

1 **Title of the invention:**

2 Amine and Nitroxide based Additive Composition for control and inhibition of
3 polymerization of styrene, and method of use thereof.

4
5 **Field of the invention:**

6 The present invention relates to amine and nitroxide based additive composition
7 for control and inhibition of polymerization of aromatic vinyl monomers, wherein
8 aromatic vinyl monomer include styrene.

9 In one embodiment, the present invention relates to use of amine and nitroxide
10 based additive composition of present invention to control and inhibit polymerization
11 of aromatic vinyl monomers including styrene.

12 In another embodiment, the present invention relates to method of preparation
13 of amine and nitroxide based additive composition of present invention for control and
14 inhibition of polymerization of aromatic vinyl monomers including styrene.

15 In still another embodiment, the present invention relates to method of
16 controlling and inhibiting polymerization of aromatic vinyl monomers including
17 styrene by employing amine and nitroxide based additive composition of present
18 invention.

19
20 **Background of the invention:**

21 The polymerization of aromatic vinyl monomers including styrene during
22 processing is a matter of concern, because it causes formation of unwanted polymers
23 and results in loss of yield of end product and makes the process un-economical.

24 In the art use of inhibitors and retarders, and combination thereof to overcome
25 problem of polymerization of styrene has been reported.

26 The problem of using the inhibitors alone is that these are to be added
27 continuously or at regular interval, because once they are consumed, the polymerization
28 will re-start.

29 The problem of using the retarders alone is that these are not very effective to
30 reduce polymerization of styrene to a level of substantial inhibition or to the acceptable
31 level of inhibition.

32 The prior art [US 5,254,760 (US'760)] discloses the polymerization inhibition
33 of vinyl monomers using a combination of nitroxides (i.e. nitroxyl compounds)
34 including 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (4HT) and aromatic nitro

1 compounds including dinitro-butylphenol [*re abstract, Col. 3, lines 26-32; Col. 4, lines*
2 *1-2, 12 of US'760*] as the polymerization inhibitor.

3 The US'760 discloses and teaches use of combination of nitroxides (i.e.
4 nitroxyl) compound and aromatic nitro compound. The US'760 discloses and teaches
5 against the use of either of nitroxides (i.e. nitroxyl) compound or of aromatic nitro
6 compound [*Re Col. 5, lines 50-56; Col. 6, lines 10-14 and 42-46; Col. 7, lines 36-41 of*
7 *US'760*].

8 However, the aromatic nitro compounds including DNBP are to be used in
9 higher amounts and/or are also known for their toxic nature for human exposure [*re*
10 *Col. 1, lines 64-68 of US'760*].

11 Therefore, the industry is aiming for additive composition wherein the aromatic
12 nitro compounds can be avoided. Any effort to avoid consumption of aromatic nitro
13 compounds will lessen the problem of industry.

14 15 **Need of the Invention:**

16 Therefore, there is still a need of an effective additive composition and method
17 of its use and preparation, and method of controlling and inhibiting polymerization of
18 vinyl aromatic monomers by employing said composition, wherein the additive
19 composition is not only suitable for substantial control and inhibition of polymerization
20 of aromatic vinyl monomers including styrene, but also does not comprise aromatic
21 nitro compounds.

22 23 **Problem to be solved by the Invention:**

24 Therefore, the present invention aims at providing a solution to above-described
25 existing industrial problems by providing effective additive composition and method of
26 its use and preparation, and method of controlling and inhibiting polymerization of
27 vinyl aromatic monomers, wherein the additive composition is not only suitable for
28 substantial control and inhibition of polymerization of aromatic vinyl monomers
29 including styrene, but also does not comprise aromatic nitro compounds.

30 In-addition to above aim, the present invention also aims at providing an
31 effective additive composition and method of its use and preparation, and method of
32 controlling and inhibiting polymerization of vinyl aromatic monomers, wherein the
33 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 amount of nitroxides (i.e. nitroxyl) 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 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 does not comprise aromatic nitro compounds.

Another main object of present invention is to provide an effective 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 reduced or minimized amount of nitroxides (i.e. nitroxyl) compounds.

This is also an object of present invention to provide an effective 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 reduced or minimized amount of one or more of nitroxides (i.e. nitroxyl) compounds, and does not comprise aromatic nitro 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 nitroxides (i.e. nitroxyl) compounds alone for achieving the same or better acceptable level of control and inhibition of polymerization of aromatic vinyl monomers including styrene.

This is also an object of present invention to provide an effective 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 nitroxides (i.e. nitroxyl) compounds, and does not comprise aromatic nitro 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 nitroxides (i.e. nitroxyl) compounds

1 alone for achieving the same or better acceptable level of control and inhibition of
2 polymerization of aromatic vinyl monomers including styrene, and wherein the amine
3 is aliphatic amine.

4 The present invention particularly aims at providing an effective additive
5 composition and method of its use and preparation, and method of controlling and
6 inhibiting polymerization of vinyl aromatic monomers, wherein the additive
7 composition comprises one or more of amines and reduced or minimized amount of
8 one or more of nitroxides (i.e. nitroxyl) compounds, and does not comprise aromatic
9 nitro compounds, and is still suitable for substantial control and inhibition of
10 polymerization of aromatic vinyl monomers including styrene, and is still required in
11 relatively lower dosage as compared to dosage of nitroxides (i.e. nitroxyl) compounds
12 alone for achieving the same or better acceptable level of control and inhibition of
13 polymerization of aromatic vinyl monomers including styrene, and wherein the amine
14 is aliphatic amine, which is selected from a group comprising tertiary amines,
15 secondary amines and primary amines, preferably the amine is tertiary amine, and
16 therefore, the composition of present invention is not only economical, but is also
17 environment friendly.

18 The present invention also aims at improving the performance of nitroxide (i.e.
19 nitroxyl) compounds at a wider range of temperature including the higher temperature
20 and in presence of air, wherein the composition further comprises one or more aliphatic
21 amines.

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

25 26 **Description and Preferred Embodiments of the Invention:**

27 With aim to overcome above-described problems of prior art and to achieve
28 above-described objects of the invention, the inventor has found that when an aliphatic
29 amine is added to composition consisting of nitroxide (i.e. nitroxyl) compounds even
30 without aromatic nitro compounds, then not only polymerization controlling and
31 inhibiting efficiency of nitroxides is substantially improved, but polymerization of
32 aromatic vinyl monomers including styrene, surprisingly and unexpectedly, is also
33 controlled and inhibited to the acceptable level at substantially reduced dosages of
34 composition comprising one or more of nitroxide compounds and one or more of

1 aliphatic amine compounds, which makes the composition economical as well as
2 environment friendly.

3 With aim to overcome above-described problems of prior art and to achieve
4 above-described objects of the invention, the inventor has found that when one or more
5 of aliphatic tertiary amines, or aliphatic tertiary amines containing one or more
6 hydroxyl groups or one or more of secondary amines or one or more of primary amines
7 or mixture thereof is added to composition consisting of one or more of nitroxide (i.e.
8 nitroxyl) compounds without aromatic nitro compounds, then not only polymerization
9 controlling and inhibiting efficiency of nitroxides is substantially improved, but
10 polymerization of aromatic vinyl monomers including styrene, surprisingly and
11 unexpectedly, is also controlled and inhibited to the acceptable level at substantially
12 reduced dosages of composition comprising nitroxide and aliphatic amine compounds,
13 which makes the composition economical as well as environment friendly.

14 Accordingly, the present invention relates to additive composition for
15 controlling and inhibition of polymerization of aromatic vinyl monomers including
16 styrene comprising:

- 17 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
18 characterized in that the said composition further comprises one or more of
19 (b) aliphatic amines selected from a group comprising tertiary amines, secondary
20 amines and primary amines, preferably the amine is tertiary amine.

21 Accordingly, in one embodiment, the present invention relates to additive
22 composition for controlling and inhibition of polymerization of aromatic vinyl
23 monomers including styrene comprising:

- 24 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
25 characterized in that the said composition further comprises one or more of
26 (b) tertiary amines.

27 Accordingly, in another embodiment, the present invention relates to additive
28 composition for controlling and inhibition of polymerization of aromatic vinyl
29 monomers including styrene comprising:

- 30 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
31 characterized in that the said composition further comprises one or more of
32 (b) amines selected from a group consisting of primary amines and secondary
33 amines.

1 In accordance with present invention, the aliphatic amine is an aliphatic tertiary
2 amine, which contains one or more hydroxyl groups in the alkyl chain of the tertiary
3 amine, preferably it contains three hydroxyl groups in the alkyl chain of the tertiary
4 amine, more preferably the hydroxyl groups are hydroxyalkyl groups.

5 In accordance with one of the most preferred embodiments of the present
6 invention, the said amine is hydroxyl alkyl tertiary amine.

7 In accordance with one of the preferred embodiments of the present invention,
8 the said amine is ethylene oxide treated amine.

9 In accordance with one of the preferred embodiments of the present invention,
10 the said amine is propylene oxide treated amine.

11 In accordance with one of the preferred embodiments of the present invention,
12 the said amine is tertiary alkyl amine.

13 In accordance with one of the preferred embodiments of the present invention,
14 the said amine is mixture of one or more of hydroxyl alkyl tertiary amines, ethylene
15 oxide treated amines, propylene oxide treated amines, tertiary alkyl amines.

16 In accordance with one of the most preferred embodiments of the present
17 invention, the said hydroxyl alkyl tertiary amine is tris(2-hydroxypropyl)amine (TIPA).

18 In accordance with one of the preferred embodiments of the present invention,
19 the said ethylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-
20 diamine) (THEED).

21 In accordance with one of the preferred embodiments of the present invention,
22 the said propylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxypropyl)
23 ethylene-diamine) (Quadrol).

24 In accordance with one of the preferred embodiments of the present invention,
25 the said hydroxyl alkyl tertiary amine is triethanolamine (TEA).

26 In accordance with one of the preferred embodiments of the present invention,
27 the said tertiary alkyl amine is Tris[N-butylamine] (TBA).

28 In accordance with one of the embodiments of the present invention, the said
29 primary amine is selected from a group comprising hydroxyl alkyl primary amine and
30 alkyl primary amine.

31 In accordance with one of the embodiments of the present invention, the said
32 secondary amine is alkyl secondary amine.

33 In accordance with one of the embodiments of the present invention, the said
34 hydroxyl alkyl primary amine is monoethanolamine (MEA).

1 In accordance with one of the embodiments of the present invention, the said
2 alkyl primary amine is octyl amine (OA).

3 In accordance with one of the embodiments of the present invention, the said
4 alkyl secondary amine is dibutyl amine (DBA).

5 It has been found that when composition of present invention comprises one or
6 more of said amines, the efficiency of nitroxide compounds to control and inhibit
7 polymerization of aromatic vinyl monomers including styrene is, surprisingly and
8 unexpectedly, substantially improved to the acceptable level that's too at substantially
9 reduced dosages of nitroxide compounds and that's too without aromatic nitro
10 compounds, thereby making the composition of present invention relatively more
11 economical and environment friendly.

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

- 14 a) about 40 to about 99.75 % by weight of *I*) said nitroxide (i.e. nitroxyl)
15 compounds; and
16 b) about 0.25 to about 60 % by weight of *II*) said amines or mixture
17 thereof.

18 In accordance with one of the preferred embodiments of the present invention,
19 the composition of present invention is added to the stream containing aromatic vinyl
20 monomers including styrene in an amount varying from about 0.01 ppm to about 2000
21 ppm, preferably from about 1 ppm to about 2000 ppm by weight of the stream of
22 monomer including styrene.

23 In accordance with present invention, the nitroxide (or nitroxyl) compound is
24 selected from the group comprising di-tert-butyl nitroxyl, 1-oxyl-2,2,6,6-
25 tetramethylpiperidine, 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol, 1-oxyl-2,2,6,6-
26 tetramethylpiperidin-4-one, and derivatives thereof; and di-nitroxides and derivatives
27 comprising bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, bis(1-oxyl-2,2,6,6-
28 tetramethylpiperidin-4-yl)succinate, bis(1-oxyl-2,2,6,6-tetramethylpiperidin-4-
29 yl)adipate, and mixture thereof.

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

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

4 In accordance with one of the preferred embodiments of the present invention,
5 the present composition does not comprise aromatic nitro compound.

6 Accordingly, in another embodiment, the present invention also relates to
7 method of using amine and nitroxide based additive composition of present invention
8 described herein, a reference to which is drawn in entirety, to control and inhibit
9 polymerization of aromatic vinyl monomers including styrene, wherein the stream
10 comprising aromatic vinyl monomer including styrene is treated with an additive
11 composition comprising one or more of nitroxides (i.e. nitroxyls) compounds and one
12 or more of said amines.

13 In particular, in second embodiment, the present invention relates to a method
14 of using additive composition of the present invention described herein, a reference to
15 which is drawn in entirety, for controlling and inhibition of polymerization of aromatic
16 vinyl monomers including styrene, wherein said composition comprises:

- 17 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
18 characterized in that the said composition further comprises one or more of
19 (b) aliphatic amines selected from a group comprising tertiary amines, secondary
20 amines and primary amines, preferably the amine is tertiary amine; and
21 said monomers are treated with said composition.

22 Accordingly, in this second embodiment, the present invention particularly
23 relates to a method of using additive composition of the present invention described
24 herein, a reference to which is drawn in entirety, for controlling and inhibition of
25 polymerization of aromatic vinyl monomers including styrene, wherein said
26 composition comprises:

- 27 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
28 characterized in that the said composition further comprises one or more of
29 (b) tertiary amines; and
30 said monomers are treated with said composition.

31 Accordingly, in this second embodiment, the present invention also relates to a
32 method of using additive composition of the present invention described herein, a
33 reference to which is drawn in entirety, for controlling and inhibition of polymerization
34 of aromatic vinyl monomers including styrene, wherein said composition comprises:

1 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
2 characterized in that the said composition further comprises one or more of
3 (b) amines selected from a group consisting of primary amines and secondary
4 amines; and
5 said monomers are treated with said composition.

6 It may be noted that the stream comprising aromatic vinyl monomers including
7 styrene may be referred to as stream or monomers stream or as aromatic vinyl
8 monomers stream.

9 In accordance with one of the embodiments of the present invention, the method
10 of using said additive composition of the present invention comprises treating said
11 monomers stream with about 0.01 ppm to about 2000 ppm, preferably from about 1
12 ppm to about 2000 ppm of said composition based on weight of monomers.

13 It may be noted that all the features of the composition of the present invention
14 described herein, a reference to which is drawn in entirety, are deemed to have been
15 included in present method of using said additive composition of the present invention.

16 Accordingly, in third embodiment, the present invention also relates to method
17 for controlling and inhibiting polymerization of aromatic vinyl monomers including
18 styrene by employing amine and nitroxide based additive composition of present
19 invention described herein, a reference to which is drawn in entirety, wherein the
20 stream comprising aromatic vinyl monomers including styrene is treated with an
21 additive composition comprising one or more of nitroxides (i.e. nitroxyls) compounds
22 and one or more of said amines.

23 In particular, in third embodiment, the present invention relates to a method for
24 controlling and inhibition of polymerization of aromatic vinyl monomers including
25 styrene by employing additive composition of the present invention described herein, a
26 reference to which is drawn in entirety, wherein said composition comprises:

27 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
28 characterized in that the said composition further comprises one or more of
29 (b) aliphatic amines selected from a group comprising tertiary amines, secondary
30 amines and primary amines, preferably the amine is tertiary amine; and
31 said composition is added to said monomers.

32 Accordingly, in this third embodiment, the present invention particularly relates
33 to a method for controlling and inhibition of polymerization of aromatic vinyl
34 monomers including styrene by employing additive composition of the present

1 invention described herein, a reference to which is drawn in entirety, wherein said
2 composition comprises:

3 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and
4 characterized in that the said composition further comprises one or more of

5 (b) tertiary amines; and
6 said composition is added to said monomers.

7 Accordingly, in this third embodiment, the present invention also relates to a
8 method for controlling and inhibition of polymerization of aromatic vinyl monomers
9 including styrene by employing additive composition of the present invention described
10 herein, a reference to which is drawn in entirety, wherein said composition comprises:

11 (a) one or more of nitroxides (i.e. nitroxyls) compounds; and

12 characterized in that the said composition further comprises one or more of

13 (b) amines selected from a group consisting of primary amines and secondary
14 amines; and

15 said composition is added to said monomers.

16 It may be noted that the stream comprising aromatic vinyl monomers including
17 styrene may be referred to as stream or monomers stream or as aromatic vinyl
18 monomers stream.

19 In accordance with one of the embodiments of the present invention, the method
20 for controlling and inhibition of polymerization of aromatic vinyl monomers including
21 styrene by employing said additive composition of the present invention comprises
22 adding from about 0.01 ppm to about 2000 ppm, preferably from about 1 ppm to about
23 2000 ppm of said composition to the aromatic vinyl monomers stream including
24 styrene based on weight of monomers.

25 It may be noted that all the features of the composition of the present invention
26 described herein, a reference to which is drawn in entirety, are deemed to have been
27 included in present method for controlling and inhibition of polymerization of aromatic
28 vinyl monomers including styrene by employing said additive composition of the
29 present invention.

30 In accordance with one of the embodiments of the present invention, the
31 composition of present invention may be mixed with or added to the monomers stream
32 containing aromatic vinyl monomers including styrene either before the stream enters
33 into processing system or after the stream has entered into processing system, but
34 preferably the composition is added to the stream containing aromatic vinyl monomers

1 before its processing starts so that polymerization of aromatic vinyl monomers is
2 avoided.

3 In accordance with one of the embodiments of the present invention, the
4 nitroxide compounds and the amine compounds may be mixed with or added to the
5 monomers stream individually or after mixing.

6 In accordance with one of the embodiments of the present invention, the present
7 composition may be used in or employed with or added to monomers stream over a
8 wide range of temperature varying from about 50 degree C to about 180 degree C,
9 preferably from about 60 degree C to about 180 degree C.

10 The composition of present invention may be prepared in any known manner to
11 prepare the compositions.

12 Accordingly, in fourth embodiment, the present invention also relates to method
13 of preparing amine and nitroxide based additive composition of present invention
14 described herein, a reference to which is drawn in entirety, for controlling and
15 inhibiting polymerization of aromatic vinyl monomers including styrene, wherein the
16 nitroxide and said amine compounds are added individually or after mixing.

17 In particular, in fourth embodiment, the present invention relates to a method
18 for preparation of additive composition of the present invention described herein, a
19 reference to which is drawn in entirety, for controlling and inhibition of polymerization
20 of aromatic vinyl monomers including styrene, wherein the method comprises:

21 (A) mixing one or more of said nitroxide (i.e. nitroxyl) compounds,
22 characterized in that said nitroxide compound or mixture thereof is further mixed with
23 one or more of

24 (B) aliphatic amines selected from a group comprising tertiary amines, secondary
25 amines and primary amines, preferably the tertiary amines.

26 Accordingly, in this fourth embodiment, the present invention particularly
27 relates to a method for preparation of additive composition of the present invention
28 described herein, a reference to which is drawn in entirety, for controlling and
29 inhibition of polymerization of aromatic vinyl monomers including styrene, wherein
30 the method comprises:

31 (A) mixing one or more of said nitroxide (i.e. nitroxyl) compounds,
32 characterized in that said nitroxide compound or mixture thereof is further mixed with
33 one or more of

34 (B) tertiary amines.

1 Accordingly, in this fourth embodiment, the present invention also relates to a
2 method for preparation of additive composition of the present invention described
3 herein, a reference to which is drawn in entirety, for controlling and inhibition of
4 polymerization of aromatic vinyl monomers including styrene, wherein the method
5 comprises:

6 (A) mixing one or more of said nitroxide (i.e. nitroxyl) compounds,
7 characterized in that said nitroxide compound or mixture thereof is further mixed with
8 one or more of

9 (B) amines selected from a group consisting of primary amines and secondary
10 amines.

11 It may be noted that the stream comprising aromatic vinyl monomers including
12 styrene may be referred to as stream or monomers stream or as aromatic vinyl
13 monomers stream.

14 It may be noted that all the features of the composition of the present invention
15 described herein, a reference to which is drawn in entirety, are deemed to have been
16 included in present method for preparation of additive composition of the present
17 invention.

18 In one of the embodiments, the inventor has found that when present
19 composition comprises any one of the amines selected from a group consisting of
20 N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED) and N,N,N',N'-
21 Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol), then efficiency for controlling
22 and inhibition of polymerization of aromatic vinyl monomers including styrene of the
23 nitroxides is substantially improved, however, the efficiency improvement is not as
24 substantial as for the composition comprising tris(2-hydroxypropyl)amine (TIPA).
25 Therefore, as per most preferred embodiment of the present invention, tris(2-
26 hydroxypropyl)amine (TIPA) is most preferred amine.

27 In another embodiment, the inventor has found that when present composition
28 comprises any one of the amines selected from a group consisting of triethanolamine
29 (TEA), Tris[N-butylamine] (TBA), monoethanolamine (MEA), octyl amine (OA),
30 dibutyl amine (DBA), then efficiency for controlling and inhibition of polymerization
31 of aromatic vinyl monomers including styrene of the nitroxides is improved, however,
32 the efficiency improvement is not as substantial as for the composition comprising
33 N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED) or N,N,N',N'-
34 Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol). Therefore, as per more

1 preferred embodiment of the present invention, N,N,N',N'-Tetrakis (2-hydroxyethyl)
2 ethylene-diamine) (THEED) and N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-
3 diamine) (Quadrol) are the more preferred amines. It has been found that dibutyl amine
4 (DBA), surprisingly and unexpectedly, demonstrates better efficiency when used in
5 compositions of dosages of about 200 ppm or more.

6 In still another embodiment, the inventor has found that when present
7 composition comprises any one of the amines selected from a group consisting of
8 N,N-disec-butyl-para-phenylene diamine (UOP5), ethylene diamine (EDA),
9 tetraethylenepentamine (TEPA), dipropyl amine (DPA), or diethanol amine (DEA),
10 then efficiency for controlling and inhibition of polymerization of aromatic vinyl
11 monomers including styrene of the nitroxides is not improved. Therefore, in one
12 embodiment, the present composition does not comprise any one of the amines selected
13 from a group consisting of N,N-disec-butyl-para-phenylene diamine (UOP5), ethylene
14 diamine (EDA), tetraethylenepentamine (TEPA), dipropyl amine (DPA), or diethanol
15 amine (DEA). It may be noted that some of these amines result in very marginal
16 improvement in efficiency of nitroxides, but same is not commercially viable.

17 Further advantages and embodiments of the present invention will become more
18 apparent from the following examples.

19 The present invention is now described with the help of following examples,
20 which are not intended to limit scope of the present invention, but have been
21 incorporated to illustrate mode and best mode of performing the present invention.

22 23 **Experiments:**

24 **Main Experiment:**

25 In the following experiments, weighed amount of distilled styrene and additives
26 were taken in a reactor (tube reactor or round bottom reactor) equipped with
27 thermometer and nitrogen inlet and outlet. In these experiments a tube reactor was used
28 without any mechanical stirrer, and enough N₂ flow was maintained to ensure proper
29 agitation. The reactions were carried out at about 120°C for about 2 hours. After the
30 selected duration, the reactor was cooled to below about 10°C by immersing in crushed
31 ice. The contents of the reactor were then poured in a beaker. To this same beaker,
32 approximately for 1.5-2g chilled polymerization mixture, about 80g methanol was used
33 to precipitate the polymer formed in the styrene solution. The precipitate obtained was
34 filtered, dried to remove methanol, and weighed.

The weight of the precipitate was reported as % polymer formed in following tables.

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

In following examples, the prior additive is a nitroxide, which is 1 oxyl-2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT), which was taken in an amount of about 100, 200, 300, 500, or 1000 ppm by weight of styrene.

In the following examples, the present additive is a composition comprising nitroxide which is 1-oxyl-2,2,6,6, tetramethylpiperidin-4-ol (4 Hydroxy Tempo or 4-HT), and aliphatic tertiary amine, which is tri-isopropanol amine (TIPA) containing three hydroxyl groups, wherein from about 1 to about 20 ppm of TIPA is added to the weighed amount of nitroxide.

Experiment 1 –

The results of above Main Experiment when performed with 10g of distilled styrene by heating to 120°C for 2h are provided in Table 1.

Table-I

Active Dosage of Prior Art Additive Composition (ppm) ↓	%polymer formed with Prior art Additive	Active Dosage of Present Additive Composition (ppm) ↓	%polymer formed with Present composition	Technical Effects of present composition
100 ppm	13.19	100 + 4 TIPA	11.22	Polymerization inhibition efficiency of nitroxide is improved, and %polymer formed is reduced substantially on addition of aliphatic tertiary amine in nitroxide
		100 + 10 TIPA	10.9	
		100 + 15 TIPA	6.28	
		100 + 20 TIPA	4.3	
200 ppm	9.38	100 + 15 TIPA	6.28	
		100 + 20 TIPA	4.3	
300 ppm	5.1	100 + 20 TIPA	4.3	

1 It is understood from above Table-I that when just 4 ppm to 20 ppm of TIPA is
2 added to 100 ppm of 4HT (prior art additive), the efficiency of 4-HT to control and
3 inhibit polymerization of styrene is, surprisingly and unexpectedly, improved
4 substantially.

5 It can also be seen from Table-I that polymerization of styrene is, surprisingly
6 and unexpectedly, substantially reduced just on addition of 4 to 20 ppm of TIPA in 100
7 ppm of 4HT (prior art additive).

8 It may be noted, the %polymer formed with 100 ppm of 4-HT alone is
9 substantially reduced from 13.19% to 11.22%, to 10.9%, to 6.28%, and to 4.3%,
10 respectively when 4 ppm (3.85% of total composition), 10 ppm (9.09% of total
11 composition), 15 ppm (13.04% of total composition) and 20 ppm (16.67% of total
12 composition) of TIPA is added to 100 ppm of 4HT.

13 It can also be seen from Table-I that for composition comprising 100 ppm of
14 4HT and 15 ppm of TIPA (13.04% of TIPA of total composition), the %polymer
15 formed is, surprisingly and unexpectedly, substantially less than %polymer formed
16 with composition consisting of 200 ppm of 4-HT, meaning thereby, the present
17 composition results in saving of half of dosage of 4-HT, and hence is economical and
18 environment friendly.

19 It can also be seen from Table-I that for composition comprising 100 ppm of
20 4HT and 20 ppm of TIPA (16.67% of TIPA of total composition), the %polymer
21 formed is, surprisingly and unexpectedly, substantially less than %polymer formed
22 with composition consisting of 300 ppm of 4-HT, meaning thereby, the present
23 composition results in saving of two-third of dosage of 4-HT, and hence, is economical
24 and environment friendly.

25 26 **Experiment 2 –**

27 The results of above Main Experiment when performed with 10g of distilled
28 styrene by heating to 135°C for 2h are provided in Table-II.
29
30

Table-II

Active Dosage of Prior Art Additive Composition (ppm) ↓	%polymer formed with Prior art Additive	Active Dosage of Present Additive Composition (ppm) ↓	%polymer formed with Present composition	Technical Effects of present composition
500 ppm	16.7	500 + 5 TIPA	6.45	Polymerization inhibition efficiency of nitroxide is improved, and %polymer formed is reduced substantially on addition of aliphatic tertiary amine in nitroxide
		500 + 10 TIPA	6.05	
		500 + 15 TIPA	5.72	
		500 + 20 TIPA	4.9	
1000 ppm	6.13	500 + 10 TIPA	6.05	
		500 + 15 TIPA	5.72	
		500 + 20 TIPA	4.9	

2

3 It is understood from above Table-II that when just 5 ppm to 20 ppm of TIPA is
4 added even to higher dosage of 500 ppm of 4HT (prior art additive) and styrene stream
5 with additive is treated even at higher temperature of 135⁰C, the efficiency of 4-HT to
6 control and inhibit polymerization of styrene is, surprisingly and unexpectedly,
7 improved substantially.

8 It can also be seen from Table-II that polymerization of styrene is, surprisingly
9 and unexpectedly, substantially reduced just on addition of 5 to 20 ppm of TIPA in 500
10 ppm of 4HT (prior art additive).

11 It may be noted the %polymer formed with 500 ppm of 4-HT alone is
12 substantially reduced even at higher temperature of about 135⁰C from 16.7% to 6.45%,
13 to 6.05%, to 5.72%, and to 4.9%, respectively when 5 ppm (just 0.99% of total
14 composition), 10 ppm (just 1.96% of total composition), 15 ppm (just 2.91% of total
15 composition) and 20 ppm (just 3.85% of total composition) of TIPA is added to 500
16 ppm of 4HT. The reduction achieved is even greater than about 3 times.

17 It can also be seen from Table-II that for composition comprising 500 ppm of
18 4HT and 10 ppm of TIPA (just 1.96% of TIPA of total composition), the %polymer
19 formed is, surprisingly and unexpectedly, less than %polymer formed with composition

consisting of 1000 ppm of 4-HT, meaning thereby, the present composition results in saving of half of dosage of 4-HT, and hence is economical and environment friendly.

Experiments 3 to 5:

In following examples, for above Main Experiment, the prior art additive composition is 4HT, which is taken in an amount of about 100, 200, and 300 ppm, and the present additive composition is a composition comprising 4HT being nitroxide, and additionally comprising TIPA, THEED, Quadrol, TEA, TBA, MEA, OA, DBA being amines of the present invention, which are taken in weight ratio of 99:1, 98:2, 95:5, 90:10, 85:15, 80:20, 70:30 and 50:50, the composition is made to 100, 200 and 300 ppm.

The inventor has further compared the results of present compositions with additive compositions comprising 4HT and amine selected from a group consisting of UOP5, EDA, TEPA, DPA, or DEA for comparative purposes.

As can be seen from data in Tables III, IV and V, with addition of about 1 to about 150 ppm of TIPA, THEED, Quadrol, TEA, TBA, MEA, OA or DBA to 4HT making total of 100, 200 and 300 ppm of the composition so as to have 4HT : Amine in a weight ratio of 99:1, 98:2, 95:5, 90:10, 85:15, 80:20, 70:30 and 50:50, the efficiency of prior art additive composition consisting of 4HT to control and inhibit polymerization of styrene is, surprisingly and unexpectedly, generally improved.

As can be seen, when present composition comprises any one of the amines selected from a group consisting of N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED) and N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol), then efficiency for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene of the nitroxides is substantially improved, however, the improvement is not as substantial as for the composition comprising tris(2-hydroxypropyl)amine (TIPA). Therefore, as per most preferred embodiment of the present invention, tris(2-hydroxypropyl)amine (TIPA) is most preferred amine.

As can also be seen, when present composition comprises any one of the amines selected from a group consisting of triethanolamine (TEA), Tris[N-butylamine] (TBA), monoethanolamine (MEA), octyl amine (OA), dibutyl amine (DBA), then efficiency for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene of the nitroxides is improved, however, the improvement is not as substantial as for the composition comprising N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-

diamine) (THEED) or N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol). Therefore, as per more preferred embodiment of the present invention, N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED) and N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol) are the more preferred amines.

As can be seen, dibutyl amine (DBA), surprisingly and unexpectedly, demonstrates better efficiency when used in compositions of dosages of about 200 ppm or more.

As can also be seen, when the composition comprises any one of the comparative amines selected from a group consisting of N,N-disec-butyl-para-phenylene diamine (UOP5), ethylene diamine (EDA), tetraethylenepentamine (TEPA), dipropyl amine (DPA), or diethanol amine (DEA), then efficiency for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene of the nitroxides is not improved. Therefore, in one embodiment, the present composition does not comprise any one of the amines selected from a group consisting of N,N-disec-butyl-para-phenylene diamine (UOP5), ethylene diamine (EDA), tetraethylenepentamine (TEPA), dipropyl amine (DPA), or diethanol amine (DEA). It may be noted that some of these amines result in very marginal improvement in efficiency of nitroxides, but same is not commercially viable.

It may be noted that, surprisingly and unexpectedly, with increase in concentration of amine, i.e. when about 20% or more of the amine is added to 4HT, the polymerization inhibition efficiency of present additive composition reduces marginally, the reasons for which are not known at present.

Accordingly, in view of above experimental data and analysis thereof, it can be concluded that only the additive compositions of the present invention comprising 4HT and amine selected from a group consisting of TIPA, THEED, Quadrol, TEA, TBA, MEA, OA and DBA, surprisingly and unexpectedly, result in improvement of control and polymerization inhibition efficiency of prior art additive composition consisting of 4HT, and these findings confirm synergistic effect of present compositions.

Experiment 6:

The above Main Experiment was also carried out with round bottom reactor for prior art additive composition consisting of 4HT; and present additive composition comprising 4HT and TIPA, and it has been found that with addition of present amine additives, the efficiency of prior art additive composition to control and inhibit

polymerization of styrene is, surprisingly and unexpectedly, generally improved even in round bottom reactor.

Table - VI

Composition	Dosage, active, ppm	% Polymer
4HT	100	13.27
4HT	200	9.11
4HT	300	6.79
4HT	400	2.32
4HT + TIPA (90:10)	100	10.17
4HT + TIPA (90:10)	200	4.42
4HT + TIPA (95:5)	200	5.15

The above experimental data confirms the synergistic effects, and the surprising and unexpected technical effects and advantages of the additive composition of the present invention over the prior art additive composition and comparative compositions.

All of above findings confirm synergistic, surprising and unexpected effects of present composition at lower as well as at higher temperatures.

All of above findings also confirm that there is successive increase in efficiency of prior art additive to control and inhibit polymerization of styrene.

All of above findings also confirm that present composition is capable of achieving far better efficiency to control and inhibit polymerization of styrene with same dosage of the prior art additive, meaning thereby, the present invention results in economical and environmental benefits.

Above experimental results confirm that presently provided composition is far superior than prior art additive, and hence, has technical advantages and surprising effects over the prior art additive.

1 It may be noted that the term “about” as employed herein is not intended to
2 enlarge scope of claimed invention, but has been incorporated only to include
3 experimental errors permissible in the field of the art.

Table IV

	4HT	4HT/ TIPA	4HT/ THEED	4HT/ Quadrol	4HT/ TEA	4HT/ MEA	<u>4HT/ DBA</u>	4HT/ TBA	4HT/ Octyl amine	4HT/ DPA	4HT/ DEA	4HT/ UOP5	4HT/ EDA	4HT/ TEPA
	9.38	3.05	4.49	4.5	8.86	8.2	6.47	9.09	8.8	9.10	9.21	9.33	9.52	9.64
	9.38	2.5	3.87	3.94	7.08	7.87	6.66	8.83	8.33	8.53	9.08	9.67	9.8	9.92
	9.38	2.14	3.47	3.53	5.26	7.41	6.90	8.45	8.03	8.39	9.27	9.82	9.91	10.20
	9.38	1.91	3.12	3.06	4.11	7.21	7.25	8.08	7.42	8.11	9.54	10.02	10.22	10.55
	9.38	1.74	2.75	2.86	3.58	7.08	7.55	7.60	7.11	8.62	9.76	10.33	10.5	10.77
	9.38	1.80	2.42	2.49	3.22	7.25	7.82	7.96	7.66	9.35	10.2	10.52	10.71	11.88
	9.38	2.53	3.22	3.18	4.06	7.64	8.21	8.24	8.11	9.91	10.9	11.0	11.14	12.07
	9.38	3.10	3.65	3.62	4.98	8.25	9.02	9.65	8.95	10.28	11.5	11.5	11.26	12.79

5.1	0.75	1.70	1.66	3.22	4.82	4.36	4.33	4.55	9.9	9.7	6.55	9.26	10.05
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Claims

1. Additive composition for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene comprising:
 - (a) one or more of nitroxide (i.e. nitroxyl) compounds; and characterized in that the said composition further comprises one or more of
 - (b) amines, wherein said amine is aliphatic amine, and wherein the aliphatic amine is tertiary amine.
2. Additive composition as claimed in claim 1, wherein said amine is selected from the group comprising hydroxyl alkyl tertiary amine, ethylene oxide treated amine, propylene oxide treated amine, and tertiary alkyl amine, or combination thereof.
3. Additive composition as claimed in claim 1 or 2, wherein said hydroxyl alkyl tertiary amine is tris(2-hydroxypropyl)amine (TIPA).
4. Additive composition as claimed in any one of claims 1 to 3, wherein said ethylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED).
5. Additive composition as claimed in any one of claims 1 to 4, wherein said propylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol).
6. Additive composition as claimed in any one of claims 1 to 5, wherein said hydroxyl alkyl tertiary amine is triethanolamine (TEA).
7. Additive composition as claimed in any one of the preceding claims 1 to 6, wherein said tertiary alkyl amine is Tris[N-butylamine] (TBA).
8. Additive composition for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene comprising:
 - (a) one or more of nitroxide (i.e. nitroxyl) compounds; and characterized in that the said composition further comprises
 - (b) one or more of amines, wherein said amine is aliphatic amine, and wherein the aliphatic amine is selected from a group consisting of primary and secondary amines.

9. Additive composition as claimed in claim 8, wherein said primary amine is selected from a group comprising hydroxyl alkyl primary amine and alkyl primary amine.
- 5 10. Additive composition as claimed in claim 8 or 9, wherein said secondary amine is alkyl secondary amine.
11. Additive composition as claimed in any one of claims 8 to 10, wherein said hydroxyl alkyl primary amine is monoethanolamine (MEA).
12. Additive composition as claimed in any one of claims 8 to 11, wherein said
10 alkyl primary amine is octyl amine (OA).
13. Additive composition as claimed in any one of claims 8 to 12, wherein said alkyl secondary amine is dibutyl amine (DBA).
14. Additive composition as claimed in any one of claims 1 to 13, wherein said composition comprises:
- 15 a) about 40 to about 99.75 % by weight of *I*) said nitroxide (i.e. nitroxyl) compounds; and
- b) about 0.25 to about 60 % by weight of *II*) said amines, or mixture thereof.
15. Additive composition as claimed in any one of claims 1 to 14, wherein about 0.01 to about 2000 ppm of said composition is added to aromatic vinyl
20 monomers stream based on weight of monomer.
16. Additive composition as claimed in any one of claims 1 to 15, wherein said nitroxide (i.e. nitroxyl) compound is selected from the group comprising di-tert-butyl nitroxyl, 1-oxy-2,2,6,6-tetramethylpiperidine, 1-oxy-2,2,6,6-tetramethylpiperidin-4-ol, 1-oxy-2,2,6,6-tetramethylpiperidin-4-one, and
25 derivatives thereof; and di-nitroxides and derivatives comprising bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)sebacate, bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)succinate, bis(1-oxy-2,2,6,6-tetramethylpiperidin-4-yl)adipate, and mixture thereof.

30

17. Additive composition as claimed in any one of claims 1 to 16, 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.
18. Additive composition as claimed in any one of claims 1 to 17, wherein said nitroxide (i.e. nitroxyl) compound is 1 oxyl -2,2,6,6, tetramethylpiperidin-4-ol (or 4 Hydroxy Tempo or 4-HT).
19. Additive composition as claimed in any one of claims 1 to 18, wherein said composition does not comprise aromatic nitro compound.
20. A method for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene by adding additive composition as claimed in any one of the preceding claims 1 to 19 to monomers stream, wherein said composition comprises:
- (a) one or more of nitroxide (i.e. nitroxyl) compounds; and characterized in that the said composition further comprises one or more of
 - (b) said amines; and said composition is added to said monomers.
21. The method as claimed claim 20, wherein about 0.01 to about 2000 ppm of said composition is added to aromatic vinyl monomers stream based on weight of monomer.
22. A method of using additive composition as claimed in any one of the preceding claims 1 to 19 for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene, wherein said composition comprises:
- (a) one or more of nitroxide (i.e. nitroxyl) compounds; and characterized in that the said composition further comprises one or more of
 - (b) said amines, and said monomers are treated with said composition.

23. The method as claimed claim 22, wherein said aromatic vinyl monomers stream is treated with about 0.01 to about 2000 ppm of said composition based on weight of monomer.
- 5 24. A method for preparing additive composition as claimed in any one of the preceding claims 1 to 19 for controlling and inhibiting polymerization of aromatic vinyl monomers including styrene, wherein the method comprises:
- (A) mixing one or more of said nitroxide (i.e. nitroxyl) compounds, characterized in that said nitroxide (i.e. nitroxyl) compound or mixture thereof
- 10 is further mixed with one or more of
- (B) said amines.
25. The method as claimed claim 24, wherein said one or more of nitroxide compounds, and said one or more amines are added to monomer stream individually.
- 15 26. The method as claimed in any one of the preceding claims 20 to 23, wherein said composition is used over a range of temperature varying from about 50 degree C to about 180 degree C.