including ~~1 oxyl 2,2,6,6, tetramethylpiepridin-4-ol~~ 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (4HT) and aromatic nitro compounds including dinitro-butylphenol [re abstract, Col. 3, lines 26-32; Col. 4, lines 1-2, 12] as the polymerization inhibitor. However, the aromatic nitro compounds including DNBP are to be used in higher amounts and/or are also known for their toxic nature for human exposure [re Col. 1, lines 64-68].

Therefore, the industry is aiming for additive composition wherein the dosage of components of composition of US'760, particularly of DNBP and 4HT can be minimized or reduced. Any effort in the direction of lowering the consumption of these components will lessen the problem of industry.

Need of the Invention:

Therefore, there is still a need of an effective additive composition and method of its use, and method of its preparation and method of controlling and inhibiting polymerization of aromatic vinyl monomers including styrene by employing said composition, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers incluidng styrene, but also comprises reduced or minimized amounts of nitroxides (i.e. nitroxyls) and aromatic nitro compounds.

Problem to be solved by the Invention:

Therefore, the present invention aims at providing a solution to above-described existing industrial problem by providing effective additive composition and method of its use, and method of its preparation and method of controlling and inhibiting polymerization of aromatic vinyl monomers including styrene by employing said composition, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, but also comprises reduced or minimized amounts of nitroxides (i.e. nitroxyls) and aromatic nitro compounds.

Objects of the Invention:

Accordingly, the main object of present invention is to provide an effective additive composition and method of its use, and method of its preparation, and method of controlling and inhibiting polymerization of aromatic vinyl monomers including

a) about 50 to about 99.5 % by weight of *I)* mixture of said nitroxide (i.e. nitroxyl) compounds and said aromatic nitro compounds; and

b) about 0.5 to about 50 % by weight of *II)* said amines.

In accordance with one of the embodiments of the present invention, the nitroxide (or nitroxyl) compound is selected from the group comprising di-tert-butylnitroxyl, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, and derivatives thereof; and di-nitroxides and derivatives comprising 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, and mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the nitroxide (or nitroxyl) compound is selected from the group comprising bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate and 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol~~1- oxyl 2,2,6,6, tetramethylpiepridin 4 ol~~ or 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (or 4 Hydroxy Tempo or 4-HT) , and mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the nitroxide (or nitroxyl) 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).

In accordance with one of the preferred embodiments of the present invention, the aromatic nitro compound contains a phenolic group or derivative thereof as well as the nitro group.

In accordance with one of the preferred embodiments of the present invention, the aromatic nitro compound is selected from a group comprising 4,6-dinitro-2-sec-butylphenol (DNBP) and 4,6-dinitro-ortho cresol or 4,6-dinitro-2-hydroxytoluene (DNOC), and mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the aromatic nitro compound is 4,6-dinitro-2-sec-butylphenol (DNBP).

Accordingly, in another embodiment, the present invention also relates to method of using amine based additive composition of the present invention described herein, a reference to which is drawn in entirety, to control and inhibit polymerization of aromatic vinyl monomers including styrene, wherein the stream comprising aromatic vinyl monomer including styrene is treated with said composition comprising one or

In following examples, the prior art additive composition is a composition comprising aromatic nitro compound and nitroxide compound, wherein aromatic nitro compound is 4,6-dinitro-2-sec-butylphenol (DNBP); 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, 200, 300, 400, 500, 1000 ppm in various weight ratios of 90:10 [referred as DNBP:4HT (90:10)], 80:20 [referred as DNBP:4HT (80:20)], 70:30 [referred as DNBP:4HT (70:30)], 50:50 [referred as DNBP:4HT (50:50)], 30:70 [referred as DNBP:4HT (30:70)], and 20:80 [referred as DNBP:4HT (20:80)].

In following examples, the present additive composition is a composition comprising 4,6-dinitro-2-sec-butylphenol (DNBP) being aromatic nitro compound; ~~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 (DNBP and 4HT); and additionally comprising TIPA, Quadrol, THEED, TBA, or MEA being amine of the present invention.

The inventor has further compared the results of present compositions with additive compositions comprising (DNBP and 4HT), and triethanolamine (TEA), N,N,disec-butyl-para-phenylene diamine (UOP5), ethylene diamine (EDA), tetraethylenepentamine (TEPA), dibutyl amine (DBA), octyle amine, dipropyl amine (DPA), or diethanol amine (DEA) for comparative purposes.

In following examples, from about 1 to about 25 ppm of amine of the present invention and of amine for the comparative purpose is added to about 100, 200, 300, 400, 500, 1000 ppm of above-said mixture of nitroxide and aromatic nitro compounds, wherein said mixture of nitroxide and aromatic nitro compounds is taken in weight ratios of 90:10, 80:20, 70:30, 50:50, 30:70 and 20:80.

Experiment 1 –

The results of above Main Experiment when performed in a tube reactor with 10g of distilled styrene for heating to 120^0C for 2h are provided in Table I for 100 ppm dosage and in Table II for 200, 300 and 400 ppm dosages of mixture of nitroxide and aromatic nitro compounds taken in weight ratios of 90:10, 80:20, 70:30, 50:50, 30:70 and 20:80, wherein 1 to 25 ppm of amine of the present invention and of amine for the comparative purpose has been added.

8. Additive composition as claimed in any one of claims 1 to 7, wherein said nitroxide (i.e. nitroxyl) compound is selected from the group comprising di-tert-butylnitroxyl, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, and derivatives thereof; and di-nitroxides and derivatives comprising bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipate, and mixture thereof.

9. Additive composition as claimed in any one of claims 1 to 8, wherein said nitroxide (i.e. nitroxyl) compound is selected from the group comprising bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate and ~~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 4-HT) , and mixture thereof.

10. Additive composition as claimed in any one of claims 1 to 9, wherein said nitroxide (i.e. nitroxyl) 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).

11. Additive composition as claimed in any one of claims 1 to 10, wherein said aromatic nitro compound contains a phenolic group or derivative thereof as well as the nitro group.

12. Additive composition as claimed in any one of claims 1 to 11, wherein said aromatic nitro compound is selected from a group comprising 4,6-dinitro-2-sec-butylphenol (DNBP) and 4,6-dinitro-ortho cresol or 4,6-dinitro-2-hydroxytoluene (DNOC) , and mixture thereof.

13. Additive composition as claimed in any one of claims 1 to 12, wherein said aromatic nitro compound is 4,6-dinitro-2-sec-butylphenol (DNBP).

14. Additive composition as claimed in any one of claims 1 to 13, wherein said composition does not comprise triethanolamine (TEA), N,N,disec-butyl-para-phenylene diamine (UOP5), ethylene diamine (EDA), tetraethylenepentamine (TEPA), dibutyl amine (DBA), octyle amine, dipropyl amine (DPA), and diethanol amine (DEA).

15. A method for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene by adding amine based additive composition as

polymerization of aromatic vinyl monomers including styrene, wherein the method comprises:

(A) mixing one or more of said nitroxide (i.e. nitroxyl) compounds and one or more of said aromatic nitro compounds,

characterized in that said mixture of said nitroxide (i.e. nitroxyl) compounds and said aromatic nitro compounds is further mixed with one or more of

(B) said amines,

wherein said amine is selected from a group comprising:

(i) hydroxyl alkyl tertiary amines,

(i) tertiary alkyl amines,

(iii) hydroxyl alkyl primary amine; and

(iv) mixture thereof.

20. The method as claimed claim 19, wherein said one or more of nitroxide compounds, said one or more of aromatic nitro compounds, and said one or more amines are mixed individually.

~~21. Amine based additive composition for control and inhibition of polymerization of aromatic vinyl monomers including styrene substantially as herein described and illustrated with the help of foregoing examples.~~

~~22. 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.~~

~~23. A method of using amine based additive composition substantially as herein described and illustrated with the help of foregoing examples.~~

~~24. A method for preparing amine based additive composition substantially as herein described and illustrated with the help of foregoing examples.~~

including 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (4HT) and aromatic nitro compounds including dinitro-butylphenol [re abstract, Col. 3, lines 26-32; Col. 4, lines 1-2, 12] as the polymerization inhibitor. However, the aromatic nitro compounds including DNBP are to be used in higher amounts and/or are also known for their toxic nature for human exposure [re Col. 1, lines 64-68].

Therefore, the industry is aiming for additive composition wherein the dosage of components of composition of US'760, particularly of DNBP and 4HT can be minimized or reduced. Any effort in the direction of lowering the consumption of these components will lessen the problem of industry.

Need of the Invention:

Therefore, there is still a need of an effective additive composition and method of its use, and method of its preparation and method of controlling and inhibiting polymerization of aromatic vinyl monomers including styrene by employing said composition, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers incluidng styrene, but also comprises reduced or minimized amounts of nitroxides (i.e. nitroxyls) and aromatic nitro compounds.

Problem to be solved by the Invention:

Therefore, the present invention aims at providing a solution to above-described existing industrial problem by providing effective additive composition and method of its use, and method of its preparation and method of controlling and inhibiting polymerization of aromatic vinyl monomers including styrene by employing said composition, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of aromatic vinyl monomers including styrene, but also comprises reduced or minimized amounts of nitroxides (i.e. nitroxyls) and aromatic nitro compounds.

Objects of the Invention:

Accordingly, the main object of present invention is to provide an effective additive composition and method of its use, and method of its preparation, and method of controlling and inhibiting polymerization of aromatic vinyl monomers including

a) about 50 to about 99.5 % by weight of *I)* mixture of said nitroxide (i.e. nitroxyl) compounds and said aromatic nitro compounds; and

b) about 0.5 to about 50 % by weight of *II)* said amines.

In accordance with one of the embodiments of the present invention, the nitroxide (or nitroxyl) compound is selected from the group comprising di-tert-butylnitroxyl, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, and derivatives thereof; and di-nitroxides and derivatives comprising 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, and mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the nitroxide (or nitroxyl) compound is selected from the group comprising bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate and 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol or 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (or 4 Hydroxy Tempo or 4-HT) , and mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the nitroxide (or nitroxyl) compound is 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT).

In accordance with one of the preferred embodiments of the present invention, the aromatic nitro compound contains a phenolic group or derivative thereof as well as the nitro group.

In accordance with one of the preferred embodiments of the present invention, the aromatic nitro compound is selected from a group comprising 4,6-dinitro-2-sec-butylphenol (DNBP) and 4,6-dinitro-ortho cresol or 4,6-dinitro-2-hydroxytoluene (DNOC), and mixture thereof.

In accordance with one of the preferred embodiments of the present invention, the aromatic nitro compound is 4,6-dinitro-2-sec-butylphenol (DNBP).

Accordingly, in another embodiment, the present invention also relates to method of using amine based additive composition of the present invention described herein, a reference to which is drawn in entirety, to control and inhibit polymerization of aromatic vinyl monomers including styrene, wherein the stream comprising aromatic vinyl monomer including styrene is treated with said composition comprising one or

In following examples, the prior art additive composition is a composition comprising aromatic nitro compound and nitroxide compound, wherein aromatic nitro compound is 4,6-dinitro-2-sec-butylphenol (DNBP); 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, 200, 300, 400, 500, 1000 ppm in various weight ratios of 90:10 [referred as DNBP:4HT (90:10)], 80:20 [referred as DNBP:4HT (80:20)], 70:30 [referred as DNBP:4HT (70:30)], 50:50 [referred as DNBP:4HT (50:50)], 30:70 [referred as DNBP:4HT (30:70)], and 20:80 [referred as DNBP:4HT (20:80)].

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In following examples, from about 1 to about 25 ppm of amine of the present invention and of amine for the comparative purpose is added to about 100, 200, 300, 400, 500, 1000 ppm of above-said mixture of nitroxide and aromatic nitro compounds, wherein said mixture of nitroxide and aromatic nitro compounds is taken in weight ratios of 90:10, 80:20, 70:30, 50:50, 30:70 and 20:80.

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8. Additive composition as claimed in any one of claims 1 to 7, wherein said nitroxide (i.e. nitroxyl) compound is selected from the group comprising di-tert-butylnitroxyl, 1-oxyl-2,2,6,6-tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-one, and derivatives thereof; and di-nitroxides and derivatives comprising bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)adipate, and mixture thereof.

9. Additive composition as claimed in any one of claims 1 to 8, wherein said nitroxide (i.e. nitroxyl) compound is selected from the group comprising bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate and 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol or 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (or 4 Hydroxy Tempo or 4-HT) , and mixture thereof.

10. Additive composition as claimed in any one of claims 1 to 9, wherein said nitroxide (i.e. nitroxyl) compound is 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT).

11. Additive composition as claimed in any one of claims 1 to 10, wherein said aromatic nitro compound contains a phenolic group or derivative thereof as well as the nitro group.

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13. Additive composition as claimed in any one of claims 1 to 12, wherein said aromatic nitro compound is 4,6-dinitro-2-sec-butylphenol (DNBP).

14. Additive composition as claimed in any one of claims 1 to 13, wherein said composition does not comprise triethanolamine (TEA), N,N,disec-butyl-para-phenylene diamine (UOP5), ethylene diamine (EDA), tetraethylenepentamine (TEPA), dibutyl amine (DBA), octyle amine, dipropyl amine (DPA), and diethanol amine (DEA).

15. A method for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene by adding amine based additive composition as

polymerization of aromatic vinyl monomers including styrene, wherein the method comprises:

(A) mixing one or more of said nitroxide (i.e. nitroxyl) compounds and one or more of said aromatic nitro compounds,

characterized in that said mixture of said nitroxide (i.e. nitroxyl) compounds and said aromatic nitro compounds is further mixed with one or more of

(B) said amines,

wherein said amine is selected from a group comprising:

(i) hydroxyl alkyl tertiary amines,

(i) tertiary alkyl amines,

(iii) hydroxyl alkyl primary amine; and

(iv) mixture thereof.

20. The method as claimed claim 19, wherein said one or more of nitroxide compounds, said one or more of aromatic nitro compounds, and said one or more amines are mixed individually.