

1 **Title of the invention:**

2 Composition for control and inhibition of polymerization of monomers, and
3 method of use and preparation thereof.

4 **Field of the invention:**

5 The present invention relates to additive composition for control and inhibition
6 of polymerization of monomers, and method of use and preparation thereof.

7 Particularly, the present invention relates to additive composition for control and
8 inhibition of polymerization of monomers, wherein the monomers may comprise
9 styrene, indene, di-vinyl benzene, alpha-methyl styrene, and other higher ring
10 compounds or monomers, or derivatives thereof, and method of use and preparation
11 thereof.

12 More particularly, the present invention relates to additive composition
13 comprising (a) a phenol compound, and (b) one or more aliphatic tertiary amine and/or
14 oxide treated derivative thereof for control and inhibition of polymerization of
15 monomers, wherein the monomers may comprise styrene, indene, di-vinyl benzene,
16 alpha-methyl styrene, and other higher ring compounds or monomers, or derivatives
17 thereof, and method of use and preparation thereof.

18 **Background of the invention:**

19 The polymerization of monomers comprising (or including) styrene indene, di-
20 vinyl benzene, alpha-methyl styrene, and other higher ring compounds or monomers, or
21 derivatives thereof, during processing is a matter of concern, because it causes
22 formation of unwanted polymers and results in problems of fouling and also loss of
23 yield of end product and makes the process un-economical.

24 Further, the inventor of the present invention has found that formation of the
25 polymerization products of the monomers get deposited at a very rapid rate not only on
26 upper tray surfaces, but also beneath tray surfaces of a primary fractionator, which may
27 also be termed a quench tower, for example, in an ethylene plant, wherein the process
28 would require additional additive, such as, one or more anti-foulants.

29 The inventor of the present invention has further observed that due to the fouling
30 problem, an increase in 'column pressure drop' along with reduction in 'fractionation
31 efficiency' are also experienced.

1 In the prior art use of inhibitors and retarders, and combination thereof to
2 overcome problem of polymerization of the monomers including styrene has been
3 reported.

4 The problem of using the inhibitors alone is that these are to be added
5 continuously or at regular intervals, because once they are consumed, the
6 polymerization will re-start.

7 The problem of using the retarders is that these are not very effective to reduce
8 polymerization of monomers including styrene to a level of substantial inhibition or to
9 the commercially viable level of inhibition.

10 The prior art discloses compositions for control and inhibition of polymerization
11 of monomers comprising styrene, wherein the composition either consists of a phenol
12 compound, such as catechol compound, for example tertiary butyl catechol (TBC), or
13 comprises a combination of a) phenol compound with b1) quinone methide (QM),
14 particularly 7-aryl-quinone methide; or b2) quinone methide (QM) derivative; or b3) a
15 phenylenediamine; or b4) a hydroxylamine compound; or b5) a mixture thereof, which
16 are required in higher dosage.

17 **Need of the Invention:**

18 Therefore, there is still a need of an additive composition which is not only
19 suitable for substantial control and inhibition of polymerization of monomers, wherein
20 the monomers may comprise styrene, indene, di-vinyl benzene, alpha-methyl styrene,
21 and other higher ring compounds or monomers, or derivatives thereof, but is also
22 required in comparatively low dosage, or at least, relatively requires low dosage of the
23 phenol compound to achieve same or better polymerization inhibition efficiency.

24 Therefore, there is also a need of an additive composition which (i) can avoid
25 formation of polymerization products of the monomers, and hence, (ii) can avoid
26 deposition of polymerization products of the monomers in a primary fractionator, or a
27 quench tower, and thereby (iii) result in increased efficiency of the ethylene plant by
28 avoiding fouling, and/or (iv) extend a run-length of the primary fractionator or of the
29 ethylene plant.

30 Therefore, there is also a need of an additive composition which (v) can avoid
31 fouling problems, and hence (vi) can avoid an increase in "column pressure drop" and
32 (vii) can avoid reduction in "fractionation efficiency".

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

1 Therefore, the present invention aims at providing a solution to above-described
2 existing industrial problems by providing an additive composition which is found to be
3 suitable for controlling and inhibiting polymerization of monomers, wherein the
4 monomers may comprise styrene, indene, di-vinyl benzene, alpha-methyl styrene, and
5 other higher ring compounds or monomers, or derivatives thereof, and is also required
6 in comparatively low dosage, or at least relatively requires low dosage of the phenol
7 compound to achieve same or better polymerization inhibition efficiency.

8 Therefore, the present invention also aims at providing a solution to above-
9 described existing industrial problems of the primary fractionator, that is, to provide an
10 additive composition which (i) would avoid formation of polymerization products of the
11 monomers, and hence, (ii) would avoid deposition of polymerization products of the
12 monomers in the primary fractionator, or the quench tower, and thereby (iii) would
13 result in increased efficiency of the ethylene plant by avoiding fouling, and/or (iv)
14 extend a run-length of the primary fractionator or of the ethylene plant.

15 Therefore, the present invention also aims at providing a solution to above-
16 described existing industrial problems of the primary fractionator, that is, to provide an
17 additive composition which (v) would avoid fouling problems, and hence (vi) would
18 avoid an increase in 'column pressure drop' and (vii) would avoid reduction in
19 'fractionation efficiency'.

20 **Objects of the Invention:**

21 Accordingly, the main object of present invention is to provide an additive
22 composition which is suitable for controlling and inhibiting polymerization of
23 monomers, wherein the monomers may comprise styrene, indene, di-vinyl benzene,
24 alpha-methyl styrene, and other higher ring compounds or monomers, or derivatives
25 thereof, and is required in comparatively low dosage as compared to dosage of prior art
26 additive or its individual components for achieving the same or better level of inhibition
27 of polymerization of the monomers.

28 Accordingly, the other object of the present invention is to provide an additive
29 composition which is suitable (i) for avoiding formation of polymerization products of
30 the monomers, and hence, (ii) for avoiding deposition of polymerization products of the
31 monomers in the primary fractionator, or the quench tower, and thereby (iii) to result in
32 increased efficiency of the ethylene plant by avoiding fouling, and/or (iv) extend a run-
33 length of the primary fractionator or of the ethylene plant.

1 Accordingly, the still another object of the present invention is to provide an
2 additive composition which is suitable (v) to overcome the fouling problems, and hence
3 (vi) to avoid an increase in “column pressure drop” and (vii) to avoid reduction in
4 “fractionation efficiency”.

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

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

9 As discussed herein, it is known that while manufacturing lighter hydrocarbon
10 products such as ethylene, heavier hydrocarbons such as naphtha, condensate or diesel
11 oil are cracked in pyrolysis heaters at higher temperatures, generally at a temperature of
12 about 850°C and form mixtures of smaller molecules including, but not limited to,
13 ethylene, propylene, and butadiene. Such mixtures, commonly termed as cracked gases,
14 are cooled and compressed in various stages of the ethylene plant until they are
15 separated in the fractionation section of the ethylene plant.

16 During primary heat recovery, the cracked gases pass through and are cooled by
17 a series of heat exchangers, also termed transfer line exchangers, before being quenched
18 with an oil, preferably an heavy oil. The heavy oil, which is commonly known as
19 quench oil, pyrolysis fuel oil or bottoms quench oil, accumulates in the bottom section
20 of the primary fractionator. The primary fractionator contains varying components of
21 fuel oil species ranging from the bottom section of the column to the beginning of what
22 is called the rectification section of the column.

23 The rectification section of the column is prone to severe fouling problems
24 caused due to presence of various monomers, such as styrene, indene, di-vinyl benzene,
25 alpha-methyl styrene, indene derivatives, and other higher ring compounds/monomers
26 or derivatives thereof, and polymers thereof.

27 The polymerization products of the said monomers get deposited at a very rapid
28 rate not only on upper tray surfaces, but also beneath tray surfaces. Due to this fouling
29 problem, an increase in ‘column pressure drop’ along with reduction in ‘fractionation
30 efficiency’ are experienced.

31 Therefore, the quality of the gasoline condensing in the quench tower and also
32 the quality of the fuel oil made from the system are negatively affected.

1 Typically, the problem of fouling in the rectification section is also accompanied
2 by poor viscosity control in the bottom section of the quench tower due to improper
3 operations of the primary fractionator.

4 Further, the deposition of the fouling substances, commonly known as polymers,
5 obstructs the vapor and liquid flow inside the fractionator and due to the reduced surface
6 area available, the environment is also conducive to increased froth/foam generation in
7 the column.

8 As the fouling continues to occur, the polymers deposit also continues to occur
9 inside the column trays thus resulting in forcing the plant operators to reduce unit feed
10 rates significantly and, ultimately, to shut down the plant for cleaning and/or
11 maintaining the primary fractionator.

12 With aim to overcome above-described problems of prior art and to achieve
13 above-described objects of the invention, the inventor has found that when (a) a phenol
14 compound comprising catechol compound is combined with (b1) an aliphatic tertiary
15 amine and/or (b2) oxide treated derivative thereof, preferably with aliphatic tertiary
16 amine having one or more hydroxyl groups in the alkyl chain of said aliphatic tertiary
17 amine, the polymerization inhibition efficiency of the phenol compound comprising
18 catechol compound surprisingly and unexpectedly increases.

19 The prior art does not disclose composition for control and inhibition of
20 polymerization of monomers, wherein the monomers may comprise styrene, indene, di-
21 vinyl benzene, alpha-methyl styrene, and other higher ring compounds or monomers, or
22 derivatives thereof to overcome above discussed existing problems of the industry
23 particularly the above-discussed problems of formation of deposits and fouling in the
24 primary fractionator, wherein the composition comprises a combination of:

25 (a) a phenol compound comprising catechol compound; and
26 (b1) an aliphatic tertiary amine and/or (b2) oxide treated derivative thereof,
27 preferably an aliphatic tertiary amine having one or more hydroxyl groups in the
28 alkyl chain of said aliphatic tertiary amine;

29 with aim to increase polymerization inhibition efficiency of the phenol compound
30 including catechol compound and/or to reduce amount of the phenol compound
31 including catechol compound for controlling and inhibiting polymerization of the
32 monomers.

33 Therefore, the present invention provides a composition which has been found to
34 be suitable in reducing the formation of polymers of the monomers, and hence, has also
35 been found to be suitable in preventing the fouling in the primary fractionator or

1 ethylene plant, and thereby, to extend a run-length of the primary fractionator or of the
2 ethylene plant.

3 Accordingly, in one embodiment, the present invention provides an additive
4 composition for control and inhibition of polymerization of monomers, wherein the
5 composition comprises a combination of:

- 6 (a) a phenol compound comprising catechol compound; and
7 (b) an aliphatic tertiary amine, oxide treated derivative of the aliphatic
8 tertiary amine, or a mixture thereof.

9 Accordingly, in one of the preferred embodiments, the present invention
10 provides an additive composition for control and inhibition of polymerization of
11 monomers, wherein the composition comprises a combination of:

- 12 (a) a phenol compound comprising catechol compound; and
13 (b) an aliphatic tertiary amine, oxide treated derivative of the aliphatic
14 tertiary amine, or a mixture thereof,

15 wherein the aliphatic tertiary amine contains (or has) one or more hydroxyl
16 groups in the alkyl chain of the aliphatic tertiary amine.

17 In accordance with one of the preferred embodiments of the present invention,
18 the aliphatic tertiary amine contains three or more hydroxyl groups in the alkyl chain of
19 the aliphatic tertiary amine.

20 In accordance with one of the preferred embodiments of the present invention,
21 the aliphatic tertiary amine comprises tri-isopropanol amine (TIPA).

22 In accordance with one of the preferred embodiments of the present invention,
23 the oxide treated derivative of the aliphatic tertiary amine comprises:

- 24 (i) ethyl oxide treated derivative of tri-isopropanol amine (EO-TIPA);
25 (ii) propyl oxide treated derivative of tri-isopropanol amine (PO-TIPA); or
26 (iii) a mixture thereof.

27 In accordance with one of the preferred embodiments of the present invention,
28 the phenol compound comprises a catechol compound.

29 In accordance with one of the preferred embodiments of the present invention,
30 the catechol compound comprises a tertiary butyl catechol (TBC).

31 In accordance with one of the preferred embodiments of the present invention,
32 the tertiary butyl catechol (TBC) may be selected from the group comprising 4-tert-
33 butyl catechol; 3,5-di-tert-butylcatechol; or a mixture thereof.

34 It may be noted that it is understood from the present description that the present
35 invention aims at reducing the amount of TBC (the prior art additive) in the present

1 compositions. Therefore, the TBC is a primary component of the present composition,
2 and the TIPA, the EO-TIPA or the PO-TIPA is the additive component of the present
3 composition, and it is the additive component which is added to the primary component,
4 or say, to the composition comprising or consisting of TBC. Therefore, generally, it is
5 the primary component of the present invention which is present in a major percent by
6 weight amount and it is the additive component of the present invention which is
7 present in a minor percent by weight amount. However, one of an ordinary skill in the
8 art may use the present composition in reverse order.

9 In accordance with the present invention, the monomers comprising or including
10 styrene may be referred to as monomers or a monomer stream, which are intended to
11 include or comprise but not limited to styrene.

12 In accordance with one of the embodiments of the present invention, the phenol
13 compound and the aliphatic tertiary amine or the oxide treated derivative thereof may be
14 taken in a weight percent ratio varying from about 99.99:0.01 to about 0.01: 99.99.

15 In accordance with one of the preferred embodiments of the present invention,
16 the phenol compound and the aliphatic tertiary amine or the oxide treated derivative
17 thereof may be taken in a weight percent ratio varying from about 90:10 to about 10:90.

18 In accordance with another embodiment of the present invention, the phenol
19 compound and the aliphatic tertiary amine or the oxide treated derivative thereof may be
20 taken in a weight percent ratio varying from about 80:20 to about 20:80.

21 In accordance with still another embodiment of the present invention, the phenol
22 compound and the aliphatic tertiary amine or the oxide treated derivative thereof may be
23 taken in a weight percent ratio varying from about 70:30 to about 30:70.

24 In accordance with yet another embodiment of the present invention, the phenol
25 compound and the aliphatic tertiary amine or the oxide treated derivative thereof may be
26 taken in a weight percent ratio varying from about 60:40 to about 40:60.

27 In accordance with yet another embodiment of the present invention, the phenol
28 compound and the aliphatic tertiary amine or the oxide treated derivative thereof may be
29 taken in a weight percent ratio of about 50:50.

30 In accordance with one of the embodiments of the present invention, about 0.01
31 to about 5000 ppm of the present composition may be used based on weight of the
32 reacting material in polymerization of monomers.

33 In accordance with another embodiment of the present invention, about 0.20 to
34 about 5000 ppm of the present composition may be used based on weight of the reacting
35 material in polymerization of monomers.

1 In accordance with still another embodiment of the present invention, about 0.50
2 to about 5000 ppm of the present composition may be used based on weight of the
3 reacting material in polymerization of monomers.

4 In accordance with yet another embodiment of the present invention, about 1.0
5 to about 5000 ppm of the present composition may be used based on weight of the
6 reacting material in polymerization of monomers.

7 In accordance with yet another embodiment of the present invention, about 5.0
8 to about 5000 ppm of the present composition may be used based on weight of the
9 reacting material in polymerization of monomers.

10 In accordance with yet another embodiment of the present invention, about 10.0
11 to about 5000 ppm of the present composition may be used based on weight of the
12 reacting material in polymerization of monomers.

13 In accordance with one of the embodiments of the present invention, the additive
14 composition of the present invention may be used or employed at a temperature range
15 varying from about 60⁰C to about 180⁰C, or preferably at a temperature range varying
16 from about 80⁰C to about 150⁰C.

17 In one embodiment, the present invention relates to a method for controlling and
18 inhibiting polymerization of monomers, wherein the method comprises a step of treating
19 a monomer stream with the additive composition of the present invention.

20 In another embodiment, the present invention also relates to a method of using
21 the additive composition of the present invention for controlling and inhibiting
22 polymerization of monomers, wherein the method comprises a step of using the additive
23 composition of the present invention in a monomer stream.

24 It may be noted that the present composition may be used for controlling and
25 inhibition of polymerization of monomers of any composition.

26 In one of the exemplary embodiments, the present composition is used for
27 controlling and inhibition of polymerization of monomers, wherein the monomers may
28 comprise styrene, indene, di-vinyl benzene, alpha-methyl styrene, and other higher ring
29 compounds or monomers, or derivatives thereof.

30 In another exemplary embodiment, the present composition is used for
31 controlling and inhibiting polymerization of the monomers in the primary fractionator
32 or the ethylene plant.

33 Accordingly, in still another embodiment, the present invention also relates to a
34 method for controlling and inhibiting polymerization of monomers in a primary

1 fractionator (or an ethylene plant), wherein the method comprises a step of treating a
2 monomer stream with the additive composition of the present invention.

3 Accordingly, in yet another embodiment, the present invention also relates to a
4 method for operating a primary fractionator by controlling and inhibiting
5 polymerization of monomers in the primary fractionator (or an ethylene plant), wherein
6 the method comprises a step of using the additive composition of the present invention
7 in a monomer stream.

8 Accordingly, in yet another embodiment, the present invention also relates to a
9 method for reducing fouling and polymer deposits in a primary fractionator by
10 controlling and inhibiting polymerization of monomers in the primary fractionator (or
11 an ethylene plant), wherein the method comprises a step of treating a monomer stream
12 with the additive composition of the present invention.

13 Accordingly, in yet another embodiment, the present invention also relates to a
14 method to extend a run-length of a primary fractionator or of an ethylene plant by
15 reducing fouling and polymer deposits in the primary fractionator by controlling and
16 inhibiting polymerization of monomers in the primary fractionator (or an ethylene
17 plant), wherein the method comprises a step of treating a monomer stream with the
18 additive composition of the present invention.

19 It may also be noted that 'in percent ratio' means 'in weight percent ratio' or 'in
20 percent ratio by weight' unless specifically otherwise provided.

21 It may also be noted that the term 'about' is intended to include experimentally
22 permissible errors in the field of the present invention.

23 The present invention is now further illustrated with the help of accompanying
24 examples, which are not intended to limit its scope.

25 **Examples:**

26 **Example - I:**

27 The pyrolysis gasoline sample was taken in a tube with provision for nitrogen
28 gas purging and the sample was treated at temperatures of about 90°C, about 120°C and
29 about 150°C for about 2 hrs. and the polymer formed was separated by methanol
30 precipitation and the percent polymerization in blank (without an additive),
31 comparative sample (with 100 ppm additive consisting of TBC) and the invention
32 sample (with 100 ppm of additive comprising TBC and TIPA in 40:10 weight percent
33 ratio) was measured and has been presented in Table - I.

1 It may be noted that as per the present invention and as described herein, the
 2 TIPA, the EO-TIPA and the PO-TIPA are the additive components of the present
 3 composition, and it is the additive component which is added to the primary component,
 4 or say, to the composition comprising or consisting of TBC. Therefore, as per the
 5 present examples, it is 10 % by wt. of the TIPA which is mixed with 40 % by wt. of the
 6 TBC to arrive at the invention composition of these examples.

Table – I

Expt.	90 ⁰ C		120 ⁰ C		150 ⁰ C	
Additive	% Polymer by OD	% Polymer by methanol	% Polymer by OD	% Polymer by methanol	% Polymer by OD	% Polymer by methanol
Blank	0.15	Nil	1.62	0.18	3.15	1.21
TBC (Comparative Example)	0.47	0.18	0.93	0.11	2.50	0.93
TBC+TIPA (Present Invention)	0.42	0.10	0.48	0.07	1.95	0.43

7 Example - II:

8 The pyrolysis gasoline sample was taken in a tube and this time without nitrogen
 9 gas purging and the sample was treated at temperatures of 120°C and 150°C for 2 hrs.
 10 and the polymer formed was separated by methanol precipitation and the percent
 11 polymerization in blank (without an additive), comparative sample (with 100 ppm
 12 additive consisting of TBC) and the invention sample (with 100 ppm of additive
 13 comprising TBC and TIPA in 40:10 weight percent ratio) was measured and has been
 14 presented in Table - II.

Table – II

Expt.	120 ⁰ C		150 ⁰ C	
Additive	% Polymer by OD	% Polymer by methanol	% Polymer by OD	% Polymer by methanol
Blank	1.46	0.13	3.05	1.14
TBC (Comparative Example)	0.82	0.09	2.34	0.86
TBC+TIPA (Present Invention)	0.43	0.04	1.80	0.41

1 The above experiments confirm surprising, unexpected and synergistic effects of
2 the presently provided compositions, because the efficiency of the phenol compound to
3 control and inhibition of polymerization of monomers has increased on combining it
4 with an aliphatic tertiary amine, and/or oxide treated derivative thereof.

5 The above findings also confirm that compositions of present invention have
6 technical advantages and surprising effects over the prior art additives and
7 compositions, because the efficiency of the phenol compound to control and inhibition
8 of polymerization of monomers has increased on combining it with an aliphatic tertiary
9 amine, and/or oxide treated derivative thereof.

Claims:

- 1 1. An additive composition for control and inhibition of polymerization of
2 monomers, wherein the composition comprises a combination of:
 - 3 (a) a phenol compound comprising catechol compound; and
 - 4 (b) an aliphatic tertiary amine, oxide treated derivative of the aliphatic
5 tertiary amine, or a mixture thereof.
- 6 2. The additive composition as claimed in **Claim 1**, wherein the aliphatic tertiary
7 amine contains one or more hydroxyl groups in the alkyl chain of the aliphatic
8 tertiary amine.
- 9 3. The additive composition as claimed in **Claim 1**, wherein the aliphatic tertiary
10 amine contains three or more hydroxyl groups in the alkyl chain of the aliphatic
11 tertiary amine.
- 12 4. The additive composition as claimed in any one of the preceding **Claims**,
13 wherein the aliphatic tertiary amine comprises tri-isopropanol amine (TIPA).
- 14 5. The additive composition as claimed in any one of the preceding **Claims**,
15 wherein the oxide treated derivative of the aliphatic tertiary amine comprises:
 - 16 (i) ethyl oxide treated derivative of tri-isopropanol amine (EO-TIPA);
 - 17 (ii) propyl oxide treated derivative of tri-isopropanol amine (PO-TIPA); or
 - 18 (iii) a mixture thereof.
- 19 6. The additive composition as claimed in any one of the preceding **Claims**,
20 wherein the phenol compound comprises a catechol compound.
- 21 7. The additive composition as claimed in **Claim 6**, wherein the catechol
22 compound comprises a tertiary butyl catechol (TBC).
- 23 8. The additive composition as claimed in **Claim 7**, wherein the tertiary butyl
24 catechol (TBC) is selected from the group comprising 4-tert-butyl catechol; 3,5-
25 di-tert-butylcatechol; or a mixture thereof.
- 26 9. A method for controlling and inhibiting polymerization of monomers, wherein
27 the method comprises a step of treating a monomer stream with the additive
28 composition as claimed in any one of the preceding **claims 1 to 8**.
- 29 10. A method of using the additive composition as claimed in any one of the
30 preceding **claims 1 to 8** for controlling and inhibiting polymerization of
31 monomers, wherein the method comprises a step of using the additive
32 composition as claimed in any one of the preceding claims 1 to 8.
- 33 11. A method for controlling and inhibiting polymerization of monomers in a
34 primary fractionator (or an ethylene plant), wherein the method comprises a step

- 1 of treating a monomer stream with the additive composition as claimed in any
2 one of the preceding **claims 1 to 8**.
- 3 12. A method for operating a primary fractionator by controlling and inhibiting
4 polymerization of monomers in the primary fractionator (or an ethylene plant),
5 wherein the method comprises using the additive composition as claimed in any
6 one of the preceding **claims 1 to 8**.
- 7 13. A method for reducing fouling and polymer deposits in a primary fractionator by
8 controlling and inhibiting polymerization of monomers in the primary
9 fractionator (or an ethylene plant), wherein the method comprises a step of
10 treating a monomer stream with the additive composition as claimed in any one
11 of the preceding **claims 1 to 8**.
- 12 14. A method to extend a run-length of a primary fractionator or of an ethylene plant
13 by reducing fouling and polymer deposits in the primary fractionator by
14 controlling and inhibiting polymerization of monomers in the primary
15 fractionator (or an ethylene plant), wherein the method comprises a step of
16 treating a monomer stream with the additive composition as claimed in any one
17 of the preceding **claims 1 to 8**.