These 7-alkyl quinone methide compounds, however, are not stable enough for sustained use in industrial settings especially in the case of emergency shutdown. Stable quinone methides are more desirable. Other applications of quinone methides are found in US Patent Numbers 5,583,247, and 7,045,647. Previous examples of inhibitor-retarder combinations that use DNP are disclosed in US Patent Numbers 5,446,220 and 6,024,894. These combinations were found to be more effective than DNP alone.

As taught in US Patents 5,750,765, 5,670,692, 6,926,820 and 7,651,635 some quinone methides have proven effective and are a "green" non-toxic inhibitor-retarder combination for use in preventing the premature polymerization of styrene and other vinyl aromatic monomers. US Published Patent Application 2009/0287013 discusses the synthesis of one such quinone methide, a manufacturing method that involves the use of highly toxic cyanide that has to be handled with great care. Therefore there is a clear utility and novelty in effective methods of synthesizing other efficient quinone methides. Equally as important, there is a need for retarders that are as efficient as DNBP but as safe as prior art quinone methide compounds.

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.

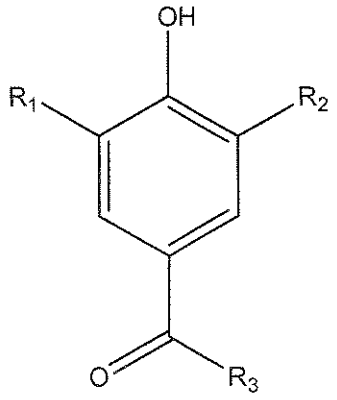
Brief Summary ~~of the Invention~~

~~At least o~~One aspect~~embodiment~~ of the present disclosure~~invention~~ is directed towards a method for the synthesis of 7-Acetyleno quinone methides. The method comprises the steps of: a) performing a condensation reaction between a 3,5-di-substituted-4-hydroxybenzaldehyde and a secondary

amine thereby forming a secondary amine quinone methide intermediate; b) removing water from the secondary amine quinone methide intermediate in a high boiling point ~~aliphatic and also aromatic~~ hydrocarbon solvent by azeotropic distillation at a temperature of between 100 and 160 °C, said hydrocarbon solvent being one from the group consisting of an aliphatic solvent, an aromatic solvent, and any combination thereof; c) adding the dehydrated secondary amine quinone methide intermediate to an organic medium containing a metal acetylide to form a Mannich base intermediate, and d) adding a release agent to the Mannich base intermediate to yield a 7-Acetyleno quinone methide.

In another aspect, there is provided a method for the synthesis of 7-Acetyleno quinone methides, the method comprising the steps of: a) performing a condensation reaction between a 3,5-di-substituted-4-hydroxybenzaldehyde and a secondary amine thereby forming a secondary amine quinone methide intermediate; b) removing water from the secondary amine quinone methide intermediate in a high boiling point hydrocarbon solvent by azeotropic distillation at a temperature of between 100 and 160°C; c) adding the dehydrated secondary amine quinone methide intermediate to an organic medium containing a metal acetylide to form a Mannich base intermediate, and d) adding a release agent to the Mannich base intermediate to yield a 7-Acetyleno quinone methide.

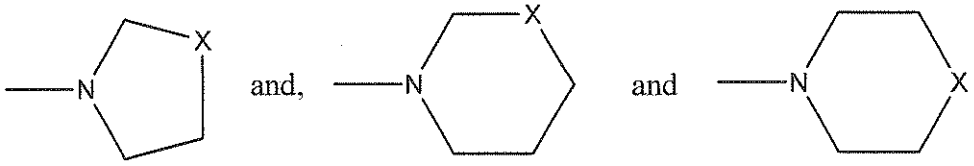
The 3,5-di-substituted-4-hydroxybenzaldehyde may have the formula:



where R_1 and R_2 are independently selected from C_4-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl and C_7-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. R_3 is H.

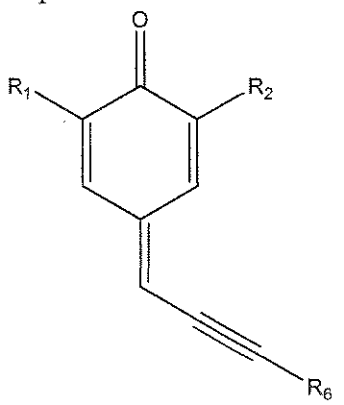
The secondary amine may be an N,N-disubstitutedamino group, and more specifically a 5-membered heterocyclic group and also a 6-membered heterocyclic group with the structures:

phenylalkyl. Z may be a secondary N,N-disubstitutedamino group, and more specifically may be a 5-membered and 6-membered heterocyclic groups with the structures:



X may be CH_2, O, S, NR_4, and R_4 is selected from C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl and C_7-C_{15} phenylalkyl, and any combination thereof. Z may be a 5-membered heterocyclic group and/or a 6-membered heterocyclic group in which X is CH_2 and O. More preferably X in claim 9 is CH_2. The release agent may be an acid. More preferably the releasing agent is *p*-toluene sulfonic acid.

At least one embodiment of the present disclosure~~invention~~ is directed towards a method for retarding the polymerization of vinyl monomers in a liquid comprising said monomers and a quinone methide compound with the formula:



where R_1 and R_2 are independently selected from C_4-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl and C_7-C_{15} phenylalkyl. More 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. R_6

Claims

1. A method for the synthesis of 7-Acetyleno quinone methides, the method comprising the steps of:

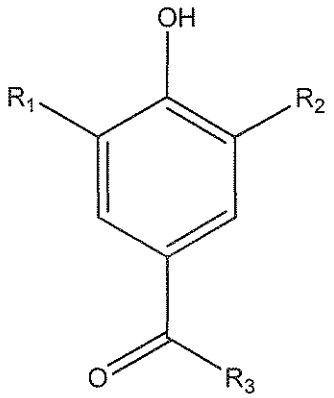
a) performing a condensation reaction between a 3,5-di-substituted-4-hydroxybenzaldehyde and a secondary amine thereby forming a secondary amine quinone methide intermediate;

b) removing water from the secondary amine quinone methide intermediate in a high boiling point ~~aliphatic and also aromatic~~ hydrocarbon solvent by azeotropic distillation at a temperature of between 100 and 160 °C, said hydrocarbon solvent being one from the group consisting of an aliphatic solvent, an aromatic solvent, and any combination thereof;

c) adding the dehydrated secondary amine quinone methide intermediate to an organic medium containing a metal acetylide to form a Mannich base intermediate, and

d) adding a release agent to the Mannich base intermediate to yield a 7-Acetyleno quinone methide.

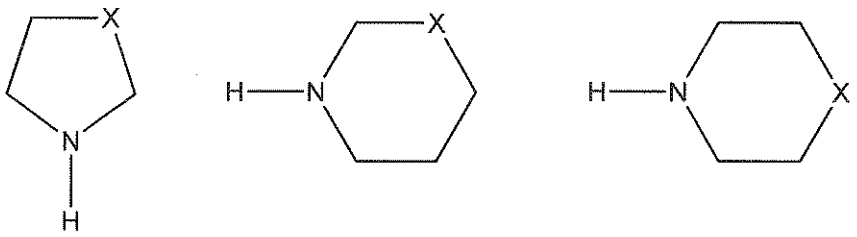
2. The method of claim 1 in which the 3,5-di-substituted-4-hydroxybenzaldehyde has the following formula:



where R_1 and R_2 are independently selected from C_4-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl and C_7

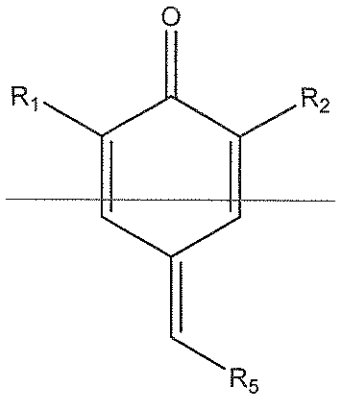
-C_{15} phenylalkyl ~~and preferably, R_1 and R_2 are *tert*-butyl, *tert*-amyl, *tert*-octyl, cyclohexyl, α-methylbenzyl or α,α-dimethylbenzyl, with *tert*-butyl, *tert*-amyl or *tert*-octyl most preferred. R_3 is H~~.

3. The method of claim 1 in which the secondary amine is ~~a N,N-disubstitutedamino group, and more specifically~~ at least one of the group consisting of: a 5-membered heterocyclic group and/or a 6-membered heterocyclic group with the following structures, respectively:



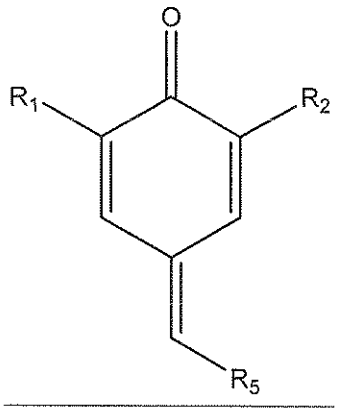
~~and any combination thereof,~~ where X is one selected from CH_2, O, S, or NR_4, where R_4 is one selected from C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, and C_7-C_{15} phenylalkyl~~, and any combination thereof, and the heterocyclic secondary amine group is an amine in which X is CH_2 and O~~.

~~4. The method of claim 1 in which the secondary amine quinone methide intermediate is a 4-((N,N-disubstitutedamino)methylene)cyclohexa-2,5-dienone quinone methide molecule with the following structural formula:~~

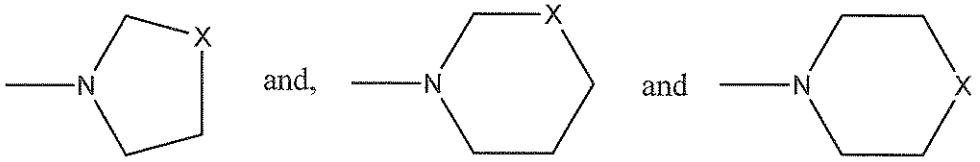


~~where R_1 and R_2 are one item selected from the list of: C_4-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl, and any combination thereof, and R_1 and R_2 are *tert*-butyl, *tert*-amyl, *tert*-octyl, cyclohexyl, α-methylbenzyl or α,α-dimethylbenzyl.~~

~~5~~4. The method of claim ~~4~~ 1 in which the secondary amine quinone methide intermediate is a 4-((N,N-disubstitutedamino)methylene)cyclohexa-2,5-dienone quinone methide molecule with the following structural formula:

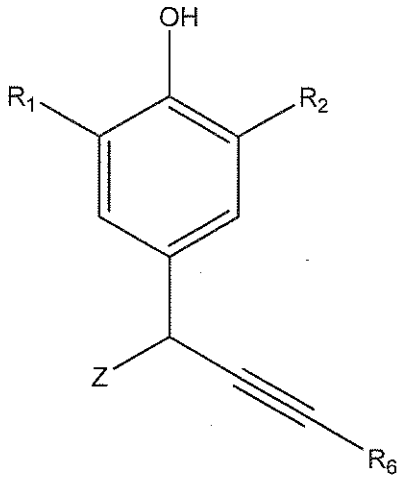


where each of R_1 and R_2 are each one item selected from the list of: C_4-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl, and any combination thereof, and ~~has an~~ R_5 ~~which~~ is a N,N-disubstitutedamino group~~s~~, or a 5-membered or 6-membered heterocyclic group~~s~~ with the following structures:

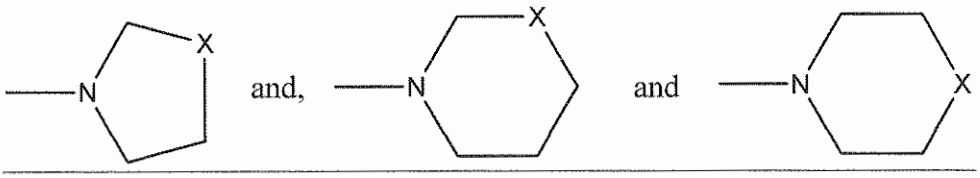


~~and any combination thereof,~~ where X is CH_2, O, S, or NR_4, and R_4 is selected from C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl, and any combination thereof ~~and R_5 is a 5-membered heterocyclic group and/or a 6-membered heterocyclic group in which X is CH_2 and O~~.

65. The method in claim 1 whereby the Mannich base intermediate has the following molecular formula:



where R_1 and R_2 are independently selected from C_4-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl, and R_6 is one item selected from: H, C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl, substituted phenyl group -Ph-R_7, and Z is a secondary N,N-disubstitutedamino group and/or a 5-membered or 6-membered heterocyclic groups with the following structures:

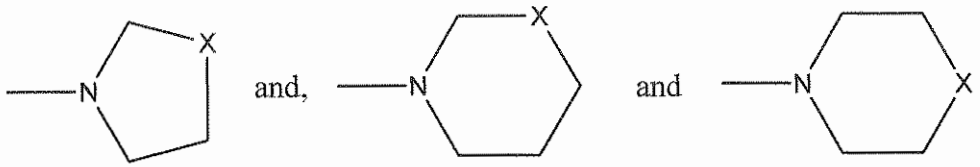


in which X is CH_2, O, S, and NR_4, and any combination thereof, and R_4 is selected from C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, and C_7-C_{15} phenylalkyl~~and any combination thereof~~.

~~7~~6. The method of claim ~~6~~5 in which R_1 and R_2 are selected from: *tert*-butyl, *tert*-amyl, *tert*-octyl, cyclohexyl, α-methylbenzyl, α,α-dimethylbenzyl, and any combination thereof.

~~8~~7. The method of claim ~~6~~5 in which R_6 is selected ~~form~~from: H, C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl, substituted phenyl group -Ph-R_7, and any combination thereof, and preferably R_7 is –COOH, and –$COOR_8$ in which R_8 is independently selected from C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl and C_7-C_{15} phenylalkyl.

~~9~~8. The method in claim ~~6~~5 in which Z is a ~~secondary N,N-disubstitutedamino group and/or a~~ 5-membered or 6-membered heterocyclic groups with the following structures:



and any combination thereof.

~~10~~9. The method of claim ~~9~~8 in which X is ~~CH_2, O, S, and NR_4, and any combination thereof, and R_4 is selected from C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl, and any combination thereof~~.

~~11~~10. The method of claim ~~9~~8 in which Z is selected from the group consisting of a 5-membered heterocyclic group and a 6-membered heterocyclic group in which X is CH_2 and O, and any combination thereof.

~~12~~11. The method of claim 1 in which the release agent is an acid and/or *p*-toluene-sulfonic acid.

12. A method for the synthesis of 7-Acetyleno quinone methides, the method comprising the steps of:

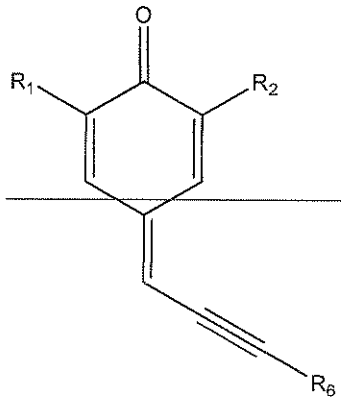
a) performing a condensation reaction between a 3,5-di-substituted-4-hydroxybenzaldehyde and a secondary amine thereby forming a secondary amine quinone methide intermediate;

b) removing water from the secondary amine quinone methide intermediate in a high boiling point hydrocarbon solvent by azeotropic distillation at a temperature of between 100 and 160°C;

c) adding the dehydrated secondary amine quinone methide intermediate to an organic medium containing a metal acetylide to form a Mannich base intermediate, and

d) adding a release agent to the Mannich base intermediate to yield a 7-Acetyleno quinone methide.

~~13. A method for retarding the polymerization of vinyl monomers in a liquid comprising said monomers and a quinone methide compound with the formula:~~



~~where R_1 and R_2 are independently selected from C_4-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl and C_7-C_{15} phenylalkyl. More 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.~~

~~14. The method of claim 13 in which R_6 is H, C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl, C_7-C_{15} phenylalkyl and substituted phenyl group –Ph-R_7, where Ph is a phenyl group –C_6H_4–. R_7 is –COOH and –$COOR_8$ in which R_8 is independently selected from C_1-C_{18} alkyl, C_5-C_{12} cycloalkyl, phenyl and C_7-C_{15} phenylalkyl.~~

~~15. The method of claim 13 in which the amount of said quinone methide added to the monomer varies from 1 to 10,000 parts per million of said monomer.~~