METHODS FOR INHIBITING THE POLYMERIZATION OF ETHYLENICALLY UNSATURATED MONOMERS

TECHNICAL FIELD

This invention relates to methods for inhibiting polymerization of ethylenically unsaturated monomers. The methods are particularly effective at inhibiting polymerization of these monomers during storage conditions in the presence of oxygen.

BACKGROUND ART

It is well known that ethylenically unsaturated monomers readily polymerize when heated and that the polymerization rate increases with increasing temperature. For this reason, the monomers are stabilized by the addition of substances which act as inhibitors or retarders of polymerization, or which block the initiation mechanism leading to the formation of radicals.

Certain ethylenically unsaturated (diolefin) monomers such as butadiene and isoprene polymerize when left in storage tanks and during transportation at temperatures as low as room temperature. This polymerization is initiated by reaction of the diolefin monomer with oxygen present in the monomer containing system. This reaction forms peroxides and free radical species which can further react with the diolefin monomer.

To prevent this polymerization from taking place, diolefin monomer manufacturers frequently add tert-butyl catechol (TBC) as a polymerization inhibitor. However, TBC is a toxic compound and can cause tissue damage when it contacts skin. These characteristics make it desirable to utilize an inhibitor compound that avoids these difficulties as well as being water and caustic extractable so that it could be easily removed from the finished product before use or additional processing.

The present inventor has discovered that dihydroxycinnamic acid and its derivatives effectively inhibit the polymerization of ethylenically unsaturated monomers during storage and transportation. These compounds prove particularly effective in the presence of oxygen and at temperatures up to 100°C.

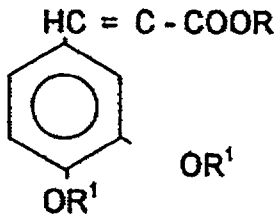
EP 89-402156 discloses a cosmetic preparation containing an antioxidant system based on a stabilized ascorbic acid ester. The antioxidant system also contains tocopherol or mixtures of tocopherol, caffeic acid or its derivatives, a complexing agent and a non-thiol polypeptide.

JP Kokai JP 59015477 teaches a food antioxidant composition effective for oils and fats which comprises 3,4-dihydroxycinnamic acid esters and one or more of ascorbic acid-stearic acid ester, citric acid, malic acid, and ascorbic acid.

DISCLOSURE OF INVENTION

The present invention relates to methods for inhibiting the polymerization of ethylenically unsaturated monomers comprising adding an effective inhibiting amount of a dihydroxycinnamic acid or derivative thereof.

The dihydroxycinnamic acid or derivatives thereof generally have the formula:



wherein R is H, CH_3 or C_2H_5; R^1 is H, CH_3 or C_2H_5 with the proviso that at least one of R^1 is H. The preferred compounds for use in the present invention are dihydroxycinnamic acid and dihydroxydihydrocinnamic acid.

The ethylenically unsaturated monomers are characterized as polymerizable ethylenically unsaturated hydrocarbons and include olephins such as alpha olephins containing 2 to 20 carbon atoms and preferably 2 to 8 carbon atoms, and conjugated di-olephins, preferably those containing 4 to 6 carbon atoms such as isoprene and butadiene.

For purposes of this invention, the term "effective amount" refers to the amount of dihydroxycinnamic acid or derivative thereof necessary to inhibit polymerization of ethylenically unsaturated monomers. This amount will vary according to the conditions under which the ethylenically unsaturated monomer is subjected during storage and/or handling thereof. At higher temperatures and higher monomer contamination, larger amounts of polymerization inhibiting compound are generally required.

Preferably the effective amount of dihydroxycinnamic acid or derivative added to the ethylenically unsaturated monomer ranges from about 1 part to about 1000 parts per million parts of monomer. More preferably, the amount of dihydroxycinnamic acid or derivative thereof added to the monomer ranges from about 10 parts to about 200 parts per million parts monomer.

The dihydroxycinnamic acid derivatives may be used in combination with the dihydroxycinnamic acid or as a mixture of the dihydroxycinnamic acid derivatives when utilized in the methods of the present invention.

The dihydroxycinnamic acid or derivative thereof may be added to the ethylenically unsaturated monomer as either a dispersion or as a solution using a suitable liquid carrier or solvent. Any solvent that is compatible with the dihydroxycinnamic acid or derivative thereof and the ethylenically unsaturated monomer may be employed.

MODES FOR CARRYING OUT THE INVENTION

The invention will now be described with reference to a number of specific examples which are to be regarded solely as illustrative, and not as restricting the scope of the invention.

EXAMPLES

Testing was performed to determine the effectiveness of the present invention at inhibiting the polymerization of ethylenically unsaturated monomers.

Tests were run in a stainless steel pressure vessel fitted with a glass sample container and cover, a stem, a pressure gauge with a continuous recorder, and the appropriate valves and fittings. A solution of 10 mL of isoprene in 40 mL of heptane and the designated treatment were placed in the glass sample container and inside the pressure vessel. The vessel was closed, filled with oxygen at 100 psig and heated in a water bath at 100°C. The pressure was recorded continuously until a break point in the pressure-time curve (i.e., steepest slope of the curve) was reached. The induction time was calculated as the time elapsed between the placing of the vessel in the bath and the breaking point. The results of this testing are reported in Table I.

TABLE I

Polymerization Inhibition Testing

Treatment	Dose (ppm)	Induction Time (min.)
Blank	——	25
TBC	10	40
BHT	10	31
	40	32
DHHCA	10	85
	25	144
Blank	——	21
TBC	40	90
DHHCA	40	110
DHCA	40	54
Blank	——	25
DHCA	50	102
	100	127

TBC is tert-butyl catechol

BHT is 2,6-di-t-butyl-4-methylphenol

DHCA is 3,5-dihydroxycinnamic acid

DHHCA is 3,4-dihydroxyhydrocinnamic acid

These results demonstrate that the compounds of the present invention are effective at inhibiting the polymerization of ethylenically unsaturated monomers under conditions approximating storage. The commercially available inhibitors, TBC and BHT proved less effective than the inventive compounds.

INDUSTRIAL APPLICABILITY

The dihydroxycinnamic acid or derivatives thereof are effective at inhibiting the polymerization of ethylenically unsaturated monomers during their storage or under transportation conditions. These conditions are typically found to have oxygen atmospheres present and monomer temperatures up to about 100°C. The present inventor anticipates that the methods of the present invention can inhibit the polymerization of ethylenically unsaturated monomers during the processing thereof. These processing conditions, such as purification and distillation processes, typically employ heat and will often cause fouling of the monomer.

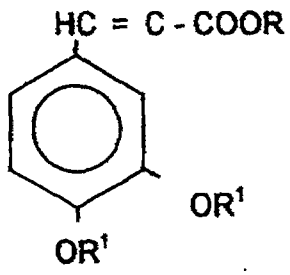
While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

THIS SHEET HAS BEEN REPLACED

Having thus described the invention, what I claim is:

1. A method for inhibiting the polymerization of ethylenically unsaturated monomers comprising adding to the monomers an effective polymerization inhibiting amount of a dihydroxycinnamic acid or derivative thereof.

2. The method as claimed in claim 1 wherein said dihydroxycinnamic acid or derivative thereof has the formula:



wherein R is H, CH_3 or C_2H_5; R^1 is H, CH_3 or C_2H_5 with the proviso that at least one of R^1 is H.

3. The method as claimed in claim 2 wherein said dihydroxycinnamic acid or derivative thereof is selected from the group consisting of dihydroxycinnamic acid and dihydroxydihydrocinnamic acid.

4. The method as claimed in claim 1 wherein said dihydroxycinnamic acid or derivative thereof is added to said monomers in an amount ranging from about 1 part to about 1000 parts per million parts of monomer.

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

* C L M S *

5. The method as claimed in claim 1 wherein said ethylenically unsaturated monomer is selected from the group consisting of isoprene and butadiene.

6. The method as claimed in claim 1 wherein said monomer is exposed to oxygen atmospheres.

7. The method as claimed in claim 1 wherein said monomer has a temperature ranging from ambient to about 100°C.

8. A composition comprising an ethylenically unsaturated monomer and a dihydroxycinnamic acid or derivative thereof.

9. The composition as claimed in claim 8 wherein said ethylenically unsaturated monomer is selected from the group consisting of isoprene and butadiene.

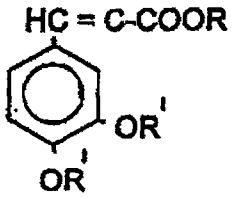
10. The composition as claimed in claim 8 wherein said dihydroxycinnamic acid or derivative thereof is selected from the group consisting of dihydroxycinnamic acid and dihydroxydihydrocinnamic acid.

This Sheet Has Been Replaced

PCT/US 97/06099
IPEA/US 02 JAN 1998

* C L M S *

1. A method for inhibiting the polymerization of isoprene comprising adding to the isoprene an effective polymerization inhibiting amount of a dihydroxycinnamic acid or derivative thereof having the formula



wherein R is H, CH_3 or C_2H_5; R' is H, CH_3 or C_2H_5 with the proviso that at least one of R' is H.

2. The method as claimed in claim 2 wherein said dihydroxycinnamic acid or derivative thereof is selected from the group consisting of dihydroxycinnamic acid and dihydroxydihydrocinnamic acid.

3. The method as claimed in claim 1 wherein said dihydroxycinnamic acid or derivative thereof is added to said isoprene in an amount ranging from about 1 part to about 1000 parts per million parts of isoprene.

4. The method as claimed in claim 1 where said isoprene is exposed to oxygen atmospheres.

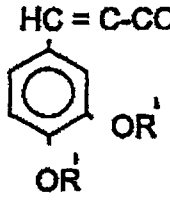
5. The method as claimed in claim 1 wherein said isoprene has a temperature ranging from ambient to about 100°C.

AMENDED SHEET

~~SUBSTITUTE SHEET~~

PCT/US 97/06099
IPEA/US 02 JAN 1998

6. A composition comprising isoprene and a dihydroxycinnamic acid or derivative thereof having the formula



wherein R is H, CH_3 or C_2H_5; R' is H, CH_3 or C_2H_5 with the proviso that at least one of R' is H.

7. The composition as claimed in claim 6 wherein said dihydroxycinnamic acid or derivative thereof is selected from the group consisting of dihydroxycinnamic acid and dihydroxydihydrocinnamic acid.

AMENDED SHEET

~~SUBSTITUTE SHEET~~

9802686-7
IBM COPY

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07C 7/20 — A1

(11) International Publication Number: WO 97/42146

(43) International Publication Date: 13 November 1997 (13.11.97)

(21) International Application Number: PCT/US97/06099

(22) International Filing Date: 4 April 1997 (04.04.97)

(30) Priority Data:
08/642,836 3 May 1996 (03.05.96) US

(71) Applicant: BETZDEARBORN INC. [US/US]; 4636 Somerton Road, Trevose, PA 19053-6783 (US).

(72) Inventor: ARHANCET, Graciela, B.; 20607 Castle Bend Drive, Katy, TX 77459 (US).

(74) Agents: VON NEIDA, Philip, H. et al.; BetzDearborn Inc., 4636 Somerton Road, Trevose, PA 19053-6783 (US).

(81) Designated States: BR, CA, CN, SG, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.

(54) Title: METHODS FOR INHIBITING THE POLYMERIZATION OF ETHYLENICALLY UNSATURATED MONOMERS

(57) Abstract

The polymerization of an ethylenically unsaturated monomer such as isoprene and butadiene is inhibited during storage or handling thereof by the addition of a dihydroxycinnamic acid or derivative thereof.