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(54) Title:

**METHODS AND COMPOSITIONS FOR INHIBITING VINYL
AROMATIC MONOMER POLYMERIZATION**

(57) Abstract:

Methods and compositions are provided for inhibiting the polymerization of a vinyl aromatic monomer, such as styrene monomer, during elevated temperature processing thereof or during storage or shipment of polymer containing product. The compositions comprise a combination of a quinone methide derivative A) and a phenol compound B). The methods comprise adding from about 1-10,000 ppm of the combination to the monomer containing medium, per one million parts of the monomer.

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(54) Title: METHODS AND COMPOSITIONS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION

(57) Abstract: Methods and compositions are provided for inhibiting the polymerization of a vinyl aromatic monomer, such as styrene monomer, during elevated temperature processing thereof or during storage or shipment of polymer containing product. The compositions comprise a combination of a quinone methide derivative A) and a phenol compound B). The methods comprise adding from about 1-10,000 ppm of the combination to the monomer containing medium, per one million parts of the monomer.



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METHODS AND COMPOSITIONS FOR INHIBITING VINYL AROMATIC MONOMER POLYMERIZATION

FIELD OF THE INVENTION

[0001] The invention pertains to methods and compositions for inhibiting the undesired polymerization of vinyl aromatic monomers, such as styrene monomer, during processes such as monomer preparation, and purification, and during storage and shipment of products containing such monomers.

BACKGROUND OF THE INVENTION

[0002] Polystyrene is a thermoplastic with many desirable characteristics. It is clear, transparent, readily colored and easily fabricated. The family of styrene polymers includes polystyrene itself, copolymers of styrene with other vinyl monomers, polymers of derivatives of styrene and mixtures of polystyrene and styrene-containing copolymers with elastomers.

[0003] ABS (acrylonitrile, butadiene-styrene) resins have enjoyed tremendous commercial popularity for many years as durable, temperature and solvent resistant elastomers. On the other hand, styrene plastics are commonly used for packaging, including foams and films, coatings, in appliance fabrication, for housewares and toys, lighting fixtures and in construction materials.

[0004] It is well known that styrene monomer readily polymerizes when heated or exposed to light. Heat polymerization is rapid. In fact, polymerization increases with increasing temperature. This polymerization is undesirable during many stages of the manufacturing, processing, handling, storage and use of styrene monomers.

[0005] Common industrial methods for producing styrene include a variety of purification processes, including distillation, to remove impurities. Unfortunately, purification operations carried out at elevated temperatures result in an increased rate of undesired polymerization. Polymerization, such as thermal polymerization, during the monomer purification process, results not only in loss of desired monomer end-product, but also in loss of production efficiency caused by polymer formation or agglomeration on process equipment. In heat requiring operations, such agglomeration adversely affects heat transfer efficiency.

SUMMARY OF THE INVENTION

[0006] In accordance with aspect of the invention, a method is provided for inhibiting the polymerization of a vinyl aromatic monomer such as styrene monomer, i.e., ethylbenzene. The method comprises adding an effective polymerization inhibiting amount of a combined treatment to the monomer medium. The combined treatment comprises (A) a quinone methide derivative and (B) a phenol compound. From about 1-10,000 ppm of (A) and (B) collectively is brought into contact with the requisite vinyl aromatic monomer based on 1 million parts of the monomer. The method may, in other aspects of the invention, comprise the step of heating the monomer and, in another aspect of the invention, the monomer may be distilled to remove impurities therefrom.

[0007] In another aspect of the invention, a vinyl aromatic monomer anti-polymerization composition is provided which comprises a liquid carrier and dissolved or dispersed therein (A) a quinone methide derivative and (B) a phenol compound.

[0008] In another embodiment, the quinone methide derivative is 2,6-di-tert-butyl-4-benzylidene-cyclohexa-2,5-dienone.

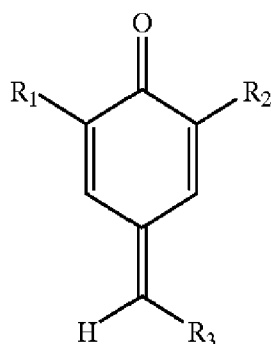
[0009] In another aspect of the invention, the phenol compound (B) is 2,6-di-tert-butylphenol.

[0010] In another exemplary embodiment, a liquid carrier such as a non-polar organic solvent is provided with the combined treatment (A) and (B) dissolved or dispersed therein.

DETAILED DESCRIPTION OF EXEMPLARY EMBODIMENTS

[0011] In accordance with the invention, both a quinone methide derivative (A) and a phenol compound (B) are conjointly utilized to inhibit polymerization of a vinyl aromatic monomer such as styrene.

[0012] The quinone methide derivatives generally have the formula:



wherein:

[0013] R_1 and R_2 are independently H, C_4 to C_{18} alkyl; C_5 to C_{12} cycloalkyl; or C_7 to C_{15} phenylalkyl.

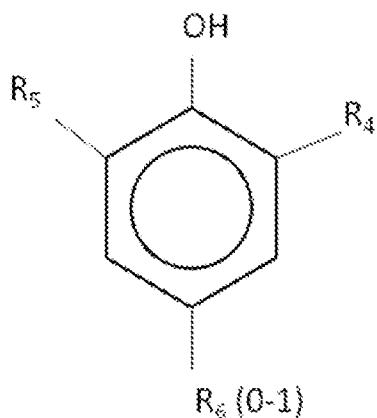
[0014] Preferably, R_1 and R_2 are tert-butyl, tert-amyl, tert-octyl, cyclohexyl, α -methylbenzyl or α,α -dimethylbenzyl; with tert-butyl, tert-amyl or tert-octyl most preferred.

[0015] R_3 is preferably aryl, or aryl substituted with C_1 to C_6 alkyl, alkoxy, hydroxy, nitro, amino, carboxy, or mixtures thereof.

[0016] Means for preparing these compounds may be found in U.S. Patent 4,032,547, the contents of which are wholly incorporated by reference to herein.

[0017] Preferably, the quinone methide derivative is 2,6-di-tert-butyl-4-benzylidene-cyclohexa-2,5-dienone.

[0018] The phenol compounds B) that may be utilized generally have the formula:



wherein R₄ and R₅ may be the same or different and are chosen from C₁-C₂₀ alkyl, C₁-C₃₀ alkaryl and substituted C₁-C₃₀ alkaryl, R₆, when present, is selected from C₁-C₂₀ alkyl, thiophenol, substituted thiophenol, C₁-C₄₀ alkanoic acid ester, C₁-C₃₀ alkaryl, substituted C₁-C₃₀ alkaryl, C₁-C₆ alkylamino, C₁-C₆ alkoxy, amine, polynuclear aryl and substituted polynuclear aryl.

[0019] At present, the preferred phenol B) compound is 2,6-di-*t*-butylphenol. Exemplary phenols include 2,6-dipropylphenol, 2,6-diethylphenol and 2,6-dimethylphenol. Also mentioned as exemplary are the hindered phenols in accord with the above formula wherein R₄, R₅ and R₆ are all present. These include:

2,6-di-*t*-butyl-4-methylphenol
 4,4'-thiobis-(6-*t*-butyl-2-methylphenol)
 octadecyl 3-(3',5'-di-*t*-butyl-4'-hydroxyphenyl)propionate
 4,4'-methylenebis(2,6-di-*t*-butylphenol)
 1,3,5-trimethyl-2,4,6-tris(3,5-di-*t*-butyl-4-hydroxybenzyl)benzene
 2,6-di-*t*-butyl- α -dimethylamino-*p*-cresol
 2,6-di-*t*-butyl-4-secbutylphenol
 2,2'-methylenebis(4-ethyl-6-*t*-butylphenol)
 2,2'-methylenebis(4-methyl-6-*t*-butylphenol)
 2,2'-methylenebis(6-(1-methylcyclohexyl)-*p*-cresol; and
 2,2'-methylenebis(4-methyl-6-cyclohexylphenol)

[0020] The compositions of the present invention are effective at inhibiting polymerization of vinyl aromatic monomers under processing conditions. These processing conditions include but are not limited to preparation, purification, distillation and vacuum distillation processes.

[0021] Styrene, for example, is typically processed at temperatures between 95° and 125° C. The compositions of the present invention are effective at inhibiting the polymerization of styrene over this range of temperatures.

[0022] The vinyl aromatic monomers that are treated by the compositions of the present invention include but are not limited to styrene, bromostyrene, divinylbenzene, and α -

methylstyrene. The compositions of the present invention are particularly efficacious at inhibiting the polymerization of styrene monomer.

[0023] The total amount of quinone methide derivative A) and phenolic compound B) used in the methods of the present invention is that amount which is sufficient to inhibit polymerization of vinyl aromatic monomers. This amount will vary according to the conditions under which the vinyl aromatic monomer is being processed, contaminants in the system and the temperature of the system. At higher processing temperatures and higher monomer contamination, larger amounts of the inhibiting composition are required.

[0024] For purposes of the present invention, the term "effective inhibiting amount" is that amount which is effective at inhibiting vinyl aromatic monomer polymerization. Preferably, this amount ranges from about 1 part to about 10,000 parts of quinone methide derivative and phenolic compound, collectively, per 1 million parts of monomer. Most preferably, this amount will range from about 1 to 1,000 parts per million parts monomer.

[0025] Accordingly, it is possible to produce a more effective vinyl aromatic monomer polymerization inhibiting treatment than is obtained by the use of either compound by itself when measured at comparable treatment levels. This synergism or enhanced activity between components allows for the concentration of each of the components to be lowered and the total quantity of polymerization inhibitor required, particularly at higher temperatures, may be lowered while achieving a commensurate level of polymerization inhibition.

[0026] As such, the weight ratio of quinone methide derivative to phenolic compound will generally range from about 90:10 to about 10:90. Most preferred is a weight ratio of about 70:30.

[0027] The compositions of the present invention can be introduced into the vinyl aromatic monomer by any conventional method at any point of the processing system, either as separate and individual ingredients or as a combination of ingredients.

[0028] The compositions of the present invention may be added to the vinyl aromatic monomer as either a dispersion or as a solution using a suitable liquid carrier or solvent. Any solvent that is compatible with the individual ingredients of the composition and the vinyl aromatic monomer to be treated may be employed. It is often desirable to dissolve the inhibitors in the monomer to which the inhibitor is being added to avoid introducing additional impurities

in the monomer. Exemplary liquid carriers include non-polar organic solvents, such as heavy aromatic naphtha and xylene.

[0029] The method of the present invention can control the fouling of processing equipment, such as the equipment used in separation and purification processes of styrene monomer, which is due to or caused by the polymerization of the monomer. The instant invention may be used as both a process inhibitor, which is employed during preparation and processing (e.g., employing heat) of the styrene monomer (i.e., ethylbenzene), and as a product inhibitor, which is combined with the styrene monomer in order to inhibit polymerization during storage and handling.

[0030] The invention will now be described in conjunction with the following examples which should be viewed as being illustrative of the invention and should not be deemed to limit the invention in any manner.

EXAMPLES

[0031] The effect of a combined treatment of QM (Quinone Methide) and 2,6-di-tert butyl phenol on the thermal polymerization of styrene at 115-120 °C was evaluated by comparing polymer formation utilizing the following procedure.

[0032] A 250 ml RB flask-equipped with an Ar gas inlet, water cooled condenser and sample outlet was charged with 110 ml of styrene and the candidate polymerization inhibitor(s). [600 ppm (w/v)]. The flask was purged with Argon for 10 minutes. The flask was then immersed into an oil-bath thermostatically controlled at 115-120 °C and heated with purging Ar continuously. Once the temperature reached 115 °C, the stop clock was started and this time was considered as time zero. About 5 ml of the sample was removed from the flask at varying time intervals for up to 4 hours and measured precisely before pouring into about 40 ml methanol to precipitate out the styrene polymer. The precipitated polystyrene was filtered with a gas membrane filter that was pre-weighed before use. The polymer was dried at 100 °C and weighed.

[0033] Styrene Polymerization Results are Shown in Table I.

Table I: Amount of polystyrene formation at 115-120 °C as a function of time for a resultant retarder dosage of about 600 ppm with different ratios of 2,6-tertiary butyl phenol (DTBP) and QM.

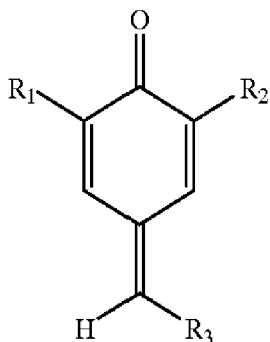
Time in minutes	Polymer wt. in mg						
	QM (pure) 600 ppm	QM+2,6- DTBP (569.3 ppm: 31.68 ppm)	QM+2,6- DTBP (479.98 ppm: 119.07 ppm)	QM+2,6- DTBP (450.24 ppm: 149.94 ppm)	QM+2,6- DTBP (420.22 ppm: 180.45 ppm)	QM+2,6- DTBP (387.3 ppm: 210.78 ppm)	QM+2,6- DTBP (300.07 ppm: 298.71 ppm)
60	19.58	15.80	12.60	10.1	6.8	13.60	16.20
120	42.85	34.90	24.80	23.2	15.0	29.00	34.50
180	70.75	59.00	41.10	40.1	26.4	50.30	58.60
240	105.85	89.20	60.60	60.5	40.0	76.20	90.30
QM (%)	100.00	94.73	80.12	75.02	69.96	64.76	50.11
2,6- DTBP (%)	0.00	5.27	19.88	24.98	30.04	35.24	49.89

[0034] While we have shown and described herein certain embodiments of the invention, it is intended that these be covered as well as any change or modification therein which may be made without departing from the spirit and scope of the invention as defined in the appended claims.

[0035] What is claimed is:

CLAIMS

1. A method for inhibiting the polymerization of vinyl aromatic monomer comprising adding to said monomer an effective polymerization inhibiting amount of a compound comprising (A) a quinone methide derivative having the formula

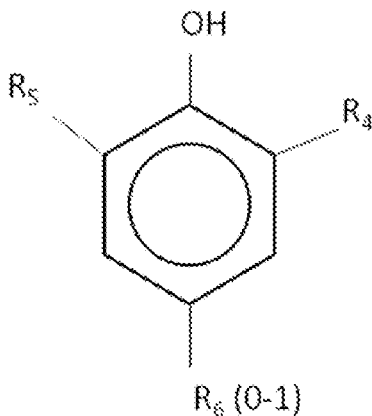


wherein:

R₁ and R₂ are independently H, C₄ to C₁₈alkyl; C₅ to C₁₂ cycloalkyl; or C₇ to C₁₅ phenylalkyl, and

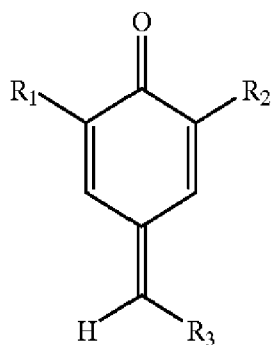
R₃ is aryl, or aryl substituted with C₁ to C₆ alkyl, alkoxy, hydroxy, nitro, amino, carboxy, or mixtures thereof; and

(B) a phenol compound having the formula



wherein R₄ and R₅ may be the same or different and are chosen from C₁-C₂₀ alkyl, C₁-C₃₀ alkaryl and substituted C₁-C₃₀ alkaryl; R₆, when present, is selected from C₁-C₂₀ alkyl, thiophenol, substituted thiophenol, C₁-C₄₀ alkanolic acid ester, C₁-C₃₀ alkaryl, substituted C₁-C₃₀ alkaryl, C₁-C₆ alkylamino, C₁-C₆ alkoxy, amine, polynuclear aryl and substituted polynuclear aryl.

2. The method as recited in claim 1 wherein the weight ratio of A to B is about 90:10 to about 10:90.
3. The method as recited in claim 2 wherein said quinone methide derivative A) is 2,6-di-tert-butyl-4-benzylidene-cyclohexa-2,5-dienone.
4. The method as recited in claim 3 wherein said phenol compound B) is 2,6-di-tert-butyl phenol.
5. The method as recited in claim 4 wherein from about 1,-10,000 ppm of A and B collectively is brought into contact with said vinyl aromatic monomer, based on 1 million parts of said vinyl aromatic monomer.
6. The method as recited in claim 5 wherein said vinyl aromatic monomer comprises styrene monomer.
7. The method as recited in claim 5 wherein the weight ratio of A:B is about 70:30.
8. The method as recited in claim 7 further comprising the step of heating said styrene monomer.
9. The method as recited in claim 7 further comprising the step of distilling said styrene monomer to remove impurities therefrom.
10. Vinyl aromatic monomer anti-polymerization composition comprising a liquid carrier and dissolved or dispersed therein A) a quinone methide derivative having the formula

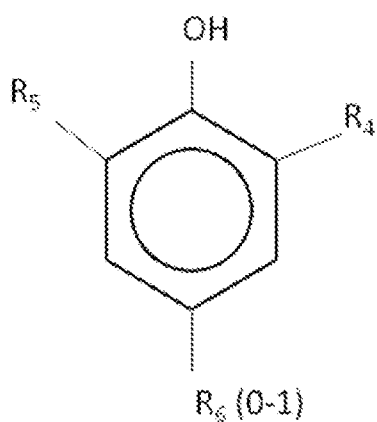


wherein:

R₁ and R₂ are independently H, C₄ to C₁₈ alkyl; C₅ to C₁₂ cycloalkyl; or C₇ to C₁₅ phenylalkyl, and

R₃ is aryl, or aryl substituted with C₁ to C₆ alkyl, alkoxy, hydroxy, nitro, amino, carboxy, or mixtures thereof; and

(B) a phenol compound having the formula



wherein R₄ and R₅ may be the same or different and are chosen from C₁-C₂₀ alkyl, C₁-C₃₀ alkaryl and substituted C₁-C₃₀ alkaryl; R₆, when present, is selected from C₁-C₂₀ alkyl, thiophenol, substituted thiophenol, C₁-C₄₀ alkanolic acid ester, C₁-C₃₀ alkaryl, substituted C₁-C₃₀ alkaryl, C₁-C₆ alkylamino, C₁-C₆ alkoxy, amine, polynuclear aryl and substituted polynuclear aryl.

11. Vinyl aromatic monomer anti-polymerization composition as recited in claim 10 wherein A) and B) are present in a weight ratio of about 90:10 to about 10:90.

12. Vinyl aromatic monomer anti-polymerization composition as recited in claim 11 wherein said quinone methide derivative A) is 2,6-di-tert-butyl-4-benzylidene-cyclohexa-2,5-dienone.

13. Vinyl aromatic monomer anti-polymerization composition as recited in claim 12 wherein said phenol compound B) is 2,6-di-tert-butyl phenol.

14. Vinyl aromatic monomer anti-polymerization composition as recited in claim 12 wherein said liquid carrier comprises a non-polar organic solvent and wherein A) and B) are both dissolved in said solvent.

15. Vinyl aromatic monomer anti-polymerization composition as recited in claim 14 wherein said non-polar organic solvent comprises heavy aromatic naphtha or xylene.

16. Vinyl aromatic monomer anti-polymerization composition as recited in claim 10 further comprising styrene monomer.