

1 **Title of the invention:**

2 Improved Additives Composition for control and inhibition of polymerization
3 of aromatic vinyl monomers, and method of use thereof.
4

5 **Field of the invention:**

6 The present invention relates to an improved additive composition for control
7 and inhibition of polymerization of aromatic vinyl monomers, wherein aromatic vinyl
8 monomer includes styrene, wherein improvement comprises a composition of one or
9 more tertiary amines and one or more of aromatic nitro compounds.

10 In one embodiment, the present invention relates to use of improved additive
11 composition of present invention to control and inhibit polymerization of aromatic
12 vinyl monomers including styrene, wherein improvement comprises use of a
13 composition comprising one or more tertiary amines and one or more of aromatic nitro
14 compounds.

15 In another embodiment, the present invention relates to method of preparation
16 of improved additive composition of present invention for control and inhibition of
17 polymerization of aromatic vinyl monomers including styrene, wherein improvement
18 comprises preparation of a composition comprising one or more tertiary amines and
19 one or more of aromatic nitro compounds.

20 In still another embodiment, the present invention relates to method of
21 controlling and inhibiting polymerization of aromatic vinyl monomers including
22 styrene by employing improved additive composition of present invention, wherein
23 improvement comprises treating the stream containing aromatic vinyl monomers with a
24 composition comprising one or more tertiary amines and one or more of aromatic nitro
25 compounds.
26

27 **Background of the invention:**

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

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

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

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

7 The prior art [US 5,254,760 (US'760)] discloses the polymerization inhibition
8 of vinyl monomers using a combination of nitroxides (i.e. nitroxyl compounds)
9 including 1 oxyl-2,2,6,6, tetramethylpiperidin-4-ol (4HT) and aromatic nitro
10 compounds including dinitro-butylphenol [*re abstract, Col. 3, lines 26-32; Col. 4, lines*
11 *1-2, 12 of US'760*] as the polymerization inhibitor.

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

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

20 Therefore, the industry is aiming for additive composition wherein the amount
21 of aromatic nitro compounds can be reduced or minimized so that the resulted
22 composition is economical as well as safe for human being. Any effort to reduce or
23 minimize consumption of aromatic nitro compounds will lessen the problems of the
24 industry.

25 **Need of the Invention:**

26 Therefore, there is still a need of an effective additive composition and method
27 of its use and preparation, and method of controlling and inhibiting polymerization of
28 vinyl aromatic monomers by employing said composition, wherein the additive
29 composition is not only suitable for substantial control and inhibition of polymerization
30 of aromatic vinyl monomers including styrene, but also comprises substantially reduced
31 or minimized amount of aromatic nitro compounds.
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33
34

1 **Problem to be solved by the Invention:**

2 Therefore, the present invention aims at providing a solution to above-described
3 existing industrial problems by providing effective additive composition and method of
4 its use and preparation, and method of controlling and inhibiting polymerization of
5 vinyl aromatic monomers, wherein the additive composition is not only suitable for
6 substantial control and inhibition of polymerization of aromatic vinyl monomers
7 including styrene, but also comprises substantially reduced or minimized amount of
8 aromatic nitro compounds.

9
10 **Objects of the Invention:**

11 Accordingly, the main object of present invention is to provide an effective
12 additive composition and method of its use and preparation, and method of controlling
13 and inhibiting polymerization of vinyl aromatic monomers, wherein the additive
14 composition is not only suitable for substantial control and inhibition of polymerization
15 of aromatic vinyl monomers including styrene, but also comprises substantially reduced
16 or minimized amount of aromatic nitro compounds.

17 Another main object of present invention is to provide an effective additive
18 composition and method of its use and preparation, and method of controlling and
19 inhibiting polymerization of vinyl aromatic monomers, wherein the additive
20 composition comprises substantially reduced or minimized amount of aromatic nitro
21 compounds, and is still suitable for substantial control and inhibition of polymerization
22 of aromatic vinyl monomers including styrene, and is still required in relatively lower
23 dosage as compared to dosage of aromatic nitro compounds alone for achieving the
24 same or better acceptable level of control and inhibition of polymerization of styrene.

25 This is also an object of present invention to provide an effective additive
26 composition and method of its use and preparation, and method of controlling and
27 inhibiting polymerization of vinyl aromatic monomers, wherein the additive
28 composition comprises one or more of amines and reduced or minimized amount of
29 one or more of aromatic nitro compounds, and is still suitable for substantial control
30 and inhibition of polymerization of aromatic vinyl monomers including styrene, and is
31 still required in relatively lower dosage as compared to dosage of aromatic nitro
32 compounds alone for achieving the same or better acceptable level of control and
33 inhibition of polymerization of styrene, and wherein the amine is one or more of
34 tertiary amines.

1 The present invention particularly aims at providing an effective additive
2 composition and method of its use and preparation, and method of controlling and
3 inhibiting polymerization of vinyl aromatic monomers, wherein the additive
4 composition comprises one or more of amines and reduced or minimized amount of
5 one or more of aromatic nitro compounds, and is still suitable for substantial control
6 and inhibition of polymerization of aromatic vinyl monomers including styrene, and is
7 still required in relatively lower dosage as compared to dosage of aromatic nitro
8 compound alone for achieving the same or better acceptable level of control and
9 inhibition of polymerization of styrene, and wherein the amine is one or more of
10 tertiary amines, and therefore, the composition of present invention is not only
11 economical, but is also environment friendly.

12 The present invention also aims at improving the performance of aromatic nitro
13 compounds at a wider range of temperature including the higher temperature, wherein
14 the composition further comprises one or more tertiary amines.

15 The present invention also aims at improving the performance of aromatic nitro
16 compounds at a wider range of temperature including the higher temperature and in
17 presence of air, wherein the composition further comprises one or more tertiary amines.

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

21 22 **Description and Preferred Embodiments of the Invention:**

23 With aim to overcome above-described problems of prior art and to achieve
24 above-described objects of the invention, the inventor has found that when one or more
25 of tertiary amines is added to composition consisting of aromatic nitro compounds, then
26 not only polymerization controlling and inhibiting efficiency of aromatic nitro
27 compounds is substantially improved, but polymerization of aromatic vinyl monomers
28 including styrene, surprisingly and unexpectedly, is also controlled and inhibited to the
29 acceptable level with substantially reduced and minimized dosage of aromatic nitro
30 compound in a composition comprising one or more of tertiary amines and one or more
31 of aromatic nitro compounds, which makes the present composition economical as well
32 as environment friendly.

33 With aim to overcome above-described problems of prior art and to achieve
34 above-described objects of the invention, the inventor has found that when one or more

1 of an aliphatic tertiary amine, or aliphatic tertiary amine containing one or more
2 hydroxyl groups is added to composition consisting of one or more of aromatic nitro
3 compounds, then not only polymerization controlling and inhibiting efficiency of
4 aromatic nitro compounds is substantially improved, but polymerization of aromatic
5 vinyl monomers including styrene, surprisingly and unexpectedly, is also controlled
6 and inhibited to the acceptable level with substantially reduced and minimized dosage
7 of aromatic nitro compound in a composition comprising one or more aromatic nitro
8 compounds and one or more of aliphatic tertiary amines or aliphatic tertiary amines
9 containing one or more hydroxyl groups, which makes the present composition
10 economical as well as environment friendly.

11 Accordingly, the present invention relates to additive composition for
12 controlling and inhibition of polymerization of aromatic vinyl monomers including
13 styrene comprising:

14 (A) one or more of aromatic nitro compounds; and

15 **characterized in that** the said composition further comprises:

16 (B) one or more of aliphatic tertiary amines, or mixture thereof.

17 In accordance with present invention, the aliphatic amine is aliphatic tertiary
18 amine, which contains one or more hydroxyl groups, preferably contains one or more
19 hydroxyl groups in the alkyl chain of the tertiary amine, more preferably the aliphatic
20 tertiary amine contains three or four hydroxyl groups in the alkyl chain of the tertiary
21 amine.

22 In accordance with present invention, in the aliphatic tertiary amine containing
23 one or more hydroxyl groups, the hydroxyl groups are hydroxyalkyl groups.

24 In accordance with present invention, the hydrocarbon in the aliphatic tertiary
25 amine may be linear, branched or cyclic.

26 In accordance with present invention, the hydrocarbon in the aliphatic tertiary
27 amine may contain one or more hydroxy alkyl groups.

28 In accordance with most preferred embodiment of the present invention, the
29 aliphatic tertiary amine containing three hydroxyl groups is tri-isopropanol amine or
30 tris(2-hydroxypropyl)amine [TIPA].

31 In accordance with one of the preferred embodiments of the present invention,
32 the aliphatic tertiary amine containing hydroxyl groups is N,N,N',N'-Tetrakis (2-
33 hydroxyethyl) ethylene-diamine) (THEED).

1 In accordance with another preferred embodiment of the present invention, the
2 aliphatic tertiary amine containing hydroxyl groups is N,N,N',N'-Tetrakis (2-
3 hydroxypropyl) ethylene-diamine) (Quadrol®).

4 In accordance with another preferred embodiment of the present invention, the
5 composition of the present invention may comprise one or more of above-said aliphatic
6 tertiary amines containing hydroxyl groups or mixture thereof.

7 Therefore, in one embodiment, the present invention relates to additive
8 composition for controlling and inhibition of polymerization of aromatic vinyl
9 monomers including styrene comprising:

10 (A) one or more of aromatic nitro compounds,

11 **characterized in that** the said composition further comprises:

12 (B) one or more of tertiary amines,

13 wherein said tertiary amine is selected from a group consisting of:

14 i) hydroxyl alkyl tertiary amine which is tris(2-hydroxypropyl)amine
15 (TIPA);

16 ii) propylene oxide treated amine which is N,N,N',N'-Tetrakis (2-
17 hydroxypropyl) ethylene-diamine) (Quadrol®); and

18 iii) ethylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxyethyl)
19 ethylene-diamine) (THEED) THEED compounds; or

20 iv) mixture thereof.

21 It has been found that when composition of present invention comprises one or
22 more said aliphatic tertiary amines, the efficiency of aromatic nitro compounds to
23 control and inhibit polymerization of aromatic vinyl monomers including styrene is,
24 surprisingly and unexpectedly, substantially improved to the acceptable level that's too
25 at substantially reduced or minimized dosages of aromatic nitro compounds, thereby
26 making the composition of present invention relatively more economical and
27 environment friendly.

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

30 a) about 40 to about 99.75 % by weight of I) one or more of said aromatic
31 nitro compounds; and

32 b) about 0.25 to about 60 % by weight of II) said amine or mixture thereof.

33 In accordance with one of the preferred embodiments of the present invention,
34 the composition of present invention is added to the stream containing aromatic vinyl

monomers including styrene in an amount varying from about 0.01 ppm to about 2000 ppm, preferably from about 1 ppm to about 2000 ppm by weight of the stream of the monomers including styrene.

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

In accordance with one of the preferred embodiments of the present invention, the present composition does not comprise nitroxide (i.e. nitroxyl) compounds including 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).

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

- i) triethanolamine (TEA);
- ii) Tris[N-butylamine] (TBA);
- iii) monoethanolamine (MEA);
- iv) octyl amine (OA);
- v) dibutyl amine (DBA);
- vi) diethanol amine (DEA);
- vii) dipropyl amine (DPA) ; and
- viii) ethylene diamine (EDA).

Accordingly, in another embodiment, the present invention also relates to method of using aliphatic tertiary amine and aromatic nitro compounds based additive composition of 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 an additive composition comprising one or more of aromatic nitro compounds and one or more of said aliphatic tertiary amines.

1 In particular, in second embodiment, the present invention relates to a method
2 of using additive composition of the present invention described herein, a reference to
3 which is drawn in entirety, for controlling and inhibition of polymerization of aromatic
4 vinyl monomers including styrene, wherein the stream comprising aromatic vinyl
5 monomer including styrene is treated with the additive composition comprising:

6 (A) one or more of aromatic nitro compounds,

7 **characterized in that** the said composition further comprises:

8 (B) one or more of tertiary amines,

9 wherein said tertiary amine is selected from a group consisting of:

10 i) hydroxyl alkyl tertiary amine which is tris(2-hydroxypropyl)amine
11 (TIPA);

12 ii) propylene oxide treated amine which is N,N,N',N'-Tetrakis (2-
13 hydroxypropyl) ethylene-diamine) (Quadrol®); and

14 iii) ethylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxyethyl)
15 ethylene-diamine) (THEED) THEED compounds; or

16 iv) mixture thereof.

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

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

24 In accordance with one of the preferred embodiments of the present invention,
25 one or more of the aromatic nitro compounds and one or more of the aliphatic tertiary
26 amine compounds are added to the monomers stream either individually or after
27 mixing.

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

31 Accordingly, in third embodiment, the present invention also relates to method
32 for controlling and inhibiting polymerization of aromatic vinyl monomers including
33 styrene by employing aliphatic tertiary amine and aromatic nitro compounds based
34 additive composition of present invention described herein, a reference to which is

drawn in entirety, wherein the stream comprising aromatic vinyl monomers including styrene is treated with the additive composition comprising one or more of aromatic nitro compounds and one or more of said aliphatic tertiary amines.

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

(A) one or more of aromatic nitro compounds,

characterized in that the said composition further comprises:

(B) one or more of tertiary amines,

wherein said tertiary amine is selected from a group consisting of:

i) hydroxyl alkyl tertiary amine which is tris(2-hydroxypropyl)amine (TIPA);

ii) propylene oxide treated amine which is N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol®); and

iii) ethylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED) THEED compounds; or

iv) mixture thereof,

and said composition is added to said monomers stream.

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

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

In accordance with one of the preferred embodiments of the present invention, one or more of the aromatic nitro compounds and one or more of the aliphatic tertiary amine compounds are added to the monomers stream either individually or after mixing.

It may be noted that all the features of the composition of the present invention described herein, a reference to which is drawn in entirety, are deemed to have been

1 included in present method for controlling and inhibition of polymerization of aromatic
2 vinyl monomers including styrene by employing said additive composition of the
3 present invention.

4 In accordance with one of the embodiments of the present invention, the
5 composition of present invention may be mixed with stream containing aromatic vinyl
6 monomers either before the stream enters into processing system or after the stream has
7 entered into processing system, but preferably the composition is added to the stream
8 containing aromatic vinyl monomers before its processing starts so that polymerization
9 of aromatic vinyl monomers is avoided or minimized.

10 In accordance with one of the embodiments of the present invention, the present
11 composition may be used over a wide range of temperature varying from about 50
12 degree C to about 180 degree C, preferably from about 60 degree C to about 180 degree
13 C.

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

16 Accordingly, in fourth embodiment, the present invention also relates to method
17 of preparing aliphatic tertiary amine and aromatic nitro compounds based additive
18 composition of the present invention described herein, a reference to which is drawn in
19 entirety, for controlling and inhibiting polymerization of aromatic vinyl monomers
20 including styrene, wherein one or more of the aromatic nitro compounds are mixed
21 with one or more of the aliphatic tertiary amine compounds either individually or after
22 mixing.

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

27 (A) mixing one or more of said aromatic nitro compounds,

28 **characterized in that** said aromatic nitro compound or mixture thereof is
29 further mixed with one or more of

30 (B) said amines selected from a group consisting of:

31 i) hydroxyl alkyl tertiary amine which is tris(2-hydroxypropyl)amine
32 (TIPA);

33 ii) propylene oxide treated amine which is N,N,N',N'-Tetrakis (2-
34 hydroxypropyl) ethylene-diamine) (Quadrol®); and

- 1 iii) ethylene oxide treated amine is N,N,N',N'-Tetrakis (2-hydroxyethyl)
2 ethylene-diamine) (THEED) THEED compounds; or
3 iv) mixture thereof.

4 In accordance with one of the embodiments of the present invention, the method
5 for preparation of additive composition of the present invention comprises mixing one
6 or more of the tertiary amines with one or more of the aromatic nitro compounds either
7 individually or after mixing.

8 In accordance with one of the embodiments of the present invention, the
9 composition prepared is used over a range of temperature varying from about 50 degree
10 C to about 180 degree C, preferably from about 60 degree C to about 180 degree C.

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

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

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

29 It may be noted that, surprisingly and unexpectedly, with increase in
30 concentration of TIPA or Quadrol® or THEED, i.e. when composition comprises about
31 50% by weight of TIPA or Quadrol® or THEED, the polymerization inhibition
32 efficiency of present additive composition reduces, the reasons for which are not
33 known at present, but compared to prior art additive composition it still demonstrates
34 improvement thereon.

1 In another embodiment, the inventor has found that when the present
2 composition comprises any one of the amines selected from a group consisting of i)
3 triethanolamine (TEA); ii) Tris[N-butylamine] (TBA); iii) monoethanolamine (MEA);
4 iv) octyl amine (OA); v) dibutyl amine (DBA); vi) diethanol amine (DEA); vii)
5 dipropyl amine (DPA); and viii) ethylene diamine (EDA), then efficiency for
6 controlling and inhibition of polymerization of aromatic vinyl monomers including
7 styrene of the aromatic nitro compounds is, surprisingly and unexpectedly,
8 substantially reduced. Therefore, in one embodiment, the present composition does not
9 comprise any one of the amines selected from a group consisting of i) triethanolamine
10 (TEA); ii) Tris[N-butylamine] (TBA); iii) monoethanolamine (MEA); iv) octyl amine
11 (OA); v) dibutyl amine (DBA); vi) diethanol amine (DEA); vii) dipropyl amine (DPA);
12 and viii) ethylene diamine (EDA). It may be noted that some of these amines result in
13 very marginal improvement in efficiency of aromatic nitro compounds at lower
14 amounts, but same is not commercially viable.

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

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

21 **Experiments:**

22 **Main Experiment:**

23 In the following experiments, measured amount of distilled styrene (or
24 hydrocarbon stream in gms) and measured amount of additives (in ppm by weight of
25 styrene or hydrocarbon stream) were taken in a tube reactor equipped with thermometer
26 and nitrogen inlet and outlet. In these experiments a tube reactor was used without any
27 mechanical stirrer, and enough N₂ flow was maintained to ensure proper agitation. The
28 reactions were carried out at either 120⁰C (Table-I, Table III, Table IV, Table V and
29 Table VI) or 135⁰C (Table-II) for 2 hours. After the selected duration, the reactor was
30 cooled to below 10⁰C by immersing in crushed ice. The contents of the reactor were
31 then poured in a beaker. To this same beaker, approximately for 1.5-2g chilled
32 polymerization mixture, about 80g methanol was used to precipitate the polymer
33 formed in the styrene solution. The precipitate obtained was filtered, dried to remove

methanol, and weighed. The weight of the precipitate was 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 aromatic nitro compound, which is 4,6-dinitro-2-sec-butylphenol (DNBP), which was taken in an amount of about 100, 200, 300, 400, 500, 600 or 1000 ppm by weight of styrene (or hydrocarbon stream).

In the following examples, the present additive is a composition comprising about 100, 200, 300, 500 or 1000 ppm of aromatic nitro compound, which is 4,6-dinitro-2-sec-butylphenol (DNBP), and from about 1 to 20 ppm of 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 aromatic nitro compound.

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 (ppm) ↓	%polymer formed with Prior art Additive	Active Dosage of Present composition (ppm) ↓	%polymer formed with Present composition	Technical Effects of present composition
100 ppm	4.8	100 + 1 TIPA	1.82	Polymerization inhibition efficiency of aromatic nitro compound is substantially improved, and %polymer formed is substantially reduced on addition of aliphatic tertiary amine in aromatic nitro compound.
		100 + 2 TIPA	1.45	
		100 + 3 TIPA	1.22	
		100 + 4 TIPA	1.08	
200 ppm	3.18	100 + 1 TIPA	1.82	
		100 + 2 TIPA	1.45	
		100 + 3 TIPA	1.22	
		100 + 4 TIPA	1.08	
300 ppm	2.03	100 + 1 TIPA	1.82	
		100 + 2 TIPA	1.45	
		100 + 3 TIPA	1.22	
		100 + 4 TIPA	1.08	

It is understood from above Table-I that when just 1 ppm, 2 ppm, 3 ppm or 4 ppm of TIPA is added to 100 ppm of DNBP (prior art additive), the efficiency of

DNBP to control and inhibit polymerization of styrene is, surprisingly and unexpectedly, improved substantially.

It can also be seen from Table-I that polymerization of styrene is, surprisingly and unexpectedly, substantially reduced just on addition of 1 ppm, 2 ppm, 3 ppm or 4 ppm of TIPA in 100 ppm of DNBP (prior art additive).

It may be noted, the %polymer formed is, surprising and unexpectedly, reduced from 4.8% with 100 ppm of DNBP, or from 3.18% with 200 ppm of DNBP, or from 2.03% with 300 ppm of DNBP to 1.82% when present composition comprises 100 ppm of DNBP and 1 ppm of TIPA, to 1.45% when present composition comprises 100 ppm of DNBP and 2 ppm of TIPA, to 1.22% when present composition comprises 100 ppm of DNBP and 3 ppm of TIPA, to 1.08% when present composition comprises 100 ppm of DNBP and 4 ppm of TIPA meaning thereby, the present composition results in substantial saving of dosage of DNBP (aromatic nitro compound), and hence, is more economical and environment friendly than a composition consisting of aromatic nitro compound.

Experiment 2 –

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

Table-II

Active Dosage of Prior art Additive (ppm) ↓	%polymer formed with Prior art Additive	Active Dosage of Present composition (ppm) ↓	%polymer formed with Present composition	Technical Effects of present composition
500 ppm	4.13	500 + 5 TIPA	2.24	Polymerization inhibition efficiency of aromatic nitro compound is substantially improved, and %polymer formed is substantially reduced on addition of aliphatic tertiary amine in aromatic nitro compound.
		500 + 10 TIPA	2.03	
		500 + 15 TIPA	1.88	
		500 + 20 TIPA	1.79	
1000 ppm	1.79	500 + 20 TIPA	1.79	

It is understood from above Table-II that when just 5 to 20 ppm of TIPA is added even to higher dosage of 500 ppm of DNBP (prior art additive), and styrene stream with additive is treated even at higher temperature of 135°C, the efficiency of DNBP to control and inhibit polymerization of styrene is, surprisingly and unexpectedly, improved substantially.

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

4 It may be noted, the %polymer formed is, surprising and unexpectedly, reduced
5 from 4.13% with 500 ppm of DNBP to 2.24% when present composition comprises
6 500 ppm of DNBP and 5 ppm of TIPA, to 2.03% when present composition comprises
7 500 ppm of DNBP and 10 ppm of TIPA, to 1.88% when present composition
8 comprises 500 ppm of DNBP and 15 ppm of TIPA, to 1.79% when present
9 composition comprises 500 ppm of DNBP and 20 ppm of TIPA, and on the contrary,
10 the efficiency of 1.79% polymer formed could only be achieved when 1000 ppm of
11 DNBP (aromatic nitro compound – prior art additive) is used, meaning thereby, the
12 present composition results in substantial saving of upto about half of the dosage of
13 DNBP (aromatic nitro compound – prior art additive), and hence, is more economical
14 and environment friendly than a composition consisting of aromatic nitro compound.

15 Experiments 3 to 5:

16 In following examples, for above Main Experiment, the prior art additive
17 composition is DNBP being aromatic nitro compound, which is taken in an amount of
18 about 100, 200, 300, 400, 500 and 600 ppm, and the present additive composition is a
19 composition comprising DNBP being aromatic nitro compound, and additionally
20 comprising TIPA, THEED or Quadrol® being amines of the present invention, which
21 are taken in weight ratio of DNBP:Amine ratio of 99:1, 95:5, 90:10, 85:15, and 50:50,
22 the composition is made to 100, 200 and 300 ppm. The inventor has further compared
23 the results of present compositions with additive compositions comprising DNBP and
24 amine selected from a group consisting of TEA, TBA, MEA, OA DBA, DEA DPA,
25 and EDA for comparative purposes. The results are given in Tables III, IV, V and VI.

26 **Table III**

Additive	Active dosage, ppm	% Polymer formed
DNBP	100	4.8
	200	3.18
	300	2.03
	400	1.17
	500	0.92
	600	0.60

1
2 As can be seen from data in Tables IV, V and VI, with addition of about 1 to
3 about 150 ppm of TIPA, THEED or Quadrol® to DNBP making total of 100, 200 and
4 300 ppm of the composition so as to have DNBP: Amine in a weight ratio of 99:1,
5 95:5, 90:10, 85:15, and 50:50, the efficiency of prior art additive composition
6 consisting of DNBP to control and inhibit polymerization of styrene is, surprisingly and
7 unexpectedly, substantially improved.

8 As can be seen, when present composition comprises any one of the amines
9 selected from a group consisting of N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-
10 diamine) (THEED) and N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine)
11 (Quadrol®), then efficiency for controlling and inhibition of polymerization of aromatic
12 vinyl monomers including styrene of the aromatic nitro compound is substantially
13 improved, however, the improvement is not as substantial as for the composition
14 comprising tris(2-hydroxypropyl)amine (TIPA). Therefore, as per most preferred
15 embodiment of the present invention, tris(2-hydroxypropyl)amine (TIPA) is most
16 preferred amine, and N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine)
17 (THEED) and N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol®) are
18 the more preferred amines of the present invention.

19 As can also be seen, when the composition comprises any one of the
20 comparative amines selected from a group consisting of TEA, TBA, MEA, OA DBA,
21 DEA DPA, and EDA, then efficiency for controlling and inhibition of polymerization
22 of aromatic vinyl monomers including styrene of the aromatic nitro compounds is not
23 improved. Therefore, in one of the embodiments, the present composition does not
24 comprise any one of the amines selected from a group consisting of TEA, TBA, MEA,
25 OA DBA, DEA DPA, and EDA. It may be noted that some of these amines result in
26 very marginal improvement in efficiency of aromatic nitro compounds, but same is not
27 commercially viable.

28 It may be noted that, surprisingly and unexpectedly, with increase in
29 concentration of amine, i.e. when about 50% of the amine is added to DNBP, the
30 polymerization inhibition efficiency of present additive composition reduces
31 marginally, the reasons for which are not known at present.

32 Accordingly, in view of above experimental data and analysis thereof, it can be
33 concluded that only the additive compositions of the present invention comprising
34 aromatic nitro compound and amine selected from a group consisting of TIPA, THEED

1 and Quadrol®, surprisingly and unexpectedly, result in improvement of control and
2 polymerization inhibition efficiency of prior art additive composition consisting of
3 aromatic nitro compound, and these findings confirm synergistic effect of present
4 compositions.

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

7 All of above findings also confirm that there is successive increase in efficiency
8 of prior art additive to control and inhibit polymerization of aromatic vinyl monomers,
9 preferably of styrene.

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

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

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

Table IV

Active Dosage Ratio of DNBP : Amine	Total Dosage (ppm)	Active Dosage DNBP+ Amine	DNBP	DNBP + TIPA	DNBP + THEED	DNBP + Quadrol [®]	DNBP + TBA	DNBP + MEA	DNBP + DBA	DNBP + TEA	DNBP + Octyl amine	DNBP + DEA	DNBP + DPA	DNBP + EDA
99:1	100	99+1	4.8	1.83	2.84	2.95	3.84	4.53	4.67	4.78	4.74	4.47	4.58	4.8
95:5	100	95+5	4.8	1.05	2.32	2.45	4.95	4.87	4.95	4.91	4.85	5.05	5.03	4.96
90:10	100	90+10	4.8	0.83	1.75	1.95	5.20	5.10	5.15	5.03	5.17	5.30	5.25	5.15
85:15	100	85+15	4.8	0.72	1.43	1.50	5.82	5.52	5.61	5.21	5.72	5.65	5.50	5.35
50:50	100	50+50	4.8	1.90	2.50	2.70	6.9	6.9	7.0	7.15	6.9	7.6	7.05	7.35

Table V

Active Dosage Ratio of DNBP : Amine	Total Dosage (ppm)	Active Dosage DNBP+ Amine	DNBP	DNBP + TIPA	DNBP + THEED	DNBP + Quadrol [®]	DNBP + TBA	DNBP + TEA	DNBP + MEA	DNBP + DPA	DNBP + DBA	DNBP + DEA	DNBP + Octyl amine	DNBP + EDA
99:1	200	198+2	3.18	0.93	1.82	1.96	3.02	3.13	3.12	3.21	3.25	3.31	3.33	3.25
95:5	200	190+10	3.18	0.65	1.40	1.52	3.25	3.33	3.35	3.40	3.45	3.60	3.51	3.40
90:10	200	180+20	3.18	0.56	0.9	1.10	3.43	3.50	3.52	3.62	3.80	3.91	3.91	3.6
85:15	200	170+30	3.18	0.35	0.75	0.9	3.85	3.75	3.8	3.85	4.1	4.1	4.5	3.8
50:50	200	100+100	3.18	0.86	1.60	1.90	4.6	5.05	5.2	4.9	5.1	5.5	5.1	5.65

Table VI

Active Dosage Ratio of DNBP : Amine	Total Dosage (ppm)	Active Dosage DNBP+ Amine	DNBP	DNBP + TIPA	DNBP + THEED	DNBP + Quadrol [®]	DNBP + MEA	DNBP + DPA	DNBP + TEA	DNBP + Octyl amine	DNBP + DBA	DNBP + TBA	DNBP + DEA	DNBP + EDA
99:1	300	297+3	2.03	0.35	0.70	0.75	1.85	1.95	2.01	1.98	2.05	2.15	2.10	2.06
95:5	300	285+15	2.03	0.20	0.45	0.50	2.05	2.15	2.10	2.10	2.20	2.30	2.35	2.19
90:10	300	270+30	2.03	0.07	0.21	0.35	2.45	2.52	2.42	2.7	2.62	2.81	2.75	2.30
85:15	300	255+45	2.03	0.05	0.15	0.30	3.0	2.9	2.8	3.2	2.92	3.09	3.25	2.45
50:50	300	150+150	2.03	0.35	0.90	0.80	4.1	3.8	3.9	4.0	3.90	3.5	4.2	4.3

Claims

1. Additive composition for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene consisting of:
 - (A) one or more of aromatic nitro compounds,
5 **characterized in that** the said composition further consists of:
 - (B) one or more of aliphatic tertiary amines, or mixture thereof,
wherein the aliphatic tertiary amine contains one or more hydroxyl groups in the alkyl chain of the tertiary amine.
2. Additive composition as claimed in claim 1, wherein the aliphatic tertiary amine
10 contains three or four hydroxyl groups in the alkyl chain of the tertiary amine.
3. Additive composition as claimed in claim 1 or claim 2, wherein said hydroxyl groups of the aliphatic tertiary amine are hydroxyalkyl groups.
4. Additive composition as claimed in any one of the preceding claims 1 to 3,
wherein said aliphatic tertiary amine containing three hydroxyl groups is tri-
15 isopropanol amine or tris(2-hydroxypropyl)amine (TIPA).
5. Additive composition as claimed in any one of the preceding claims 1 to 3,
wherein said aliphatic tertiary amine containing hydroxyl groups is N,N,N',N'-
Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED).
6. Additive composition as claimed in any one of the preceding claims 1 to 3,
20 wherein said aliphatic tertiary amine containing hydroxyl groups is N,N,N',N'-
Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol®).
7. Additive composition as claimed in any one of the preceding claims 1 to 6,
wherein the composition comprises:
 - (A) one or more of the aromatic nitro compounds,
25 **characterized in that** the said composition further comprises:
 - (B) one or more of the tertiary amines,
wherein said tertiary amine is selected from a group consisting of:
 - i) hydroxyl alkyl tertiary amine which is tris(2-hydroxypropyl)amine (TIPA);
 - 30 ii) propylene oxide treated amine which is N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol®); and
 - iii) ethylene oxide treated amine which is N,N,N',N'-Tetrakis (2-hydroxyethyl) ethylene-diamine) (THEED) compounds; or

iv) mixture thereof.

8. Additive composition as claimed in any one of claims 1 to 7, wherein said composition consists of:

a) about 40 to about 99.75 % by weight of *I*) one or more of said aromatic nitro compounds; and

b) about 0.25 to about 60 % by weight of *II*) said amine or mixture thereof.

9. Additive composition as claimed in any one of claims 1 to 8, wherein about 0.01 to about 2000 ppm of said composition is added to aromatic vinyl monomers stream based on weight of monomer.

10. Additive composition as claimed in any one of claims 1 to 9, wherein said aromatic nitro compound contains a phenolic group or derivative thereof as well as the nitro group.

11. Additive composition as claimed in any one of claims 1 to 10, 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.

12. Additive composition as claimed in any one of claims 1 to 11, wherein said aromatic nitro compound is 4,6-dinitro-2-sec-butylphenol (DNBP).

13. Additive composition as claimed in any one of claims 1 to 12, wherein said composition does not comprise nitroxide (i.e. nitroxyl) compounds including 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).

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

i) triethanolamine (TEA);

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

iii) monoethanolamine (MEA);

iv) octyl amine (OA);

v) dibutyl amine (DBA);

vi) diethanol amine (DEA);

vii) dipropyl amine (DPA) ; and

viii) ethylene diamine (EDA).

15. 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 14 to monomers stream, wherein said composition consists of:

(A) one or more of aromatic nitro compounds,

characterized in that the said composition further consists of:

(B) one or more of the aliphatic tertiary amines, or mixture thereof,

wherein the aliphatic tertiary amine contains one or more hydroxyl groups in the alkyl chain of the tertiary amine.

and said composition is added to said monomers stream.

16. The method as claimed claim 15, wherein about 0.01 to about 2000 ppm of said composition is added to aromatic vinyl monomers stream based on weight of monomer.

17. The method as claimed claim 15 or 16, wherein one or more of said aromatic nitro compounds and one or more of said tertiary amine compounds are added to said monomers stream either individually or after mixing.

18. A method of using additive composition as claimed in any one of the preceding claims 1 to 14 for controlling and inhibition of polymerization of aromatic vinyl monomers including styrene, wherein the stream comprising aromatic vinyl monomer including styrene is treated with the additive composition consisting of:

(A) one or more of aromatic nitro compounds,

characterized in that the said composition further consists of:

(B) one or more of the aliphatic tertiary amines, or mixture thereof,

wherein the aliphatic tertiary amine contains one or more hydroxyl groups in the alkyl chain of the tertiary amine.

19. The method as claimed claim 18, wherein said aromatic vinyl monomers stream is treated with about 0.01 to about 2000 ppm of said composition based on weight of monomer.

20. The method as claimed claim 18 or 19, wherein one or more of said aromatic nitro compounds and one or more of said tertiary amine compounds are added to said monomers stream either individually or after mixing.

21. A method for preparing additive composition as claimed in any one of the preceding claims 1 to 14 for controlling and inhibiting polymerization of aromatic vinyl monomers including styrene, wherein the method comprises:

(A) mixing one or more of said aromatic nitro compounds,

characterized in that said aromatic nitro compound or mixture thereof is further mixed with one or more of

(B) said the aliphatic tertiary amines, or mixture thereof, wherein the aliphatic tertiary amine contains one or more hydroxyl groups in the alkyl chain of the tertiary amine.

22. The method as claimed claim 21, wherein one or more of said amines are mixed with one or more of said aromatic nitro compounds either individually or after mixing.

23. The method as claimed in any one of the preceding claims 15 to 20, wherein said composition is used over a range of temperature varying from about 50 degree C to about 180 degree C.