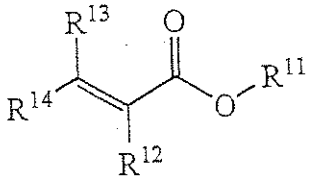
during such reduced pressure distillation operations and essentially do not inhibit polymerization of the evaporated and condensed acrylic acid-type monomers on the structures in the columns.

The chemical industry desires superior polymerization inhibitor compositions comprising a captive polymerization inhibitor and a fugitive polymerization inhibitor each independently capable of inhibiting polymerization of distillable monomers (e.g., acrylic acid-type monomers and other olefinic monomers) in vessels (e.g., distillation pots) and piping and the fugitive polymerization inhibitor preferably further capable of evaporating into headspaces in the vessels and piping and into distillation columns, condensing in a polymerization inhibiting amount with the distillable monomers, and inhibiting polymerization of the evaporated and condensed distillable monomers on structures in the headspaces (e.g., distillation columns), including structures distal from unevaporated acrylic acid-type monomers remaining in the vessels or pipes.

~~BRIEF~~ SUMMARY ~~OF THE INVENTION~~

In a first aspect, the present disclosure provides a distillable-monomer polymerization inhibitor composition comprising a liquid mixture comprising a distillable monomer, a captive polymerization inhibitor and a fugitive polymerization inhibitor, wherein:

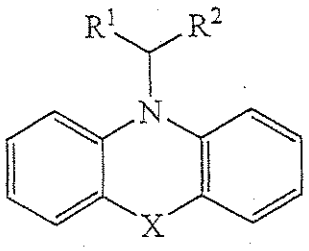
the distillable monomer is an acrylic acid-type monomer of formula (M):



(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;

the captive polymerization inhibitor comprises: (a) a manganese salt that is $Mn(HCO_2^-)_2$, $Mn((C_1$-$C_8)alkylCO_2^-)_2$, or potassium permanganate; (b) a first mixture of an N-oxyl compound and a manganese salt that is $Mn(HCO_2^-)_2$, $Mn((C_1$-$C_8)alkylCO_2^-)_2$, or potassium permanganate; (c) hydroquinone; (d) a second mixture of molecular oxygen and phenothiazine, or a first acid addition salt thereof, wherein the term "acid addition salt" means an ionic substance comprising an organic cation comprising a protonated form of phenothiazine, and an organic, or preferably inorganic anion, (e) a third mixture of a compound of formula (II):



(II)

or a second acid addition salt thereof,

wherein X is S, O, or N-R^3;

R^1 is hydrogen or (C_1-C_3)alkyl;

R^2 is phenyl; and

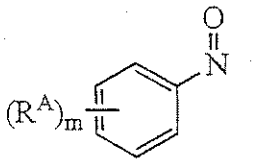
R^3 is (C_1-C_3)alkyl;

or (f) a combination of any two or more captive polymerization inhibitors of the foregoing (a) to (e),

the captive polymerization inhibitor and the fugitive polymerization inhibitor are different and not interconvertible between one another;

each of the fugitive polymerization inhibitor and the captive polymerization inhibitor independently is characterizable as being an inhibitor of polymerization of the distillable monomer; and

the fugitive polymerization inhibitor is characterizable as being capable of evaporating with the distillable monomer from a first location and condensing with the distillable monomer at a second location that is different than the first location during distillation of the distillable monomer, wherein the fugitive polymerization inhibitor is a nitroso compound of formula (I):



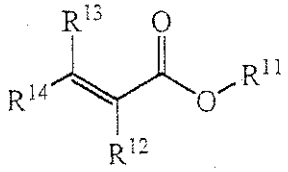
(I)

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, the nitroso compound of formula (I) is from greater than 25 parts per million to 2000 parts per million of the liquid mixture; wherein

the acrylic acid-type monomer of formula (M) and the fugitive polymerization inhibitor are characterized by either (i) respective first and second liquid vapor pressures of substantially pure forms thereof or (ii) relative volatility of a test mixture consisting of the acrylic acid-type monomer of formula (M), the fugitive polymerization inhibitor, and the captive polymerization inhibitor, wherein the first and second liquid vapor pressures are independently determined at a same elevated temperature, the elevated temperature being 50 degrees Celsius or higher, and the first liquid vapor pressure and the second liquid vapor pressure independently are at least 5 kiloPascals and are within 40 kiloPascals of each other; and the relative volatility of the test mixture is from 0.5 to 10, wherein the term "relative volatility" means a ratio of distribution coefficients, the ratio equal to (vapor phase mole fraction (y_i) divided by liquid phase mole fraction (x_i) for the fugitive polymerization inhibitor) divided by (vapor phase mole fraction (y_m) divided by liquid phase mole fraction (x_m) for the distillable monomer), determined by methods as referred to in the description.

In a first embodiment, the present ~~invention~~disclosure provides a monomer polymerization inhibitor composition ("composition") comprising a captive polymerization inhibitor and a fugitive polymerization inhibitor, wherein: the captive polymerization inhibitor and the fugitive polymerization inhibitor are different and not interconvertible between one another; each of the fugitive polymerization inhibitor and the captive polymerization inhibitor independently is characterizable as being an inhibitor of polymerization of a same distillable monomer; and the fugitive polymerization inhibitor is characterizable as being capable of evaporating with the distillable monomer from a first location and condensing with the distillable monomer at a second location that is different than the first location during distillation of the distillable monomer.

In some aspects of the first embodiment the fugitive polymerization inhibitor and the captive polymerization inhibitor are characterizable as being inhibitors of a distillable monomer that is an olefinic monomer or a free-radical polymerizable monomer. An example of the olefinic monomer is an acrylic acid-type monomer of formula (M):



(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.

In a second aspect, the present disclosure provides a method of inhibiting polymerization of a distillable monomer during a distillation thereof, the method comprising steps of:

(a) contacting together a distillable monomer polymerization inhibitor composition and an amount of a distillable monomer to give a liquid mixture thereof at a first location, wherein the composition comprises a first polymerization inhibiting amount of a fugitive polymerization inhibitor and an inhibiting amount of a captive polymerization inhibitor, wherein the captive polymerization inhibitor and the fugitive polymerization inhibitor are different, not interconvertible between one another, and each of the fugitive polymerization inhibitor and the captive polymerization inhibitor independently is characterized as being an inhibitor of polymerization of the distillable monomer;

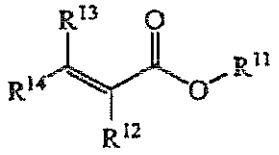
(b) evaporating from the first location at least some of the distillable monomer and at least some of the fugitive polymerization inhibitor to respectively give an evaporated distillable monomer and an evaporated fugitive polymerization inhibitor; and

(c) condensing together at least some of the evaporated distillable monomer and at least some of the evaporated fugitive polymerization inhibitor to give a condensate mixture thereof at a second location that is different than and in fluid communication with the first location, wherein the condensate mixture comprises some of the amount of the distillable monomer and a second polymerization inhibiting amount of the fugitive polymerization inhibitor;

wherein polymerization of the distillable monomer at the second location is inhibited by the second polymerization inhibiting amount of the fugitive polymerization inhibitor; and in and under conditions of distilling steps (b) and (c), the fugitive polymerization inhibitor has a vapor pressure or relative volatility distillation performance compatible with a vapor pressure or relative volatility distillation performance of the distillable monomer.

In a second embodiment, the present ~~invention~~disclosure provides a method of inhibiting polymerization of a distillable monomer during a distillation thereof, the method comprising steps of: (a) contacting together the invention composition of the first embodiment and an amount of a distillable monomer to give a liquid mixture thereof at a first location (e.g., a distillation vessel), wherein the composition comprises a first polymerization inhibiting amount of the fugitive polymerization inhibitor and an inhibiting amount of the captive polymerization inhibitor; (b) evaporating from the first location at least some of the distillable monomer and at least some of the fugitive polymerization inhibitor to respectively give an evaporated distillable monomer and an evaporated fugitive polymerization inhibitor; and (c) condensing together at least some of the evaporated distillable monomer and at least some of the evaporated fugitive polymerization inhibitor to give a condensate mixture thereof at a second location that is different than and in fluid communication with the first location, wherein the condensate mixture comprises a mixture of some of the amount of the distillable monomer and a second polymerization inhibiting amount of the fugitive polymerization inhibitor; wherein polymerization of the distillable monomer at the second location is inhibited by the second polymerization inhibiting amount of the fugitive polymerization inhibitor; and in and under conditions of distilling steps (b) and (c), the fugitive polymerization inhibitor has a vapor pressure or relative volatility distillation performance compatible with a vapor pressure or relative volatility distillation performance of the distillable monomer. The liquid mixture and the condensate mixture are different.

In some aspects of the second embodiment the distillable monomer is an olefinic monomer or a free-radical polymerizable monomer and the captive and fugitive polymerization inhibitors are each inhibitors of polymerization thereof. In some embodiments the olefinic monomer is an acrylic acid-type monomer of formula (M):



(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. In this embodiment the condensate mixture comprises an evaporated and condensed acrylic acid-type monomer of formula (M) and the second polymerization inhibiting amount of the evaporated and condensed fugitive polymerization inhibitor thereof.

The ~~invention~~disclosed composition of the first aspect~~embodiment~~ is one that is capable of functioning in the method of the second embodiment. Preferably the ~~invention~~disclosed composition is capable of functioning in such a way that should the invention composition be employed in a distillation of