

Synergistic Polymerization Inhibitor Composition and Method

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from provisional application serial number 61/450,734, filed
5 March 9, 2011, which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

Field of the Invention.

The present invention relates to a vinyl monomer polymerization inhibitor composition and
method of inhibiting polymerization of a vinyl monomer therein.

10 Description of the related art.

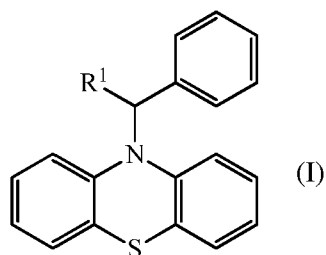
Vinyl monomers include vinyl alcohols and esters and acrylic monomers. Vinyl monomers
are widely used in chemical industry. For example, acrylic monomers are used to prepare
polyacrylate-type polymers (e.g., poly(acrylic acids) and poly(methacrylic acids)), which are useful
as, among other things, additives (e.g., for use in rubbers, coatings and adhesives) and ingredients in
15 fibers and other articles. A major problem with the vinyl monomers is premature polymerization. In
the absence of sufficient amounts of polymerization inhibitors, vinyl monomers undesirably
polymerize during manufacture, purification, handling, and storage operations. A unique solution to
this problem is mentioned in WO 2010/096512 A1, which relates to a monomer polymerization
inhibitor composition comprising a captive polymerization inhibitor and a fugitive polymerization
20 inhibitor. The fugitive polymerization inhibitor is characterizable as being capable of evaporating
with a distillable monomer from a first location (e.g., distillation pot) and condensing with the
distillable monomer at a second location (e.g., in a distillation tower).

A problem addressed by the present invention includes providing a vinyl monomer
polymerization inhibitor composition comprising a captive polymerization inhibitor that inhibits
25 polymerization of a vinyl monomer unexpectedly better than phenothiazine inhibits such
polymerization, and wherein the composition lacks a fugitive polymerization inhibitor of the vinyl
monomer.

BRIEF SUMMARY OF THE INVENTION

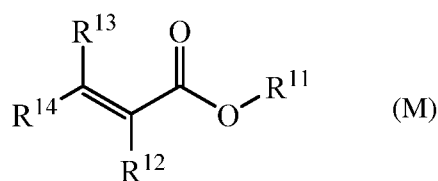
In a first embodiment the present invention provides a vinyl monomer polymerization
30 inhibitor composition comprising a liquid mixture comprising a vinyl monomer and a
polymerization inhibiting effective amount of a captive polymerization inhibitor, wherein the
composition lacks a fugitive polymerization inhibitor of polymerization of the vinyl monomer and
the captive polymerization inhibitor independently is characterizable as being a synergistically
effective inhibitor of polymerization of the vinyl monomer and polymerization of the vinyl

monomer is synergistically inhibited by the captive polymerization inhibitor, and wherein the captive polymerization inhibitor is a compound of formula (I):



, or a first acid addition salt thereof, wherein R^1 is hydrogen or (C_1-C_3) alkyl.

- 5 In some aspects of the first embodiment the vinyl monomer is an acrylic monomer, preferably an acrylic acid-type monomer of formula (M):



, wherein R^{11} is hydrogen or (C_1-C_{18}) alkyl and each of R^{12} to R^{14} independently is hydrogen or (C_1-C_8) alkyl.

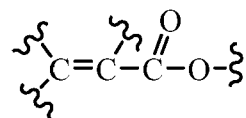
- 10 In a second embodiment, the present invention provides a method of synergistically inhibiting polymerization of a vinyl monomer, the method comprising contacting together a vinyl monomer with a polymerization inhibiting effective amount of a captive polymerization inhibitor so as to give the invention composition.

- The invention composition is one that is capable of functioning in the method of the second embodiment. The invention composition is useful in manufacture, purification, handling, and storage of vinyl monomers (e.g., vinyl alcohols and esters and acrylic monomers) as an inhibitor of polymerization of the vinyl monomers in, for example, vessels such as distillation pots, storage vessels, and transportation vessels.

Additional embodiments are described in the remainder of the specification.

DETAILED DESCRIPTION OF THE INVENTION

- 20 The embodiments of the present invention summarized previously and the Abstract are incorporated here by reference. As used herein, the term “**vinyl monomer**” means a molecule containing the structural fragment $H_2C=C(H)-$ and having a molecular weight of $< 1,000$ grams per mole (g/mol). The term “**acrylic monomer**” means a vinyl monomer with the structural fragment,



, wherein represent portions of covalent bonds. The term “**captive**

- 25 **polymerization inhibitor**” means a substance that does not evaporate from a distillation pot during

distillation of the vinyl monomer (e.g., acrylic monomer) therefrom. The term “**fugitive polymerization inhibitor**” means a substance that is capable of evaporating and condensing in a polymerization inhibiting amount with the acrylic. The term “**inhibit**” means to delay onset of, reduce degree of, or, preferably, prevent that which is being inhibited. The phrase “**synergistically effective inhibitor of polymerization**” means a substance that prevents visual appearance of solid poly(vinyl monomer) (e.g., poly(acrylic monomer)) for an average time value of at least 70 hours, which is about two times the average time value obtainable with phenothiazine *per se*. The time is determined using the following procedure: seal a glass vial containing a liquid mixture of the vinyl monomer (e.g., acrylic monomer) and 100 ppm of the substance or 100 ppm of the substance and 20 ppm of an inhibitor modifier, based on total weight of the liquid mixture. Place the vial in a mineral oil bath thermostated at 113 °C. Record time to the visual appearance of the solid poly(vinyl monomer) (e.g., poly(acrylic monomer)) anywhere in the vial (i.e., in the liquid mixture or on wall of vial above the liquid mixture). Repeat 4 times. Average the five times to give the average time value. The term “**inhibitor modifier**” means a substance (e.g., a manganese salt) that generates or regenerates the compound from a derivative thereof. The term “**lacks**” and the like (e.g., lacking) means entirely absent. The term “**polymerization inhibiting effective amount**” means an absolute weight (e.g., in grams) or relative weight (e.g., expressed in parts per million (ppm) or weight percent (wt%)) of a substance that is sufficient to delay onset of, reduce degree of, or, preferably, prevent polymerization. The phrase “**polymerization is synergistically inhibited**” and the like means where a polymerizable monomer is exposed to polymerization conditions (a chemical process resulting in bonding between two or more molecules of the polymerizable monomer to produce an organic oligomer or polymer thereof) and the polymerizable monomer is in contact with the captive polymerization inhibitor, rate of the chemical process is significantly lowered compared to a rate of the chemical process in presence of the comparator inhibitor, phenothiazine.

Conflict Resolution: what is written in the present specification controls any conflict with what is written in a patent, patent application, or patent application publication, or a portion thereof that is incorporated by reference. The structure controls any conflict with a compound name. Any non-international system of units value controls any conflict with an International System (SI) of Units value. A drawing controls any conflict with the written description thereof.

Numerical ranges: any lower limit of a range of numbers, or any preferred lower limit of the range, may be combined with any upper limit of the range, or any preferred upper limit of the range, to define a preferred aspect or embodiment of the range. Unless otherwise indicated, each range of numbers includes all numbers, both rational and irrational numbers, subsumed in that range (e.g., “from 1 to 5” includes, for example, 1, 1.5, 2, 2.75, 3, 3.81, 4, and 5).

The term “(C₁-C₁₈)alkyl” means a saturated straight or branched hydrocarbon radical of from 1 to 18 carbon atoms that is unsubstituted. Examples of (C₁-C₁₈)alkyl are (C₉-C₁₈)alkyl (e.g., a (C₁₈)alkyl such as CH₃(CH₂)₁₇-) and (C₁-C₈)alkyl, which includes (C₁-C₃)alkyl, including methyl, ethyl, 1-propyl, and 2-propyl; and (C₄-C₈)alkyl, including 1-butyl (also known as *normal*-butyl or *n*-butyl), 2-butyl, 2-methylpropyl, 1,1-dimethylethyl, 1-pentyl, 1-hexyl, 1-heptyl, and 1-octyl. The term “(C₁-C₃)alkyl-O-” means the (C₁-C₃)alkyl bonded to an oxygen atom radical.

The captive polymerization inhibitor is especially useful for inhibiting polymerization of the vinyl monomer (e.g., acrylic monomer) in a distillation vessel (pot), storage vessel, or conduit (e.g., piping and tubing).

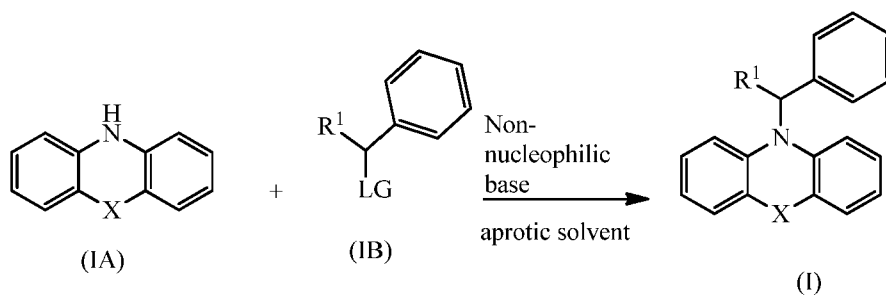
A polymerization inhibiting effective amount of the captive polymerization inhibitor (i.e., compound of formula (I)) can be varied depending on, for example, the particular vinyl monomer (e.g., acrylic monomer) and amount thereof being inhibited, conditions such as temperature and pressure, and presence or absence of other captive polymerization inhibitors. An invention process may be initiated with a larger polymerization inhibiting effective amount than is believed required. Thereafter the polymerization inhibiting effective amount can be allowed to decrease (e.g., as polymerization inhibitor is reacted) until a desirable steady-state amount of polymerization inhibitor is obtained under the conditions (e.g., as evidenced by achieving a desired time interval between vessel cleanings). A person of ordinary skill in the art would be able to determine appropriate polymerization inhibiting effective amounts under particular circumstances without undue experimentation. A preferred first polymerization inhibiting effective amount of the compound of formula (I) is from about 5 ppm to about 500 ppm, more preferably from about 10 ppm to about 250 ppm, still more preferably from about 20 ppm to about 200 ppm, and even more preferably from about 40 ppm to about 100 ppm, all based on a total weight of the liquid mixture.

The captive polymerization inhibitors do not include derivatives of the vinyl monomer (e.g., acrylic monomer).

In some embodiments the captive polymerization inhibitor is the compound of formula (I) wherein R¹ is hydrogen. In some embodiments R¹ is (C₁-C₃)alkyl. In some embodiments R¹ is ethyl, 1-propyl, or 2-propyl, and more preferably, R¹ is methyl. In some embodiments the compound of formula (I) is N-benzyl-phenothiazine, in other embodiments N-(1-phenylethyl)phenothiazine, and in still other embodiments the first acid addition salt thereof.

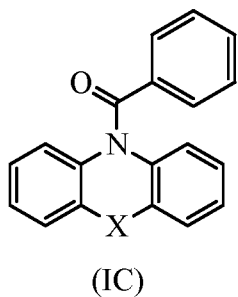
Synthesis of the compound of formula (I) is not critical to the invention and all successful syntheses are contemplated. In some embodiments the compound of formula (I) is synthesized by alkylating a corresponding intermediate amino compound of formula (IA) as shown below in Scheme 1.

Scheme 1.



wherein R^1 is as described for formula (I) and LG is a leaving group. In Scheme 1, an amino compound of formula (IA) and a compound of formula (IB) having a leaving group are contacted in the presence of a non-nucleophilic strong base and aprotic solvent at a nucleophilic displacement temperature, preferably from about 0 °C to about 100 °C, to give the compound of formula (I). Examples of aprotic solvents are tetrahydrofuran, 1,2-dimethoxyethane, and dioxane. Examples of the non-nucleophilic base are sodium hydride, potassium hydride, potassium hexamethyldisilazide (KHMDs), and lithium diisopropylamide (LDA). Examples of leaving groups are iodo, bromo, chloro, an activated hydroxyl, trifluoromethanesulfonate, trifluoroacetate, and tosylate. In some embodiments, such activated hydroxyls are prepared from a compound of formula (IB) wherein LG is HO- and a coupling agent such as, for example, triphenylphosphine with either diisopropylazodicarboxylate (DIAD), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, EDCI, or EDAC), N,N'-carbonyldiimidazole (CDI), or N,N'-dicyclohexylcarbodiimide (DCC), and optionally with 1-hydroxybenzotriazole (HOBt); and (benzotriazol-1-yloxy)tripyrrolidino-phosphonium hexafluorophosphate.

Other syntheses of the compound of formula (I) are contemplated. For example when R^1 is hydrogen, the compound of formula (I) can be synthesized by coupling the compound of formula (IA) with an acid halide of formula halo-C(=O)-phenyl or acid anhydride of formula phenyl-C(=O)-O-C(=O)-phenyl to give a penultimate carboxamide of formula (IC):

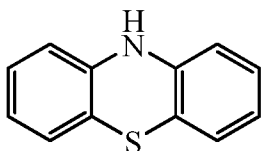


The carboxamide of formula (IC) can then be reduced (e.g., lithium aluminum hydride in tetrahydrofuran) to give the compound of formula (I) wherein R^1 is H.

The invention further contemplates employing acid addition salts of the compound of formula (I). The term "acid addition salt" means an ionic substance comprising an organic cation

and an organic, or preferably inorganic anion. The organic cation comprises a protonated form of phenothiazine or the compound of formula (I). The anion comprises a residual of an organic or, preferably, inorganic compound having at least one proton characterized by a pKa value of less than 7 (i.e., a residual of a Brønsted acid). Preferred acid addition salts comprise from 0.9 to 1.1 mole equivalents of a monoprotic Brønsted acid, from 0.45 to 0.55 mole equivalents of a diprotic Brønsted acid, or from 0.3 to 0.37 mole equivalents of a triprotic Brønsted acid, all per mole of phenothiazine or the compound of formula (I). Preferred Brønsted acids include hydrochloric, nitric, phosphoric, sulfuric, hydrobromic, hydroiodic, phosphorus, formic, and acetic acids.

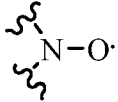
In some embodiments the invention composition further comprises at least one additional captive polymerization inhibitor of the vinyl monomer (e.g., acrylic monomer). In some embodiments the additional captive polymerization inhibitor is a manganese salt that is $\text{Mn}(\text{HCO}_2^-)_2$, $\text{Mn}((\text{C}_1\text{-C}_8)\text{alkylCO}_2^-)_2$, or potassium permanganate. In some embodiments the manganese salt is employed in a method of the second embodiment as the inhibitor modifier in combination with the captive polymerization inhibitor. In some embodiments the manganese salt is $\text{Mn}(\text{HCO}_2^-)_2$. In some embodiments the manganese salt is $\text{Mn}((\text{C}_1\text{-C}_8)\text{alkylCO}_2^-)_2$, and more preferably manganese(II) acetate, including manganese(II) acetate ($\text{Mn}(\text{O}_2\text{CCH}_3)_2$) and manganese(II) acetate tetrahydrate ($\text{Mn}(\text{O}_2\text{CCH}_3)_2 \cdot 4\text{H}_2\text{O}$). In some embodiments the manganese salt is potassium permanganate. In some embodiments the additional captive polymerization inhibitor is hydroquinone. In some embodiments the additional captive polymerization inhibitor is phenothiazine or a second mixture of molecular oxygen and phenothiazine, or a second acid addition salt thereof. The term “phenothiazine” and “phenothiazine *per se*” each mean the compound of the following formula:



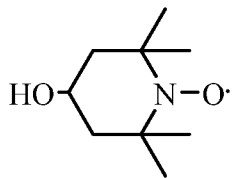
The additional captive polymerization inhibitor, when used, is employed in its own independent polymerization inhibiting effective amount. A polymerization inhibiting effective amount of the manganese salt, hydroquinone, or phenothiazine can vary depending on, for example, the particular vinyl monomer (e.g., acrylic monomer) and amount thereof being inhibited, conditions such as temperature and pressure, presence or absence of other captive polymerization inhibitors, and amount of inhibitor modifier, if any, that is present. The person of ordinary skill in the art would be able to determine appropriate polymerization inhibiting effective amounts under particular circumstances without undue experimentation. A preferred polymerization inhibiting effective amount of the manganese salt, hydroquinone, or phenothiazine independently is from about 5 ppm

to about 500 ppm, more preferably from about 10 ppm to about 250 ppm, still more preferably from about 20 ppm to about 200 ppm, and even more preferably from about 40 ppm to about 100 ppm, all based on a total weight of the liquid mixture.

In some embodiments the invention composition further comprises a first mixture of an N-oxyl compound and the manganese salt that is $\text{Mn}(\text{HCO}_2^-)_2$, $\text{Mn}((\text{C}_1\text{-C}_8)\text{alkylCO}_2^-)_2$, or potassium permanganate. The term “N-oxyl compound” means a chemical substance having a

structural fragment, , wherein the • represents a radical (electron) and each  represents a portion of a covalent bond to a quaternary carbon atom. Preferably, the N-oxyl

compound is 2,2,5,5-tetramethyl-3-oxopyrrolidine-1-oxyl; 2,2,6,6-tetramethylpiperidine-1-oxyl; tris(2,2,6,6-tetramethylpiperidine-1-oxyl-4-yl)-phosphite; and, more preferably, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl. The terms “4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl” and “4-hydroxy-TEMPO” are synonymous and each mean a compound of the following formula:



, wherein the • represents a radical (electron).

The invention further contemplates compositions further comprising a combination of any two or more of the aforementioned additional captive polymerization inhibitors.

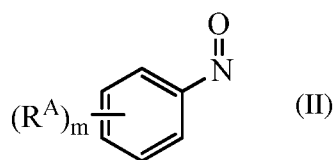
A polymerization inhibiting effective amount of 4-hydroxy-TEMPO can vary depending on, for example, the particular vinyl monomer (e.g., acrylic monomer) and amount thereof being inhibited, conditions such as temperature and pressure, presence or absence of other captive polymerization inhibitors, and amount of the manganese salt present. The person of ordinary skill in the art would be able to determine appropriate polymerization inhibiting effective amounts under particular circumstances without undue experimentation. A preferred polymerization effective inhibiting amount of the N-oxyl compound such as 4-hydroxy-TEMPO is from about 5 ppm to about 500 ppm, more preferably from about 10 ppm to about 250 ppm, still more preferably from about 20 ppm to about 200 ppm, and even more preferably from about 40 ppm to about 100 ppm, all based on a total weight of the liquid mixture.

The present invention further contemplates compositions further comprising the inhibitor modifier. Examples of the inhibitor modifier are molecular oxygen and the manganese salt (e.g., when no additional captive polymerization inhibitor is employed or when the invention composition further comprises the N-oxyl compound (e.g., the 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl).

As mentioned before, preferably the acrylic monomer is the acrylic acid-type monomers of formula (M). Preferred is the acrylic acid-type monomer of formula (M) wherein one of R^{11} to R^{14} is (C_1-C_8) alkyl and the remainder of R^{11} to R^{14} is hydrogen. In some embodiments, R^{11} is (C_1-C_8) alkyl. In some embodiments, R^{11} is (C_9-C_{18}) alkyl. In some embodiments, R^{11} is (C_1-C_8) alkyl. In some embodiments, R^{11} is (C_1-C_8) alkyl and each of R^{12} to R^{14} is hydrogen. In some embodiments, R^{12} is (C_1-C_8) alkyl and each of R^{11} , R^{13} , and R^{14} is hydrogen. In some embodiments, R^{13} is (C_1-C_8) alkyl and each of R^{11} , R^{12} , and R^{14} is hydrogen. In some embodiments, R^{14} is (C_1-C_8) alkyl and each of R^{11} to R^{13} is hydrogen. In some embodiments, each of R^{11} to R^{14} is hydrogen, i.e., the acrylic acid-type monomer of formula (M) is acrylic acid itself.

Also preferred is the acrylic acid-type monomer of formula (M) wherein two of R^{11} to R^{14} is (C_1-C_8) alkyl and the remainder of R^{11} to R^{14} is hydrogen. More preferably, R^{11} is one of the two of R^{11} to R^{14} that is (C_1-C_8) alkyl. Also preferred is the acrylic acid-type monomer of formula (M) wherein three of R^{11} to R^{14} is (C_1-C_8) alkyl and the remainder of R^{11} to R^{14} is hydrogen. Preferably in the acrylic acid-type monomer of formula (M), each (C_1-C_8) alkyl is (C_1-C_3) alkyl and, more preferably, methyl.

In some embodiments the fugitive polymerization inhibitor that is lacking in the invention composition is a nitroso compound of formula (II):



, wherein m is an integer of from 1 to 3 and each R^A independently is hydrogen, (C_1-C_3) alkyl, (C_1-C_3) alkyl-O-, fluoro, or chloro.

Compounds of formulas (I) and (M), 4-hydroxy-TEMPO, manganese salts, acid addition salts, inhibitor modifier, etc. useful in the present invention, and the fugitive inhibitor that is lacking, include solvates, including hydrates, thereof.

In the method of the second embodiment the vinyl monomer (e.g., acrylic monomer) is exposed to polymerizing conditions and thus becomes susceptible to being polymerized (e.g., susceptible to forming an oligomer or homopolymer), and any polymerization of the distillable monomer in the invention method is inhibited by the captive polymerization inhibitor(s). Examples of polymerizing conditions are exposure to a polymerizing agent (e.g., oxygen gas, water, or a free

radical or initiator) or condition (e.g., free radical generation conditions such as ultraviolet light or a high temperature zone).

A preferred method of the second embodiment employs any one of the preferred acrylic acid-type monomer polymerization inhibitor compositions described herein and any one of the preferred acrylic acid-type monomers of formula (M) described herein. Another preferred of the second embodiment employs a mixture of any two or more of the preferred acrylic acid-type monomers of formula (M) described herein such as, for example, a mixture of acrylic acid and either ethyl acrylate or *n*-butyl acrylate.

Preferably in the method of the second embodiment employing the vinyl monomer (e.g., acrylic monomer) and captive polymerization inhibitor, the step comprises evaporating at least some of the vinyl monomer (e.g., acrylic monomer) and under a reduced pressure that is less than 90 kPa and an elevated temperature of the liquid mixture (e.g., distillation pot temperature) that is greater than 50 °C, and more preferably greater than 90 °C.

In a pilot plant or manufacturing setting, a vessel (e.g., distillation pot or reactor) containing the invention composition is in fluid communication with a distillation column. A preferred distillation column is one that contains dual-flow plates or trays. An example of such a dual-flow tray column is described in U.S. Patent Number US 7,306,204 B2. Preferably, distillation columns comprise, and the liquid mixture is in sequential fluid communication with, bottom, middle and upper zones, wherein the middle zone optionally defines a feed inlet. In a method of the second embodiment, preferably during steady state operation temperature in the bottom zone is within about 5 °C of the elevated temperature of the liquid mixture and reduced pressure in the top zone is within about 30 kPa of reduced pressure in the bottom zone. For illustration, a manufacturing scale dual-flow 40-tray column during steady state operation is characterized by a temperature of about 111 °C and reduced pressure of about 35 kPa in its bottom zone, a temperature of about 46 °C and reduced pressure of about 21 kPa in its top zone, and a temperature of about 56 °C in its middle zone.

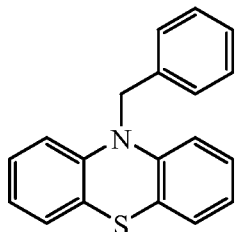
The present invention contemplates batch (single addition of vinyl monomer (e.g., acrylic monomer)) and continuous (continuous addition or multiple separate additions of vinyl monomer (e.g., acrylic monomer)) to the vessel containing the invention composition. In batch or continuous processes, especially continuous processes, preferably one or more additional polymerization inhibiting effective amounts of the captive polymerization inhibitor are added to the vinyl monomer (e.g., acrylic monomer) in the vessel. For example in a continuous process employing a distillation vessel (e.g., distillation pot) and column, such one or more additional polymerization inhibiting effective amounts can be added to the distillation vessel containing vinyl monomer (e.g., acrylic monomer) so as to replace portions of the captive polymerization inhibitor lost to reaction thereof in the distillation vessel. The additions of the captive polymerization inhibitor independently comprise

continuous or multiple separate additions and can be made by conventional means such as, for example, an addition funnel or valved feed line.

Materials: Acrylic acid, phenothiazine, 4-hydroxy-TEMPO and a number of manganese salts are commercially available from various suppliers including Sigma-Aldrich Company, St.

5 Louis, Missouri, USA.

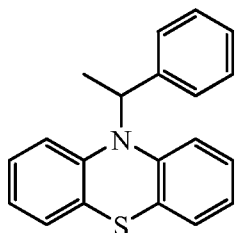
Preparation 1: synthesis of N-benzylphenothiazine (1)



(1)

. Add a solution of 2 grams (g; 0.01 mole (mol)) of phenothiazine in 10 milliliters (mL) of dry tetrahydrofuran (THF) under nitrogen gas atmosphere to a suspension of 1.0 g of sodium hydride (NaH; 0.042 mol) in 20 mL of dry THF at room temperature (Previously obtain the NaH by washing an 80% suspension of NaH in mineral oil with n-hexane.) Stir the mixture for 4 hours or until hydrogen gas is released and the color of mixture changes to orange. Then slowly add 2 mL (0.017 mol) of benzyl bromide to the orange mixture at room temperature, and stir the resulting mixture overnight. Heat the mixture to 60 °C for 1 hour. The orange color fades. Pour the reaction mixture into ice-water that has been acidified with concentrated
10 hydrochloric acid to pH 1. Extract the resulting aqueous mixture with ethyl acetate, dry it over anhydrous magnesium sulfate, and remove the solvent under vacuum. Purify the resulting extraction residue by column chromatography over neutral alumina eluting with a solvent mixture of n-hexane:ethyl acetate (50:1). Evaporate the solvents and recrystallized the residue from ethanol to give 2 g (60% yield) of N-benzylphenothiazine as white crystals. ¹H NMR spectrum is consistent
20 with pure N-benzylphenothiazine. ¹H NMR (CDCl₃) (ppm): 7.25 – 7.40 (m, 5H); 7.11 (d, 2H, *J* = 7.5 Hz); 7.00 (t, 2H, *J* = 8.0 Hz); 6.88 (t, 2H, *J* = 7.5 Hz); 6.67 (d, 2H, *J* = 8.0 Hz); 5.12 (s, 2H).

Preparation 2: synthesis of N-(1-phenylethyl)-phenothiazine (2)



(2)

. In a procedure similar to that of Preparation 1 except use (1-bromoethyl)benzene instead of benzyl bromide, prepare N-(1-phenylethyl)-phenothiazine. Product is
25 purified by column chromatography on neutral alumina using n-hexane:ethyl acetate (50 : 1) mixture of solvents as an eluent. Evaporation of solvent gave N-(1-phenylethyl)-phenothiazine as a white solid in 65 % yield. ¹H NMR spectrum is consistent with N-(1-phenylethyl)-phenothiazine. ¹H

NMR (CDCl₃) (ppm): 7.30 – 7.45 (m, 5H, Ar-CH-); 7.14 (d, 2H, *J* = 7.5 Hz, Ar-PTZ); 6.85 – 7.05 (m, 4H, Ar-PTZ); 6.74 (d, 2H, *J* = 7.0 Hz, Ar-PTZ); 5.42 (q, 1H, Ar-CH-CH₃); 1.98 (d, 3H, *J* = 7.0 Hz, CH-CH₃).

Some embodiments of the invention are described in more detail in the following Examples.

5 Examples 1 and 2: compositions of acrylic acid and compound (1) or (2).

In two separate vials, mix 5 milliliters (mL) acrylic acid and an amount of compound (1) or (2) (Preparations 1 or 2) that is sufficient to produce a mixture having 100 ppm of the captive polymerization inhibitor, the mixture being the composition of Example 1 or 2, respectively. The compositions of Examples 1 and 2 are particularly useful for inhibiting polymerization of acrylic acid. Repeat Examples 1 and 2 four more times to give 5 vials for Examples 1 and 2.

10 Examples 3 and 4: inhibition of polymerization of acrylic acid with compound (1) or (2).

For Example 3, seal vials and heat the compositions of Example 1 and for Example 4 seal vials and heat the compositions of Example 2, all at 113 degrees Celsius (°C) and record time of first appearance of change in density (gel formation) in compositions. In five separate vials heat a

15 comparative, non-invention composition comprising 5 mL acrylic acid and 100 ppm of phenothiazine *per se* (PTZ) and likewise record time to gel formation. There are a total of 5 runs for each of Examples 3 and 4 and the comparative example. Gel formation times for Example 3 ranged from 81 hours to 97 hours; for Example 4 from 94 to 99 hours; and for comparator PTZ from 31 hours to 34 hours. Average results are reported below in Table 1.

20 Table 1: time to gel formation

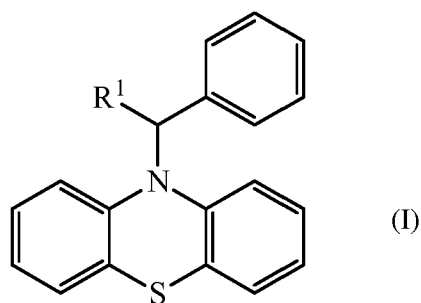
Example Number	Composition Example number	Average time to gel formation (hours)
3	1	85
4	2	97
Comparator	PTZ	33

As shown by the above data, the invention composition synergistically inhibits polymerization of vinyl monomer (e.g., acrylic monomer) and is especially useful in manufacture, purification, handling, and storage of acrylic monomers, especially acrylic acid-type monomers, as an inhibitor of polymerization of the acrylic monomers in, e.g., vessels and piping.

CLAIMS

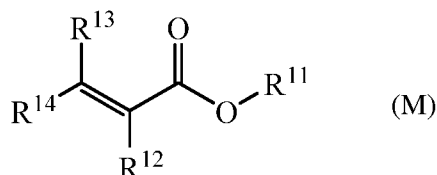
WHAT IS CLAIMED IS:

1. A vinyl monomer polymerization inhibitor composition comprising a liquid mixture comprising a vinyl monomer and a polymerization inhibiting effective amount of a captive polymerization inhibitor, wherein the composition lacks a fugitive polymerization inhibitor of polymerization of the vinyl monomer and the captive polymerization inhibitor independently is characterizable as being a synergistically effective inhibitor of polymerization of the vinyl monomer and polymerization of the vinyl monomer is synergistically inhibited by the captive polymerization inhibitor, and wherein the captive polymerization inhibitor is a compound of formula (I):



, or a first acid addition salt thereof, wherein R¹ is hydrogen or (C₁-C₃)alkyl.

2. The composition as in claim 1, wherein the vinyl monomer is an acrylic acid-type monomer of formula (M):



, wherein R¹¹ is hydrogen or (C₁-C₁₈)alkyl and each of R¹² to R¹⁴ independently is hydrogen or (C₁-C₈)alkyl.

3. The composition as in claims 1 or 2, wherein R¹ is hydrogen.
4. The composition as in claim 1 or 2, wherein R¹ is (C₁-C₃)alkyl.
5. The composition as in claim 1 or 2, wherein the captive polymerization inhibitor is N-benzyl-phenothiazine, N-(1-phenylethyl)phenothiazine, or the first acid addition salt thereof.
6. The composition as in claim 5, wherein the captive polymerization inhibitor is N-benzyl-phenothiazine or N-(1-phenylethyl)phenothiazine.

7. The composition as in any one of the preceding claims, wherein the composition further comprises: (a) a manganese salt that is $\text{Mn}(\text{HCO}_2^-)_2$, $\text{Mn}((\text{C}_1\text{-C}_8)\text{alkylCO}_2^-)_2$, or potassium permanganate; (b) a first mixture of an N-oxyl compound and a manganese salt that is $\text{Mn}(\text{HCO}_2^-)_2$, $\text{Mn}((\text{C}_1\text{-C}_8)\text{alkylCO}_2^-)_2$, or potassium permanganate; (c) 5 hydroquinone; (d) a second mixture of molecular oxygen and phenothiazine, or a second acid addition salt thereof, or (e) a combination of any two or more captive polymerization inhibitors of the foregoing (a) to (d).
8. A method of synergistically inhibiting polymerization of a vinyl monomer, the method comprising contacting together a vinyl monomer with a polymerization inhibiting effective 10 amount of a captive polymerization inhibitor so as to give the polymerization inhibitor composition as in any one of claims 1 to 7.