Objects of the Invention:

Accordingly, the main object of present invention is to provide an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, but also comprises substantially reduced or minimized amounts of aromatic and nitroxide compounds.

Another main object of present invention is to provide an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition comprises substantially reduced or minimized amount of aromatic and nitroxide compounds, and is still suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, and is still required in relatively lower dosage as compared to dosage of combination of aromatic and nitroxide compounds for achieving the same or better acceptable level of control and inhibition of polymerization of styrene.

This is also an object of present invention to provide an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition comprises one or more of amines, and reduced or minimized amount of one or more of aromatic and one or more of nitroxide compounds, and is still suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, and is still required in relatively lower dosage as compared to dosage of combination of aromatic and nitroxides compounds for achieving the same or better acceptable level of control and inhibition of polymerization of styrene, and wherein the amine is one or more of tertiary amines.

The present invention particularly aims at providing an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition comprises one or more of amines, and reduced or minimized amounts of one or more of aromatic compounds including quinone methide (QM) and one or more of nitroxides (i.e. nitroxyl) compounds including ~~1-oxyl-2,2,6,6,~~

~~tetramethylpiepridin-4-ol~~ 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4HT) and is still suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, and is still required in relatively lower dosage as compared to dosage of combination of aromatic and nitroxides compounds for achieving the same or better acceptable level of control and inhibition of polymerization of styrene, and wherein the amine is one or more of tertiary amines, and therefore, the composition of present invention is not only economical, but is also environment friendly.

The present invention aims at improving the performance of additive compositions comprising mixture of aromatic compounds and nitroxide compounds, wherein the present composition comprises one or more of aromatic compounds and one or more of nitroxide compounds, and further comprises one or more of tertiary amines.

The present invention aims at improving the performance of additive compositions comprising mixture of aromatic compounds and nitroxide compounds at a wider range of temperature including the higher temperature, wherein the composition comprises one or more of aromatic compounds and one or more of nitroxide compounds, and further comprises one or more of tertiary amines.

The present invention aims at improving the performance of additive compositions comprising mixture of aromatic compounds and nitroxide compounds at a wider range of temperature including the higher temperature and in presence of air, wherein the composition comprises one or more of aromatic compounds and one or more of nitroxide compounds, and further comprises one or more of tertiary amines.

Other objects and advantages of present invention will become more apparent from the following description when read in conjunction with examples, which are not intended to limit scope of present invention.

Description and Preferred Embodiments of the Invention:

With aim to overcome above-described problems of prior art and to achieve above-described objects of the present invention, the inventor has found that when one or more of tertiary amines is added to composition comprising one or more of aromatic and one or more of nitroxide compounds, then not only polymerization controlling and inhibiting efficiency of composition comprising aromatic and nitroxide compounds is substantially improved, but polymerization of aromatic vinyl monomers including styrene, surprisingly and unexpectedly, is also controlled and inhibited to the

styrene is, surprisingly and unexpectedly, substantially improved to the acceptable level that's too at substantially reduced or minimized dosages of aromatic and nitroxide compounds, thereby making the composition of present invention relatively more economical and environment friendly.

In accordance with one of the embodiments of the present invention, the composition of present invention comprises:

a) about 40 to about 99.9 % by weight of *I)* mixture of one or more of said quinone methide or derivatives thereof (herein after may be referred to QM) and one or more of said nitroxides (i.e. nitroxyl) compounds; and

b) about 0.1 to about 60 % by weight of *II)* one or more of said tertiary amines or mixture thereof.

In accordance with one of the embodiments of the present invention, the said quinone methide or derivatives thereof includes benzyl quinone methide, preferably 4-benzylidene,2,6-di-tert-butyl cyclohexa-2,5-dienone.

It may be noted that 'said quinone methide or derivatives thereof' herein after may be referred to as QM.

In accordance with one of the embodiments of the present invention, the said nitroxides (i.e. nitroxyl) compounds include ~~1-oxyl-2,2,6,6,-tetramethylpiepridin-4-ol~~ 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol or 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (or 4 Hydroxy Tempo or 4HT).

It may be noted that 'said nitroxides (i.e. nitroxyl) compounds including ~~1-oxyl-2,2,6,6,-tetramethylpiepridin-4-ol~~ 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4HT) herein after may be referred to as 4HT.

In accordance with one of the embodiments of the present invention, in the mixture of QM and 4HT, the QM is taken in an amount varying from about 0.5 to about 99.5 %by wt and 4HT is taken in an amount varying from about 99.5 to about 0.5 % by wt. of the mixture.

In accordance with the present invention, the mixture of QM and 4HT comprises QM and 4HT in a weight ratio varying from about 99.5:0.5 to 0.5:99.5, preferably from about 95:5 to 5:95, more preferably from about 90:10 to about 10:90.

In accordance with the present invention, the said tertiary amine or mixture thereof is taken an amount varying from about 0.01 to about 60 % by wt of the composition.

In accordance with another preferred embodiment of the present invention, the present composition does not comprise:

In the following experiments, weighed amount of distilled styrene (or hydrocarbon stream in gms) and weighed amount of additives (in ppm by weight of styrene or hydrocarbon stream) were taken in a tube reactor equipped with thermometer and nitrogen inlet and outlet. In these experiments, enough N_2 flow was maintained to ensure proper agitation. The reactions were carried out at 120^0C under continuous nitrogen flow for 2 hours. After the selected duration, the reactor was cooled to below 10^0C by immersing in crushed ice. The contents of the reactor were then poured in a beaker. To this same beaker, approximately for 1.5-2g chilled polymerization mixture, about 80g methanol was used to precipitate the polymer formed in the styrene solution. The precipitate obtained was filtered, dried to remove methanol, and weighed. The weight of the precipitate formed is reported as % polymer formed.

It may be noted that styrene was purified before use to remove the stabilizers.

In following examples, the prior additive is a composition consisting of aromatic compound and nitroxide compound, wherein aromatic compound is Quinine Methide (QM); and nitroxide compound is ~~1-oxyl-2,2,6,6,-tetramethylpiepridin-4-ol~~ 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT), which are taken in an amount of about 100, 150, 200, 300, or 400 ppm in various weight ratios of 90:10 [referred as QM:4HT (90:10)], 80:20 [referred as QM:4HT (80:20)], 70:30 [referred as QM:4HT (70:30)], 50:50 [referred as QM:4HT (50:50)], 30:70 [referred as QM:4HT (30:70)] and 20:80 [referred as QM:4HT (20:80)] of QM and 4-HT.

In following examples, the present additive composition is a composition comprising Quinine Methide (QM) being aromatic compound and ~~1-oxyl-2,2,6,6,-tetramethylpiepridin-4-ol~~ 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT) being nitroxide compound, and further comprising an amine selected from a group consisting of TIPA, Quadrol® and THEED, wherein about 1, 5, 10, 15, or 20 ppm of TIPA, Quadrol® or THEED is added to 100, 200, 300 or 400 ppm of the mixture of said QM and 4HT, and about 2 ppm of TIPA is added to 200 ppm of above-said mixture of QM and 4HT taken in above-said weight ratios of 90:10, 80:20, 70:30, 50:50, 30:70 and 20:80 of QM and 4-HT.

Experiments:-

The results of above Main Experiment when performed with 10g of distilled styrene by heating to 120^0C for 2h are provided in Table-I, Table-II and Table-III.

8. The composition as claimed in any one of the preceding claims 1 to 7, wherein said composition comprises:

a) about 40 to about 99.9 % by weight of *I)* mixture of one or more of said quinone methide or derivatives thereof and one or more of said nitroxides (i.e. nitroxyl) compounds; and

b) about 0.1 to about 60 % by weight of *II)* one or more of said tertiary amines or mixture thereof.

9. The composition as claimed in any one of the preceding claims 1 to 8, wherein said quinone methide or derivatives thereof (QM) includes benzyl quinone methide, preferably 4-benzylidene,2,6-di-tert-butyl cyclohexa-2,5-dienone.

10. The composition as claimed in any one of the preceding claims 1 to 9, wherein said nitroxides (i.e. nitroxyl) compounds include ~~1-oxyl-2,2,6,6,-tetramethylpiepridin-4-ol~~ 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4HT).

11. The composition as claimed in any one of the preceding claims 1 to 10, wherein said mixture of QM and 4HT comprises QM in an amount varying from about 0.5 to about 99.5 % by wt. and 4HT in an amount varying from about 99.5 to about 0.5 % by wt. of the said mixture.

12. The composition as claimed in any one of the preceding claims 1 to 11, wherein said mixture of QM and 4HT comprises QM and 4HT in a weight ratio varying from about 99.5:0.5 to 0.5:99.5, preferably from about 95:5 to 5:95, more preferably from about 90:10 to about 10:90.

13. The composition as claimed in any one of the preceding claims 1 to 12, wherein said tertiary amine or mixture thereof is taken an amount varying from about 0.01 to about 60 % by wt. of the composition.

14. The composition as claimed in any one of the preceding claims 1 to 13, wherein said composition does not comprise:

i) triethanolamine (TEA);

ii) Tris[N-butylamine] (TBA);

iii) monoethanolamine (MEA);

iv) dibutyl amine (DBA);

v) diethanol amine (DEA);

vi) dipropyl amine (DPA);

vii) ethylene diamine (EDA); and

viii) tetraethylenepentamine (TEPA), and

21. The method as claimed in claim 19 or 20, wherein said quinone methide or derivatives thereof, said nitroxides (i.e. nitroxyl) compounds, and said tertiary amines are added to the monomers stream either individually or after mixing.

22. The method as claimed in any one of the preceding claims 16 to 21, wherein said composition is used over a range of temperature varying from about 50 degree C to about 180 degree C.

23. A method for preparing additive composition as claimed in any one of the preceding claims 1 to 15 for controlling and inhibiting polymerization of aromatic vinyl monomers including styrene, wherein the method comprises step of mixing:

(A) one or more of said quinone methide or derivatives thereof, and

(B) one or more of said nitroxides (i.e. nitroxyl) compounds, and

characterized in that said quinone methide or derivatives thereof and said nitroxides (i.e. nitroxyl) compounds or mixture thereof is further mixed with

(C) one or more of said tertiary amines.

~~24. Additive composition for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene substantially as herein described and illustrated with the help of foregoing examples.~~

~~25. A method for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene substantially as herein described and illustrated with the help of foregoing examples.~~

~~26. A method of using additive composition substantially as herein described and illustrated with the help of foregoing examples.~~

~~27. A method for preparing additive composition substantially as herein described and illustrated with the help of foregoing examples.~~

Objects of the Invention:

Accordingly, the main object of present invention is to provide an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, but also comprises substantially reduced or minimized amounts of aromatic and nitroxide compounds.

Another main object of present invention is to provide an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition comprises substantially reduced or minimized amount of aromatic and nitroxide compounds, and is still suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, and is still required in relatively lower dosage as compared to dosage of combination of aromatic and nitroxide compounds for achieving the same or better acceptable level of control and inhibition of polymerization of styrene.

This is also an object of present invention to provide an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition comprises one or more of amines, and reduced or minimized amount of one or more of aromatic and one or more of nitroxide compounds, and is still suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, and is still required in relatively lower dosage as compared to dosage of combination of aromatic and nitroxides compounds for achieving the same or better acceptable level of control and inhibition of polymerization of styrene, and wherein the amine is one or more of tertiary amines.

The present invention particularly aims at providing an effective and improved amine based additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the additive composition comprises one or more of amines, and reduced or minimized amounts of one or more of aromatic compounds including quinone methide (QM) and one or more of nitroxides (i.e. nitroxyl) compounds including

1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4HT) and is still suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, and is still required in relatively lower dosage as compared to dosage of combination of aromatic and nitroxides compounds for achieving the same or better acceptable level of control and inhibition of polymerization of styrene, and wherein the amine is one or more of tertiary amines, and therefore, the composition of present invention is not only economical, but is also environment friendly.

The present invention aims at improving the performance of additive compositions comprising mixture of aromatic compounds and nitroxide compounds, wherein the present composition comprises one or more of aromatic compounds and one or more of nitroxide compounds, and further comprises one or more of tertiary amines.

The present invention aims at improving the performance of additive compositions comprising mixture of aromatic compounds and nitroxide compounds at a wider range of temperature including the higher temperature, wherein the composition comprises one or more of aromatic compounds and one or more of nitroxide compounds, and further comprises one or more of tertiary amines.

The present invention aims at improving the performance of additive compositions comprising mixture of aromatic compounds and nitroxide compounds at a wider range of temperature including the higher temperature and in presence of air, wherein the composition comprises one or more of aromatic compounds and one or more of nitroxide compounds, and further comprises one or more of tertiary amines.

Other objects and advantages of present invention will become more apparent from the following description when read in conjunction with examples, which are not intended to limit scope of present invention.

Description and Preferred Embodiments of the Invention:

With aim to overcome above-described problems of prior art and to achieve above-described objects of the present invention, the inventor has found that when one or more of tertiary amines is added to composition comprising one or more of aromatic and one or more of nitroxide compounds, then not only polymerization controlling and inhibiting efficiency of composition comprising aromatic and nitroxide compounds is substantially improved, but polymerization of aromatic vinyl monomers including styrene, surprisingly and unexpectedly, is also controlled and inhibited to the

styrene is, surprisingly and unexpectedly, substantially improved to the acceptable level that's too at substantially reduced or minimized dosages of aromatic and nitroxide compounds, thereby making the composition of present invention relatively more economical and environment friendly.

In accordance with one of the embodiments of the present invention, the composition of present invention comprises:

a) about 40 to about 99.9 % by weight of *I)* mixture of one or more of said quinone methide or derivatives thereof (herein after may be referred to QM) and one or more of said nitroxides (i.e. nitroxyl) compounds; and

b) about 0.1 to about 60 % by weight of *II)* one or more of said tertiary amines or mixture thereof.

In accordance with one of the embodiments of the present invention, the said quinone methide or derivatives thereof includes benzyl quinone methide, preferably 4-benzylidene,2,6-di-tert-butyl cyclohexa-2,5-dienone.

It may be noted that 'said quinone methide or derivatives thereof' herein after may be referred to as QM.

In accordance with one of the embodiments of the present invention, the said nitroxides (i.e. nitroxyl) compounds include 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol or 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (or 4 Hydroxy Tempo or 4HT).

It may be noted that 'said nitroxides (i.e. nitroxyl) compounds including 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4HT) herein after may be referred to as 4HT.

In accordance with one of the embodiments of the present invention, in the mixture of QM and 4HT, the QM is taken in an amount varying from about 0.5 to about 99.5 %by wt and 4HT is taken in an amount varying from about 99.5 to about 0.5 % by wt. of the mixture.

In accordance with the present invention, the mixture of QM and 4HT comprises QM and 4HT in a weight ratio varying from about 99.5:0.5 to 0.5:99.5, preferably from about 95:5 to 5:95, more preferably from about 90:10 to about 10:90.

In accordance with the present invention, the said tertiary amine or mixture thereof is taken an amount varying from about 0.01 to about 60 % by wt of the composition.

In accordance with another preferred embodiment of the present invention, the present composition does not comprise:

In the following experiments, weighed amount of distilled styrene (or hydrocarbon stream in gms) and weighed amount of additives (in ppm by weight of styrene or hydrocarbon stream) were taken in a tube reactor equipped with thermometer and nitrogen inlet and outlet. In these experiments, enough N_2 flow was maintained to ensure proper agitation. The reactions were carried out at 120^0C under continuous nitrogen flow for 2 hours. After the selected duration, the reactor was cooled to below 10^0C by immersing in crushed ice. The contents of the reactor were then poured in a beaker. To this same beaker, approximately for 1.5-2g chilled polymerization mixture, about 80g methanol was used to precipitate the polymer formed in the styrene solution. The precipitate obtained was filtered, dried to remove methanol, and weighed. The weight of the precipitate formed is reported as % polymer formed.

It may be noted that styrene was purified before use to remove the stabilizers.

In following examples, the prior additive is a composition consisting of aromatic compound and nitroxide compound, wherein aromatic compound is Quinine Methide (QM); and nitroxide compound is 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT), which are taken in an amount of about 100, 150, 200, 300, or 400 ppm in various weight ratios of 90:10 [referred as QM:4HT (90:10)], 80:20 [referred as QM:4HT (80:20)], 70:30 [referred as QM:4HT (70:30)], 50:50 [referred as QM:4HT (50:50)], 30:70 [referred as QM:4HT (30:70)] and 20:80 [referred as QM:4HT (20:80)] of QM and 4-HT.

In following examples, the present additive composition is a composition comprising Quinine Methide (QM) being aromatic compound and 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT) being nitroxide compound, and further comprising an amine selected from a group consisting of TIPA, Quadrol® and THEED, wherein about 1, 5, 10, 15, or 20 ppm of TIPA, Quadrol® or THEED is added to 100, 200, 300 or 400 ppm of the mixture of said QM and 4HT, and about 2 ppm of TIPA is added to 200 ppm of above-said mixture of QM and 4HT taken in above-said weight ratios of 90:10, 80:20, 70:30, 50:50, 30:70 and 20:80 of QM and 4-HT.

Experiments:-

The results of above Main Experiment when performed with 10g of distilled styrene by heating to 120^0C for 2h are provided in Table-I, Table-II and Table-III.

8. The composition as claimed in any one of the preceding claims 1 to 7, wherein said composition comprises:

a) about 40 to about 99.9 % by weight of *I)* mixture of one or more of said quinone methide or derivatives thereof and one or more of said nitroxides (i.e. nitroxyl) compounds; and

b) about 0.1 to about 60 % by weight of *II)* one or more of said tertiary amines or mixture thereof.

9. The composition as claimed in any one of the preceding claims 1 to 8, wherein said quinone methide or derivatives thereof (QM) includes benzyl quinone methide, preferably 4-benzylidene,2,6-di-tert-butyl cyclohexa-2,5-dienone.

10. The composition as claimed in any one of the preceding claims 1 to 9, wherein said nitroxides (i.e. nitroxyl) compounds include 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4HT).

11. The composition as claimed in any one of the preceding claims 1 to 10, wherein said mixture of QM and 4HT comprises QM in an amount varying from about 0.5 to about 99.5 % by wt. and 4HT in an amount varying from about 99.5 to about 0.5 % by wt. of the said mixture.

12. The composition as claimed in any one of the preceding claims 1 to 11, wherein said mixture of QM and 4HT comprises QM and 4HT in a weight ratio varying from about 99.5:0.5 to 0.5:99.5, preferably from about 95:5 to 5:95, more preferably from about 90:10 to about 10:90.

13. The composition as claimed in any one of the preceding claims 1 to 12, wherein said tertiary amine or mixture thereof is taken an amount varying from about 0.01 to about 60 % by wt. of the composition.

14. The composition as claimed in any one of the preceding claims 1 to 13, wherein said composition does not comprise:

i) triethanolamine (TEA);

ii) Tris[N-butylamine] (TBA);

iii) monoethanolamine (MEA);

iv) dibutyl amine (DBA);

v) diethanol amine (DEA);

vi) dipropyl amine (DPA);

vii) ethylene diamine (EDA); and

viii) tetraethylenepentamine (TEPA), and

21. The method as claimed in claim 19 or 20, wherein said quinone methide or derivatives thereof, said nitroxides (i.e. nitroxyl) compounds, and said tertiary amines are added to the monomers stream either individually or after mixing.

22. The method as claimed in any one of the preceding claims 16 to 21, wherein said composition is used over a range of temperature varying from about 50 degree C to about 180 degree C.

23. A method for preparing additive composition as claimed in any one of the preceding claims 1 to 15 for controlling and inhibiting polymerization of aromatic vinyl monomers including styrene, wherein the method comprises step of mixing:

(A) one or more of said quinone methide or derivatives thereof, and

(B) one or more of said nitroxides (i.e. nitroxyl) compounds, and

characterized in that said quinone methide or derivatives thereof and said nitroxides (i.e. nitroxyl) compounds or mixture thereof is further mixed with

(C) one or more of said tertiary amines.