than the linear combination of the effectiveness of an inhibitor consisting essentially of quinone diimide (compound B) with the effectiveness of an inhibitor consisting essentially of quinone methide (compound A).

13. A composition in which Compound A is a quinone methide compound with the formula;



wherein R_1 and R_2 are independently H, C_4 to C_{18} alkyl; C_5 to C_{12} cycloalkyl; or C_7 to C_{15} phenylalkyl. Preferably, R_1 and R_2 are *tert*-butyl, *tert*-amyl, *tert*-octyl, cyclohexyl, α-methylbenzyl or α,α-dimethylbenzyl; with *tert*-butyl, *tert*-amyl or *tert*-octyl most preferred, and, R_3 is also preferably nitrile, aryl, methoxy, 4-hydroxy-3,5-di-*tert*-butylphenyl, an acetylenic group, or phenyl-substituted acetyleno preferably substituted with C_1 to C_6 alkyl, alkoxy, nitro,

amino and carboxy, and (B) a quinone diimide compound of the formula



in which substituents R_1 and R_2 are the same or different and are alkyl, aryl, alkaryl, or aralkyl groups wherein the weight ratio of Compound A to Compound B is about 9:1 to about 1:9.

14. The composition in claim 13 in which the quinone methide compounds are (2-(3,5-di-*tert*-butyl-4-oxocyclohexa-2,5-dienylidene)acetonitrile (also called 7-cyano quinone methide), 2,6-di-*tert*-butyl-4-(methoxymethylene)cyclohexa-2,5-dienone (also called 7-methoxy quinone methide), 2,6-di-*tert*-butyl-4-(3,5-di-*tert*-butyl-4-hydroxybenzylidene)cyclohexa-2,5-dienone (also called 7-(4-hydroxy-3,5-di-*tert*-butylphenyl) quinone methide) and 4-benzylidene-2,6-di-*tert*-butyl-cyclohexa-2,5-dienone (also called 7-phenyl quinone methide).

15. The composition in claim 13 in which the quinone diimide compound is N,N'-(cyclohexa-2,5-diene-1,4-diylidene)dibutan-1-amine.

16. The composition in claim 13 in which the quinone diimide compound is (E)-N-((E)-4-(4-methylpentan-2-ylimino)cyclohexa-2,5-dienylidene)aniline.

17. The composition in claim 13 in which the weight ratio of Compound A and Compound B is between about 9:1 to about 1:9.

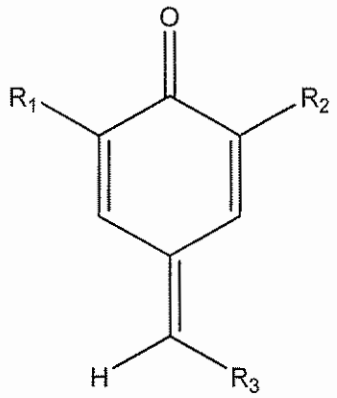
18. The composition in claim 13 in which the weight ratio of Compound A and Compound B is about 4:6 to 6:4.

19. The composition in claim 13 in which there is synergism between Compound A and Compound B as an inhibitor of vinyl monomer polymerization.

Claims

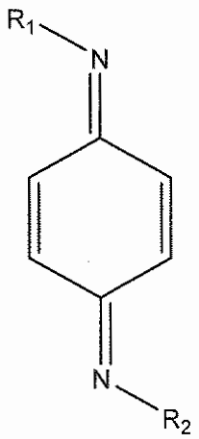
1. A method of inhibiting polymerization of vinyl monomers in a liquid, comprising adding to said liquid a composition comprising Compound A and Compound B, wherein:

Compound A is a quinone methide compound with the formula:



wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of H, C_4 to C_{18} alkyl, C_5 to C_{12} cycloalkyl, C_7 to C_{15} phenylalkyl, and any combination thereof, and R_3 is an aryl, an aryl substituted with C_1 to C_6 alkyl, an alkoxy, a nitro, an amino, a carboxy, a nitrile, a methoxy, 4-hydroxy-3,5-di-tert-butylphenyl, an acetylenic group, a phenyl-substituted acetyleno, a phenyl-substituted acetyleno substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino, carboxy, and any combination thereof;

Compound B is a quinone diimide compound of the formula:



wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of an alkyl, an aryl, an alkaryl, and an aralkyl; wherein the weight ratio of Compound A to Compound B is from about 9:1 to about 1:9, and the polymerization is inhibited within an anaerobic environment.

2. The method of claim 1, wherein Compound A is a stable quinone methide selected from the group consisting of: 2-(3,5-di-tert-butyl-4-oxocyclohexa-2,5-dienylidene)acetonitrile; 2,6-di-tert-butyl-7-cyano quinone methide; 4 benzylidene-2,6-di-tert-butyl-cyclohexa-2,5-dienone; 2,6-di-tert-butyl-4-(methoxymethylene)cyclohexa-2,5-dienone; 2,6-di-tert-butyl-4-(3,5-di-tert-butyl-4-hydroxybenzylidene)cyclohexa-2,5-dienone; and any combination thereof.

3. The method of claim 1, wherein Compound B is benzoquinonediimide compound N,N'-(cyclohexa-2,5-diene-1,4-diylidene)dibutan-1-amine.

4. The method of claim 1, wherein Compound B is benzoquinonediimide compound (E)-N-((E)-4-(4-methylpentan-2-ylimino)cyclohexa-2,5-dienylidene)aniline.

5. The method of claim 1, wherein said composition is added to the liquid in an amount of from about 1 to about 10,000 parts per million of said monomer.

6. The method of claim 1, wherein the weight proportion of Compound A to Compound B is about 1:1.

7. The method of claim 1, wherein the weight proportion of Compound A to Compound B ranges from about 6:4 to about 4:6.

8. The method of claim 1, wherein the polymerization is substantially inhibited.

9. The method of claim 1, wherein the inhibition is more effective than the linear combination of the effectiveness of an inhibitor consisting essentially of Compound B with the effectiveness of an inhibitor consisting essentially of Compound A.

10. The method of claim 1, wherein said composition is added to the liquid in an amount of from about 1 to about 1000 parts per million of said monomers.

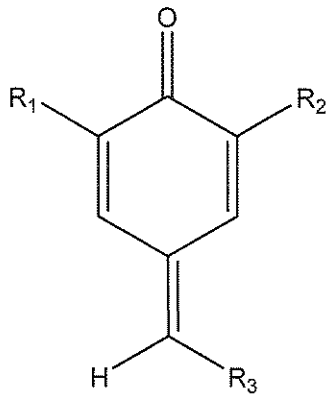
11. The method of claim 1, wherein the weight ratio of Compound A to Compound B is from about 9:1 to about 3:7.

12. The method of claim 1, wherein, when R_1 is not H, R_1 is selected from the group consisting of tert-butyl, tert-amyl, tert-octyl, cyclohexyl, α-methylbenzyl, α,α-dimethylbenzyl, and any combination thereof.

13. The method of claim 1, wherein, when R_2 is not H, R_2 is selected from the group consisting of tert-butyl, tert-amyl, tert-octyl, cyclohexyl, α-methylbenzyl, α,α-dimethylbenzyl, and any combination thereof.

14. A method of inhibiting polymerization of vinyl monomers in a liquid comprising adding to said liquid a composition comprising Compound A and Compound B, wherein:

Compound A is a quinone methide compound with the formula:



wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of H, C_4 to C_{18} alkyl, C_5 to C_{12} cycloalkyl, C_7 to C_{15} phenylalkyl, and any combination thereof, and, R_3 is aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino and carboxy, nitrile, methoxy, 4-hydroxy-3,5-di-tert-butylphenyl, an acetylenic group, or phenyl-substituted acetyleno, phenyl-substituted acetyleno substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino, carboxy, and any combination thereof;

Compound B is a quinone diimide compound selected from the group consisting of: a N,N′-dialkyl-p-benzoquinonediimide, a N-phenyl-N′-alkyl-p-benzoquinonediimide, and combinations thereof; wherein the weight ratio of Compound A to Compound B is from about 9:1 to about 1:9, and the polymerization is inhibited within an anaerobic environment.

15. The method of claim 14, wherein said composition is added to the liquid in an amount of from about 1 to about 10,000 parts per million of said monomer.

16. The method of claim 14, wherein said composition is added to the liquid in an amount of from about 1 to about 1000 parts per million of said monomer.

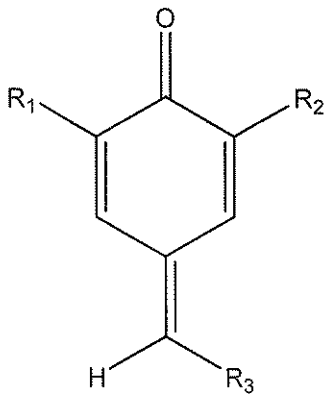
17. The method of claim 14, wherein the weight proportion of Compound A to Compound B ranges from about 9:1 to about 3:7.

18. The method of claim 14, wherein the weight proportion of Compound A to Compound B ranges from about 6:4 to about 4:6.

19. The method of claim 14, wherein the weight proportion of Compound A to Compound B is about 1:1.

20. A method of inhibiting polymerization of vinyl monomers in a liquid comprising adding to said liquid a composition comprising Compound A and Compound B, wherein:

Compound A is a quinone methide compound with the formula:



wherein R_1 and R_2 may be the same or different and each of R_1 and R_2 is selected from the group consisting of H, C_4 to C_{18} alkyl, C_5 to C_{12} cycloalkyl, C_7 to C_{15} phenylalkyl, and any combination thereof, and R_3 is aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino and carboxy, nitrile, methoxy, 4-hydroxy-3,5-di-tert-butylphenyl, an acetylenic group, or phenyl-substituted acetyleno, phenyl-substituted acetyleno substituted with C_1 to C_6 alkyl, alkoxy, nitro, amino, carboxy, and any combination thereof;

Compound B is a quinone diimide compound selected from the group consisting of: N,N'-di-sec-butyl-p-benzoquinonediimide, N-phenyl-N'-methyl-p-benzoquinonediimide, N-phenyl-N'-ethyl-p-benzoquinonediimide, N-phenyl-N'-propyl-p-benzoquinonediimide, N-phenyl-N'-n-butyl-p-benzoquinonediimide, N-phenyl-N'-iso-butyl-p-benzoquinonediimide, N-phenyl-N'-sec-butyl-p-benzoquinonediimide, N-phenyl-N'-tert-butyl-p-benzoquinonediimide, N-phenyl-N'-n-pentyl-p-benzoquinonediimide, N-phenyl-N'-(1-methylhexyl)-p-benzoquinonediimide, N-phenyl-N'-(1,3-dimethylhexyl)-p-benzoquinonediimide, N,N'-bis(1,4-dimethylpentyl)-p-benzoquinonediimide, N-phenyl-N'-(1,4-dimethylpentyl)-p-benzoquinonediimide and N-phenyl-N'-(1,4-dimethylbutyl)-p-benzoquinonediimide, and combinations thereof; wherein the weight ratio of Compound A to Compound B is from about 9:1 to about 1:9, and the polymerization is inhibited within an anaerobic environment.