

Title of the invention:

ADDITIVE COMPOSITION FOR CONTROL AND INHIBITION OF
POLYMERIZATION OF ALIPHATIC MONOMERS, AND METHODS OF
PREPARATION AND USE THEREOF.

Field of the invention:

The present invention relates to additive composition for control and inhibition
of polymerization of aliphatic monomers including butadiene, wherein the composition
comprises:

- A) one or more of first components selected from a group comprising
- a) quinone methide (QM), quinone methide (QM) derivative
including ester derivative of quinone methide,
 - b) nitroxide (i.e. nitroxyl) compounds, and
 - c) mixture thereof;

characterized in that the composition further comprises

- B) one or more of second components selected from amines and
polyamines, wherein the amine and polyamine is selected from a group
comprising:
- i) oxide treated tertiary amines,
 - ii) hydroxyl alkyl tertiary amines,
 - iii) polyether amines, and
 - iv) mixture thereof.

In one embodiment, the present invention relates to the use of said composition
of the present invention to control and inhibit polymerization of butadiene.

In another embodiment, the present invention relates to the method of
preparation of said composition of the present invention for control and inhibition of
polymerization of butadiene.

In still another embodiment, the present invention relates to the method of
controlling and inhibiting polymerization of butadiene by employing said composition
of the present invention, wherein the stream containing butadiene is treated with said
composition of the present invention.

Background of the invention:

1 The polymerization of butadiene during processing of hydrocarbons is a matter
2 of concern, because it causes formation of unwanted polymers and results in loss of
3 yield of end product and makes the process un-economical. Further, the butadiene also
4 gets dimerized, which further enhances the wastage, and thereby, further enhances cost
5 of production.

6 The prior art discloses use of quinone methide (QM) or its derivatives including
7 4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dienone, and use of nitroxide (i.e.
8 nitroxyl) compounds including 1 oxyl-2,2,6,6-tetramethylpiperidin-4-ol or 4-hydroxy-
9 2,2,6,6-tetramethylpiperidin-1-oxyl (or 4 Hydroxy Tempo or 4HT) as polymerization
10 inhibitor. However, the inventor has found [refer to examples] that main problem of
11 using the QM or its derivatives, or nitroxides including 4HT is that these have to be
12 used in higher amounts to achieve commercially acceptable level (acceptable by the
13 industry) of inhibition, and such higher amount not only results in increase of cost of
14 the process, but also results in formation of undesired products due to unstable nature of
15 QM or its derivatives and nitroxides including 4HT.

16 Therefore, the industry is aiming for additive composition wherein the dosage of
17 components of compositions of the prior art, particularly of the QM or its derivatives,
18 and the nitroxides (i.e. nitroxyl) compounds including 4HT can be minimized or
19 reduced. Any effort in the direction of lowering the consumption of these components
20 will lessen the problem of industry, and the resulted composition will be economical as
21 well as safe for human being.

22 **Need of the Invention:**

23 Therefore, there is still a need of an effective additive composition and method
24 of its use and preparation, and method of controlling and inhibiting polymerization of
25 aliphatic monomers including butadiene, and for control and inhibition of dimerization
26 of aliphatic monomers including butadiene by employing said composition, wherein the
27 additive composition is not only suitable for substantial control and inhibition of
28 polymerization of butadiene, but is also suitable for control and inhibition of
29 dimerization of aliphatic monomers including butadiene, and also comprises
30 substantially reduced or minimized amount of the QM or its derivatives, and the
31 nitroxides (i.e. nitroxyl) compounds.
32
33

Problem to be solved by the Invention:

Therefore, the present invention aims at providing a solution to the above-described existing industrial problems by providing effective additive composition and method of its use and preparation, and method of controlling and inhibiting polymerization of aliphatic monomers including butadiene, and for control and inhibition of dimerization of aliphatic monomers including butadiene, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of butadiene, but is also suitable for control and inhibition of dimerization of aliphatic monomers including butadiene, and also comprises substantially reduced or minimized amount of the QM or its derivatives, and nitroxides (i.e. nitroxyl) compounds.

Objects of the Invention:

Accordingly, the main object of present invention is to provide an effective additive composition, and methods of its use and preparation, and method of controlling and inhibiting polymerization of aliphatic monomers including butadiene, and for control and inhibition of dimerization of aliphatic monomers including butadiene, wherein the additive composition is not only suitable for substantial control and inhibition of polymerization of butadiene, but is also suitable for control and inhibition of dimerization of aliphatic monomers including butadiene, and also comprises substantially reduced or minimized amount of one or more of compounds (which may be referred to as 'first component' or as 'component A' or as 'compound A') selected from a group comprising QM or its derivatives, and nitroxides (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 4HT, hereinafter may be referred to as 4HT), and mixture thereof.

Another main object of the present invention is to provide the above-described said additive composition, and methods of its use and preparation, and method of controlling and inhibiting polymerization, and dimerization of aliphatic monomers including butadiene, wherein the additive composition is required in relatively lower dosage as compared to dosage of compositions of the prior art comprising one or more of the compounds selected from a group comprising QM or its derivatives, and nitroxides (i.e. nitroxyl) compounds including 4HT, and mixture thereof for achieving

the same or better commercially acceptable level of control and inhibition of polymerization, and dimerization of aliphatic monomers including butadiene.

This is also an object of the present invention to provide the above-described said additive composition, and methods of its use and preparation, and method of controlling and inhibiting polymerization, and dimerization of aliphatic monomers including butadiene, wherein the additive composition comprises reduced or minimized amount of one or more of the compounds (which may be referred to as 'first component' or as 'component A' or as 'compound A') selected from a group comprising quinone methide (QM) or its derivatives including ester derivatives of quinone methide, and nitroxide (i.e. nitroxyl) compounds including 4HT, and mixture thereof; and it further comprises one or more of compounds, which may be referred to as 'second component' or as 'component B' or as 'compound B' selected from amines or polyamines.

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

Brief Description and Summary of the Invention:

The present invention primarily aims at providing an additive composition, and methods of its use and preparation, and method of controlling and inhibiting polymerization, and dimerization of aliphatic monomers including butadiene, wherein the additive composition comprises reduced or minimized amount of:

one or more of first component selected from a group comprising

- a) quinone methide (QM),
- b) quinone methide (QM) derivative including ester derivative of quinone methide,
- c) nitroxide (i.e. nitroxyl) compounds, and
- d) mixture thereof;

characterized in that it further comprises one or more of second component selected from amines or polyamines, wherein the amine and polyamine is selected from a group comprising

- i) oxide treated tertiary amines,
- ii) hydroxyl alkyl tertiary amines,

1 iii) polyether amines, and
2 iv) mixture thereof, and
3 therefore, the composition of the present invention is not only economical, but is
4 also environment friendly.

5 Accordingly, the present invention also aims at improving the performance of
6 compounds selected from a group comprising QM or its derivatives, and nitroxides (i.e.
7 nitroxyl) compounds including 4HT, and mixture thereof at a wider range of
8 temperature including the higher temperature.

9 Accordingly, the present invention also aims at improving the performance of
10 compounds selected from a group comprising QM or its derivatives, and nitroxides (i.e.
11 nitroxyl) compounds including 4HT, and mixture thereof at a wider range of
12 temperature including the higher temperature and in presence of air.

13

14 **Description and Preferred Embodiments of the Invention:**

15 With aim to overcome above-described problems of the prior art and to achieve
16 the above-described objects of the present invention, the inventor has found that when
17 one or more of the amines or polyamines selected from a group comprising

- 18 i) oxide treated tertiary amines,
19 ii) hydroxyl alkyl tertiary amines,
20 iii) polyether amines, and
21 iv) mixture thereof,

22 is added to the composition comprising the compound (first component) selected from a
23 group comprising QM or its derivatives, and nitroxides (i.e. nitroxyl) compounds
24 including 4HT, and mixture thereof, then not only polymerization and dimerization
25 controlling and inhibiting efficiency of the compound (first component) is substantially
26 improved, but polymerization and dimerization of aliphatic monomers including
27 butadiene is, surprisingly and unexpectedly, also controlled and inhibited to the
28 industrially acceptable level with substantially reduced and minimized dosage of the
29 first components, which makes the present composition economical as well as
30 environment friendly.

31 Accordingly, the present invention relates to an additive composition for control
32 and inhibition of polymerization and dimerization of aliphatic monomers including
33 butadiene comprising:

- 1 A) one or more of first component selected from a group comprising
2 a) quinone methide (QM),
3 b) quinone methide (QM) derivative including ester derivative of
4 quinone methide,
5 c) nitroxide (i.e. nitroxyl) compounds, and
6 d) mixture thereof;

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

- 8 B) one or more of second component selected from amines or polyamines,
9 wherein the amine and polyamine is selected from a group comprising:
10 i) oxide treated tertiary amines,
11 ii) hydroxyl alkyl tertiary amines,
12 iii) polyether amines, and
13 iv) mixture thereof.

14 In accordance with one of the preferred embodiments of the present invention,
15 the oxide treated tertiary amine, which may be referred to as oxide treated polymeric
16 amine of propylene oxide treated amine includes N,N,N',N'-Tetrakis (2-
17 hydroxypropyl) ethylene-diamine) (Quadrol®).

18 In accordance with one of the preferred embodiments of the present invention,
19 the hydroxyl alkyl tertiary amine, which may be referred to as oxide treated polymeric
20 amine of hydroxyl alkyl tertiary amine includes tris(2-hydroxypropyl)amine (TIPA).

21 Accordingly, in accordance with one of the preferred embodiments, the present
22 invention relates to additive composition for controlling and inhibition of
23 polymerization and dimerization of aliphatic monomers including butadiene
24 comprising:

- 25 A) one or more of first component selected from a group comprising
26 a) quinone methide (QM),
27 b) quinone methide (QM) derivative including ester derivative of
28 quinone methide,
29 c) nitroxide (i.e. nitroxyl) compounds, and
30 d) mixture thereof;

31 **characterized in that** the composition further comprises

- 32 B) one or more of second component selected from amines or polyamines,
33 wherein the amine and polyamine is selected from a group comprising:

- i) oxide treated tertiary amines,
- ii) hydroxyl alkyl tertiary amines,
- iii) polyether amines, and
- iv) mixture thereof,

wherein the oxide treated tertiary amine includes N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine) (Quadrol[®]), and the hydroxyl alkyl tertiary amines includes tris(2-hydroxypropyl)amine (TIPA).

In present description above first component may be referred to as component A of the present composition and the above second component may be referred to as component B of the present composition.

In accordance with one of the preferred embodiments of the present invention, the nitroxide (i.e. nitroxyl) compounds include 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol or 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (or 4 Hydroxy Tempo or 4HT, hereinafter may be referred to as 4HT).

It has been found that when composition of the present invention comprises one or more said amines or polymeric amines (component B), the efficiency of said component A to control and inhibit polymerization and dimerization of aliphatic monomers including butadiene is, surprisingly and unexpectedly, substantially improved to the acceptable level that's too at substantially reduced or minimized dosages of said component A, thereby making the composition of the present invention relatively more economical and environment friendly.

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

- a) about 40 to about 99.75 % by weight of I) one or more of said compounds (component A); and
- b) about 0.25 to about 60 % by weight of II) said amines or polymeric amines or mixture thereof (component B).

In accordance with one of the preferred embodiments of the present invention, amount of the composition of the present invention added to the stream containing butadiene is selected from the group comprising varying from about 0.01 ppm to about 2000 ppm, and from about 1 ppm to about 2000 ppm by weight of the stream of the monomers including butadiene.

1 It may be noted that the butadiene may be present in the stream along with other
2 monomers. The present invention is applicable to control and inhibit polymerization of
3 aliphatic monomers including butadiene, and to control and inhibit dimerization of
4 aliphatic monomers including butadiene but excluding aromatic monomers.

5 Accordingly, in another embodiment, the present invention also relates to
6 method of using said additive composition of the present invention, described herein, a
7 reference to which is drawn in entirety, to control and inhibit polymerization and
8 dimerization of aliphatic monomers including butadiene, wherein to the stream
9 comprising monomers including butadiene said additive composition comprising one or
10 more of said component A and one or more of said component B is added.

11 In particular, in second embodiment, the present invention relates to a method of
12 using said additive composition of the present invention, described herein, a reference
13 to which is drawn in entirety, for controlling and inhibition of polymerization and
14 dimerization of aliphatic monomers including butadiene, wherein to the stream
15 comprising the aliphatic monomers including the butadiene and excluding aromatic
16 monomers, the additive composition comprising:

- 17 A) one or more of component A selected from a group comprising
18 a) quinone methide (QM),
19 b) quinone methide (QM) derivative including ester derivative of
20 quinone methide,
21 c) nitroxide (i.e. nitroxyl) compounds, and
22 d) mixture thereof;

23 **characterized in that** the composition further comprising

- 24 B) one or more of component B selected from amines or polyamines,
25 wherein said amine and polyamine is selected from a group comprising:
26 i) oxide treated tertiary amines,
27 ii) hydroxyl alkyl tertiary amines,
28 iii) polyether amines, and
29 iv) mixture thereof,

30 is added.

31 In accordance with one of the embodiments of the present invention, the oxide
32 treated tertiary amine includes N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-
33 diamine) (Quadrol[®]).

1 In accordance with one of the embodiments of the present invention, the
2 hydroxyl alkyl tertiary amines includes tris(2-hydroxypropyl)amine (TIPA).

3 In accordance with one of the embodiments of the present invention, the method
4 of using said additive composition of the present invention comprises adding amount
5 selected from the group comprising varying from about 0.01 ppm to about 2000 ppm,
6 and from about 1 ppm to about 2000 ppm of said composition to the monomer stream
7 including butadiene and excluding aromatic monomers based on weight of the
8 monomers.

9 In accordance with one of the preferred embodiments of the present invention,
10 one or more of the component A and one or more of the component B are added to the
11 monomers stream either individually or after mixing.

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

16 Accordingly, in third embodiment, the present invention also relates to a method
17 for controlling and inhibiting polymerization and dimerization of aliphatic monomers
18 including butadiene and excluding aromatic monomers by employing said additive
19 composition of the present invention, described herein, a reference to which is drawn in
20 entirety, wherein the stream comprising monomers including butadiene and excluding
21 aromatic monomers is treated with the additive composition of the present invention
22 comprising one or more of said component A and one or more of said component B.

23 In particular, in third embodiment, the present invention relates to a method for
24 controlling and inhibition of polymerization and dimerization of aliphatic monomers
25 including butadiene and excluding aromatic monomers, wherein said monomers are
26 treated with the additive composition of the present invention, described herein, a
27 reference to which is drawn in entirety, and wherein the additive composition
28 comprises:

- 29 A) one or more of component A selected from a group comprising
30 a) quinone methide (QM),
31 b) quinone methide (QM) derivative including ester derivative of
32 quinone methide,
33 c) nitroxide (i.e. nitroxyl) compounds, and

- 1 d) mixture thereof;
- 2 **characterized in that** the composition further comprising
- 3 B) one or more of component B selected from amines or polyamines,
- 4 wherein said amine and polyamine selected from a group comprising:
- 5 i) oxide treated tertiary amines,
- 6 ii) hydroxyl alkyl tertiary amines,
- 7 iii) polyether amines, and
- 8 iv) mixture thereof.

9 In accordance with one of the embodiments of the present invention, the oxide
10 treated tertiary amine includes N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-
11 diamine) (Quadrol®).

12 In accordance with one of the embodiments of the present invention, the
13 hydroxyl alkyl tertiary amines includes tris(2-hydroxypropyl)amine (TIPA),

14 In accordance with one of the preferred embodiments of the present invention,
15 the method for controlling and inhibition of polymerization and dimerization of
16 aliphatic monomers including butadiene and excluding aromatic monomers by
17 employing said additive compositions of the present invention comprises adding an
18 amount selected from the group comprising varying from about 0.01 ppm to about 2000
19 ppm, and from about 1 ppm to about 2000 ppm of the compositions to the monomers
20 stream including butadiene based on weight of the monomers.

21 In accordance with one of the preferred embodiments of the present invention,
22 one or more of the component A and one or more of the component B are added to the
23 monomers stream either individually or after mixing.

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

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

including butadiene before its processing starts so that polymerization and dimerization of aliphatic monomers including butadiene is avoided or minimized.

In accordance with one of the embodiments of the present invention, the present composition may be used over a wide range of temperature selected from the group comprising varying from about 50 degree C to about 180 degree C, and from about 60 degree C to about 180 degree C.

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

Accordingly, in fourth embodiment, the present invention also relates to a method of preparing additive compositions of the present invention, described herein, a reference to which is drawn in entirety, for controlling and inhibiting polymerization and dimerization of aliphatic monomers including butadiene (and excluding aromatic monomers), wherein one or more of the component A are mixed with one or more of said component B either individually or after mixing.

In particular, in fourth embodiment, the present invention relates to a method for preparation of additive compositions of the present invention, described herein, a reference to which is drawn in entirety, for controlling and inhibition of polymerization and dimerization of aliphatic monomers including butadiene and excluding aromatic monomers, wherein said method comprises:

(A) mixing one or more of the component A selected from a group comprising

- a) quinone methide (QM),
- b) quinone methide (QM) derivative including ester derivative of quinone methide,
- c) nitroxide (i.e. nitroxyl) compounds, and
- d) mixture thereof;

characterized in that the compounds are further mixed with

B) one or more of component B selected from amines or polyamines, wherein said amine and polyamine is selected from a group comprising:

- i) oxide treated tertiary amines,
- ii) hydroxyl alkyl tertiary amines,
- iii) polyether amines, and
- iv) mixture thereof.

1 In accordance with one of the embodiments of the present invention, the oxide
2 treated tertiary amine includes N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-
3 diamine) (Quadrol[®]).

4 In accordance with one of the embodiments of the present invention, the
5 hydroxyl alkyl tertiary amines includes tris(2-hydroxypropyl)amine (TIPA),

6 In accordance with one of the embodiments of the present invention, the method
7 for preparation of additive composition of the present invention comprises mixing one
8 or more of the component B with one or more of said component A either individually
9 or after mixing.

10 In accordance with one of the embodiments of the present invention, the
11 composition prepared is used over a range of temperature selected from the group
12 comprising varying from about 50 degree C to about 180 degree C, and from about 60
13 degree C to about 180 degree C.

14 It may be noted that in accordance with the present invention the stream
15 comprises aliphatic monomers including butadiene and excludes aromatic monomers,
16 and the stream may be referred to as monomer stream or as butadiene stream.

17 It may also be noted that all the features of the compositions of the present
18 invention, described herein, a reference to which is drawn in entirety, are deemed to
19 have been included in the present method for preparation of the additive compositions
20 of the present invention.

21 It may be noted that the terms or words "first component" or "first components"
22 or "compounds" or "said compounds" or "compound A" or "compounds A" or
23 "component A" or "components A" used herein are intended to mean and include:

24 one or more of the compounds selected from a group comprising

- 25 a) quinone methide (QM),
- 26 b) quinone methide (QM) derivative including ester derivative of quinone
27 methide,
- 28 c) nitroxide (i.e. nitroxyl) compounds, and
- 29 d) mixture thereof.

30 It may be noted that the terms or words "amines" or "said amines" or
31 "polyamines" or "said polyamines" or "second component" or "second components" or
32 "compound B" or "compounds B" or "component B" or "components B" used herein
33 are intended to mean and include:

- 1 i) oxide treated tertiary amines,
2 ii) hydroxyl alkyl tertiary amines,
3 iii) polyether amines, and
4 iv) mixture thereof.

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

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

10

11 **Experiments:**

12 In following experiments gel is cross linked polybutadiene or simply butadiene
13 polymer or polybutadiene, and dimer is vinyl cyclohexene, which is formed by
14 condensation of two butadiene ring compounds, and the amounts are expressed in % by
15 weight.

16

17 **Experiment - I.**

18 Condition : Autoclave (100ml Capacity)
19 Sample : 1,3-Butadiene
20 Temperature : 120°C
21 Time : 4 hrs
22 Motor speed : 1000 rpm
23 Purge gas : Nitrogen (15 kgs Blanketing, pressure at 120°C is 35-36 kgs)

24

25

26

1

Table - I

Additive	Active Dosage (ppm)	Gel (%)	Dimer (%)	Non Volatile (%)	% Efficiency of Polymerization control	% Efficiency of dimerization control
Blank	--	4.44	20.4	0.55	--	-
4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dienone (QM) – Prior art	50	2.75	18.5	0.57	38	9.8
	200	0	10.7	0.11	100	47.3
4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dienone (QM) and TIPA (Invention Composition-1)	12.5+2.5	1.79	21.2	0.49	59.7	0
	17+1.5	0	22.15	0.22	100	0
	200+50	0	6.12	0.37	100	70
	300+75	0	4.4	0.75	100	78
4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) – Prior Art	10	4.14	20.4	0.50	6.7	0
	15	0.98	22.3	0.45	77	0
	18	0	23.4	0.22	100	0
	25	0	23.8	0.23	100	0
	50	0	24.05	0.22	100	0
	200	0	23.8	0.25	100	0
4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and TIPA (Invention Composition-2)	5+1	1.2	19.6	0.45	75.2	3.9
	7.5+1.5	0	22.95	0.19	100	0
	8+1	0	22.4	0.25	100	0
	10+0.5	2.19	19.46	0.53	50.7	4.6
	10+1	0	21.7	0.32	100	0
	200+10	0	13.1	0.21	100	36.1
	200+50	0	10.5	0.35	100	48.5

2

3 The above experiment of Invention Composition – 1 of Table 1 confirms that
4 with addition of just 1.5 ppm of TIPA, only 17 ppm of QM is required as against 200
5 ppm of QM to achieve 100% control / inhibition of polymerization of 1,3-butadiene,
6 thereby results in saving of about 183 ppm (about 91.5%) of QM confirming surprising
7 and unexpected technical advantages of the present composition.

8 The above experiment of Invention Composition – 1 of Table 1 also confirms
9 that the present composition comprising QM and TIPA additionally controls the
10 dimerization of butadiene. It has been found that the present composition comprising
11 300 ppm of QM and 75 ppm of TIPA has about 78% efficiency to control the
12 dimerization of butadiene, and the present composition comprising 200 ppm of QM and
13 50 ppm of TIPA has about 70% efficiency to control the dimerization of butadiene as

1 against only about 47.3% efficiency to control the dimerization of butadiene when prior
2 art additive is used, which confirms additional surprising and unexpected technical
3 advantages of the present composition.

4 The above experiment of Invention Composition – 2 of Table 1 confirms that
5 with addition of just 1.5 ppm of TIPA, only 7.5 ppm of TEMO is required as against 18
6 ppm of TEMPO to achieve 100% control / inhibition of polymerization of 1,3-
7 butadiene, thereby results in saving of about 10.5 ppm (about 58.33%) of TEMPO
8 confirming surprising and unexpected technical advantages of the present composition.

9 The above experiment of Invention Composition – 2 of Table 1 also confirms
10 that the present composition comprising TEMPO and TIPA additionally controls the
11 dimerization of butadiene. It has been found that with the present composition
12 comprising 200 ppm of TEMPO and 50 ppm of TIPA has about 48.5% efficiency to
13 control dimerization of butadiene, and the present composition comprising 200 ppm of
14 TEMPO and 10 ppm of TIPA has about 36.1% efficiency to control dimerization of
15 butadiene as against no control of the dimerization of butadiene when prior art additive
16 is used, which also confirms additional surprising and unexpected technical advantages
17 of the present composition.

18 **Experiment - II.**

20 Condition	: Autoclave (100ml Capacity)
21 Sample	: 1,3-Butadiene (without deep tube cylinder)
22 Temperature	: 140°C
23 Time	: Varies
24 Motor speed	: 1000 rpm
25 Purge gas	: Nitrogen (15 kgs Blanketing, pressure at 140°C is 48-49 kgs).

Table – II

Additive	Time, hrs	Active Dosage (ppm)	Gel (%)	Dimer (%)	Non Volatile (%)	% Efficiency of Polymerization control
Blank	1	--	0	14.9	0.55	--
	2	--	6.4	23.2	0.35	-
	4	--	14.25	Nil	-	--
4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dienone (QM) – Prior art	4	50	8.0	20.4	0.48	43.9
4-benzylidene-2,6-di-tert-butylcyclohexa-2,5-dienone (QM) and TIPA – (Invention Composition-1)	4	40+10	3.2	23.6	0.22	77.5
	4	55+5	2.2	23.0	0.55	84.6
	4	60+15	0	25.9	0.45	100
4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) – Prior art	4	50	3.4	25.8	0.33	76.1
	4	60	0.8	30.6	0.50	94.4
	4	75	0	30.9	0.4	100
4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) and TIPA – (Invention Composition-2)	4	40+10	0	30.1	0.19	100

The above experiment of Invention Composition – 1 of Table 2 confirms that with the present composition comprising 60 ppm of QM and 15 ppm of TIPA, 100% control / inhibition of polymerization of 1,3-butadiene is achieved, and with the present composition comprising 55 ppm of QM and 5 ppm of TIPA, about 84.6% control / inhibition of polymerization of 1,3-butadiene is achieved, and with the present composition comprising 40 ppm of QM and 10 ppm of TIPA, about 77.5% control / inhibition of polymerization of 1,3-butadiene is achieved as against about 43.9% controller / inhibition of polymerization of 1,3-butadiene when 50 ppm of prior art

additive is used, which confirms surprising and unexpected technical advantages of the present composition.

The above experiment of Invention Composition – 2 of Table 2 confirms that with addition of just 10 ppm of TIPA, only 40 ppm of TEMO is required as against 75 ppm of TEMPO to achieve 100% control / inhibition of polymerization of 1,3-butadiene, thereby results in saving of 35 ppm (about 46.6%) of TEMPO, and when the prior art additive is used, then only 76.1% control / inhibition of polymerization of 1,3-butadiene is achieved, which also confirms surprising and unexpected technical advantages of the present composition.

Accordingly, all of above experimental findings confirm that a solution to the industrial problems of controlling and inhibiting polymerization of butadiene, and additionally controlling dimerization of butadiene with reduced or minimized amounts of the prior art additives has been achieved.

Further, the above experimental findings also confirm synergistic, surprising and unexpected effects of the presently provided compositions.

All of the above experiments also confirm that the present compositions are capable of achieving far better efficiency to control and inhibit polymerization of monomers stream comprising butadiene and excluding aromatic monomers, and additionally controlling dimerization of butadiene with same dosage of the prior art additives, meaning thereby, the present invention results in economical and environmental benefits.

The above experimental results also confirm that the presently provided compositions are far superior than prior art additives, and hence, have technical advantages and surprising effects over the prior art additives.

It may also be noted that the term “about” appearing before value or range of value and as employed herein is not intended to enlarge scope of the corresponding value or range of value, and the claimed invention, but is intended to include, within scope of the present invention, experimental errors permissible in the field of the invention.

It may also be noted that the present invention has been described with the help of foregoing experiments which have been performed on the laboratory scale. It is obvious to the persons skilled in the art to modify the present invention to apply it to

- 1 industrial scale without deviating from its scope, and such application of present
- 2 invention is included in its scope.
- 3

Claims

1. Additive composition for control and inhibition of polymerization of aliphatic monomers including butadiene and for control and inhibition of dimerization of aliphatic monomers including butadiene comprising:
 - A) one or more of first component selected from a group comprising
 - a) quinone methide (QM),
 - b) quinone methide (QM) derivative including ester derivative of quinone methide,
 - c) nitroxide (i.e. nitroxyl) compounds, and
 - d) mixture thereof;
 - characterized in that** the composition further comprises
 - B) one or more of second component selected from amines or polyamines, wherein the amine and polyamine is selected from a group comprising:
 - i) oxide treated tertiary amines,
 - ii) hydroxyl alkyl tertiary amines,
 - iii) polyether amines, and
 - iv) mixture thereof.
2. The additive composition as claimed in claim 1, wherein the oxide treated tertiary amine comprises N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylenediamine) (Quadrol®).
3. The additive composition as claimed in claim 1 or claim 2, wherein the hydroxyl alkyl tertiary amine comprises tris(2-hydroxypropyl)amine (TIPA).
4. The additive composition as claimed in any one of the preceding claims, wherein the nitroxide compound comprises 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol (4HT).
5. The additive composition as claimed in any one of the preceding claims, wherein the composition comprises:
 - a) about 40 to about 99.75 % by weight of I) one or more of said first component; and
 - b) about 0.25 to about 60 % by weight of II) said second component.
6. The additive composition as claimed in any one of the preceding claims, wherein amount of the composition added to stream of aliphatic monomers including butadiene is selected from the group comprising varying from about

1 0.01 ppm to about 2000 ppm, and from about 1 ppm to about 2000 ppm by
2 weight of the stream.

3 7. The additive composition as claimed in any one of the preceding claims,
4 wherein the stream excludes aromatic monomers.

5 8. A method of using additive composition for controlling and inhibition of
6 polymerization of aliphatic monomers including butadiene and for controlling
7 and inhibition of dimerization of aliphatic monomers including butadiene,
8 wherein to stream of the aliphatic monomers including the butadiene the
9 additive composition comprising:

10 A) one or more of component A selected from a group comprising

11 a) quinone methide (QM),

12 b) quinone methide (QM) derivative including ester derivative of
13 quinone methide,

14 c) nitroxide (i.e. nitroxyl) compounds, and

15 d) mixture thereof;

16 **characterized in that** the composition further comprises

17 B) one or more of component B selected from amines or polyamines,
18 wherein said amine and polyamine is selected from a group comprising:

19 i) oxide treated tertiary amines,

20 ii) hydroxyl alkyl tertiary amines,

21 iii) polyether amines, and

22 iv) mixture thereof,

23 is added.

24 9. The method as claimed in claim 8, wherein the oxide treated tertiary amine
25 comprises N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine)
26 (Quadrol®).

27 10. The method as claimed in claim 8 or claim 9, wherein the hydroxyl alkyl tertiary
28 amine comprises tris(2-hydroxypropyl)amine (TIPA).

29 11. The method as claimed in any one of the preceding claims 8 to 10, wherein the
30 nitroxide compound comprises 1-oxyl-2,2,6,6-tetramethylpiperidin-4-ol (4HT).

31 12. The method as claimed in any one of the preceding claims 8 to 11, wherein the
32 composition comprises:

- 1 a) about 40 to about 99.75 % by weight of I) one or more of said component
2 A; and
- 3 b) about 0.25 to about 60 % by weight of II) said component B.
- 4 13. The method as claimed in any one of the preceding claims 8 to 12, wherein
5 amount of the composition added to the stream of the aliphatic monomers
6 including the butadiene is selected from the group comprising varying from
7 about 0.01 ppm to about 2000 ppm, and from about 1 ppm to about 2000 ppm
8 by weight of the stream.
- 9 14. The method as claimed in any one of the preceding claims 8 to 13, wherein the
10 component A and the component B are added to the stream either individually
11 or after mixing.
- 12 15. The method as claimed in any one of the preceding claims 8 to 14, wherein the
13 stream excludes aromatic monomers.
- 14 16. A method for controlling and inhibition of polymerization of aliphatic
15 monomers including butadiene and for controlling and inhibition of dimerization
16 of aliphatic monomers including butadiene, wherein said monomers are treated
17 with the additive composition comprising:
- 18 A) one or more of component A selected from a group comprising
19 a) quinone methide (QM),
20 b) quinone methide (QM) derivative including ester derivative of
21 quinone methide,
22 c) nitroxide (i.e. nitroxyl) compounds, and
23 d) mixture thereof;
- 24 **characterized in that** the composition further comprising
- 25 B) one or more of component B selected from amines or polyamines,
26 wherein said amine and polyamine selected from a group comprising:
- 27 i) oxide treated tertiary amines,
28 ii) hydroxyl alkyl tertiary amines,
29 iii) polyether amines, and
30 iv) mixture thereof.
- 31 17. The method as claimed in claim 16, wherein the oxide treated tertiary amine
32 comprises N,N,N',N'-Tetrakis (2-hydroxypropyl) ethylene-diamine)
33 (Quadrol[®]).

- 1 18. The method as claimed in claim 16 or claim 17, wherein the hydroxyl alkyl
2 tertiary amine comprises tris(2-hydroxypropyl)amine (TIPA).
- 3 19. The method as claimed in any one of the preceding claims 16 to 18, wherein the
4 nitroxide compound comprises 1-oxy-2,2,6,6-tetramethylpiperidin-4-ol (4HT).
- 5 20. The method as claimed in any one of the preceding claims 16 to 19, wherein the
6 composition comprises:
- 7 a) about 40 to about 99.75 % by weight of I) one or more of said component
8 A; and
- 9 b) about 0.25 to about 60 % by weight of II) said component B.
- 10 21. The method as claimed in any one of the preceding claims 16 to 20, wherein
11 amount of the composition added to the stream of the aliphatic monomers
12 including the butadiene is selected from the group comprising varying from
13 about 0.01 ppm to about 2000 ppm, and from about 1 ppm to about 2000 ppm
14 by weight of the stream.
- 15 22. The method as claimed in any one of the preceding claims 16 to 21, wherein the
16 component A and the component B are added to the stream either individually
17 or after mixing.
- 18 23. The method as claimed in any one of the preceding claims 16 to 22, wherein the
19 stream excludes aromatic monomers.
- 20 24. The method as claimed in any one of the preceding claims 16 to 23, wherein the
21 temperature of the polymerization is selected from the group comprising varying
22 from about 50 degree C to about 180 degree C, and from about 60 degree C to
23 about 180 degree C.
- 24 25. A method for preparation of additive composition of any one of the preceding
25 claims 1 to 7 for controlling and inhibition of polymerization of aliphatic
26 monomers including butadiene and for controlling and inhibition of dimerization
27 of aliphatic monomers including butadiene, wherein the method comprises:
- 28 (A) mixing one or more of the component A selected from a group
29 comprising
- 30 a) quinone methide (QM),
- 31 b) quinone methide (QM) derivative including ester derivative of
32 quinone methide,
- 33 c) nitroxide (i.e. nitroxyl) compounds, and

- 1 d) mixture thereof;
- 2 **characterized in that** the compounds are further mixed with
- 3 B) one or more of the component B selected from amines or polyamines,
- 4 wherein said amine and polyamine is selected from a group comprising:
- 5 i) oxide treated tertiary amines,
- 6 ii) hydroxyl alkyl tertiary amines,
- 7 iii) polyether amines, and
- 8 iv) mixture thereof.
- 9 26. Additive composition for control and inhibition of polymerization of aliphatic
- 10 monomers including butadiene and for control and inhibition of dimerization of
- 11 aliphatic monomers including butadiene substantially as herein described with
- 12 reference to foregoing examples.
- 13 27. A method of using additive composition for controlling and inhibition of
- 14 polymerization of aliphatic monomers including butadiene and for controlling
- 15 and inhibition of dimerization of aliphatic monomers including butadiene
- 16 substantially as herein described with reference to foregoing examples.
- 17 28. A method for controlling and inhibition of polymerization of aliphatic
- 18 monomers including butadiene and for controlling and inhibition of dimerization
- 19 of aliphatic monomers including butadiene substantially as herein described
- 20 with reference to foregoing examples.
- 21 29. A method for preparation of additive composition for controlling and inhibition
- 22 of polymerization of aliphatic monomers including butadiene and for controlling
- 23 and inhibition of dimerization of aliphatic monomers including butadiene
- 24 substantially as herein described with reference to foregoing examples.
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