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Gel prevention in polymers.

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US-A- 3 984 372
US-A- 4 707 300

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Description

This invention relates to discovery that the combination of a polyhydroxyacrylate or polyhydroxy- methacrylate, such as 2-(2-hydroxy-3-tert.butyl-5-methylbenzene)-4-methyl-6-tert.butyl phenyl methacrylate, and the reaction product derived from the acid catalyzed reaction of an alkylated phenol, formaldehyde and a mercaptan, will provide elastomers with enhanced protection from the formation of hard gel, soft gel and micro-gel during the processing and storage of said elastomers.

Background Art

Gel formation in polymers can be caused during the isolation and drying of the polymers from either an aqueous system or a solvent or cement system wherein localized polymer hot-spots can result in the undesirable gelling or cross-linking phenomenon. Care must be taken to assure that during the processing of elastomers that the polymer's structure is not altered which will result in degradation of the polymer's physical properties.

The process for solution polymerization of synthetic elastomers such as polybutadiene is well known in the art. Monomer and solvent are purified and dried. The catalyst is prepared separately and then added to the reaction vessel containing the monomer or monomers, for example, butadiene and styrene. When the desired degree of polymerization has been achieved, the catalyst is deactivated, the unreacted monomer or monomers and solvent are removed, and the polymer is recovered, washed, dried and baled. It is usually during the recovery process, where the elastomer is dewatered and dried that the formation of gel occurs.

Japanese Patent No. 49,066,725 discloses gelation inhibitors that are obtained by mixing solid phenylenediamine derivatives with liquid reaction products derived from aromatic amines and acetone. This patent discloses a stable suspension consisting of 100 parts of a 1:3 mixture of 4-(isopropyl-aminomethyl) diphenylamine and a toluene-acetone condensate, 293 parts water, 2.5 parts of a 50% aqueous solution of KOH, and 4.5 parts of oleic acid. This suspension was then combined with an SBR latex at ratios of the suspension to the SBR of about 0.6:100. The rubber mixture was then flocculated to give rubber with 20% gel after 130 hours at 120 °C compared to 80% gel for rubber containing dodecylphenylamine in place of the subject suspension.

US-A-3,984,372 and 4,168,387 disclose esters of polyphenolics as polymerizable or built-in antioxidants. These patents disclose the use of compounds such as 2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6- tert.butyl phenyl methacrylate as polymerizable antioxidants for polymeric compositions. More specifically, the compounds of these two U.S. Patents are reaction products of a polyphenolic compound such as 2,6-bis-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methylphenol; and 2,2'-methylene-bis-(4-methyl-6- tert.butylphenol) with an ester forming compound of the general formula:

\[
\begin{align*}
O & \quad R^3 \quad H \\
A - C - C - & \quad CR^4 \\
0 & \quad 1 & \quad 2 & \quad 3 & \quad 4
\end{align*}
\]

wherein \(R^3\) is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms, \(R^4\) is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms, and wherein \(A\) is selected from the group consisting of chlorine, iodine and bromine.

US-A-4,707,300, relates to the reaction products of an acid catalyzed simultaneous reaction between a phenol, formaldehyde and a mercaptan in specific molar ratios under specific reaction conditions. The reaction product is normally a liquid at room temperature and exhibits excellent antidegradative properties in oxidizable materials. Further, this U.S. patent is concerned with the autosynergistic phenolic reaction product itself and its incorporation into oxidizable organic materials.

The invention of this disclosure is directed to the discovery that the combination of materials disclosed in US-A-3,984,372 and 4,168,387 with those of US-A-4,707,300 lessen or prevents the formation of gel in elastomers.

There is a need in the rubber industry for a process or system which will prevent or greatly lessen the formation of gel during the isolation and processing of natural or synthetic elastomers.
Disclosure of the Invention

As used herein the term esters of polyphenolics means the esters disclosed in US-A-3,984,372 and 4,168,387. The esters of polyphenolics are prepared by reacting a polyphenolic compound of the structural formula:

\[
\text{(I)}
\]

wherein \(R^1\) and \(R^2\) are the same or different radicals selected from the group consisting of hydrogen, alkyl radicals of 1 to 16 carbon atoms, cycloalkyl radicals of from 5 to 9 carbon atoms, aralkyl radicals of 7 to 12 carbon atoms, and substituted and unsubstituted aryl radicals of 6 to 12 carbon atoms and \(R^1\) preferably contains from 1 to 2 carbon atoms when para to the hydroxyl group;

\(X\) is the same or different radical selected from the group consisting of (1) cyclic dienes with non-adjacent carbon to carbon double bonds within the ring structure containing from 5 to 20 carbon atoms from which the divergent radicals are prepared and (2) a bivalent radical selected from the group consisting of \(-S-\), \(-O-\), \(-\text{CH}_2-\) and \(-S-S-\);

and wherein the \(n\) is selected from the group consisting of 0 and real numbers from 1 to 5;

with a compound having the general formula:

\[
\text{(II)}
\]

wherein \(R^3\) is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms, \(R^4\) is selected from the group consisting of hydrogen, alkyl radicals having from 1 to 4 carbon atoms, aralkyl radicals having from 7 to 12 carbon atoms, cycloalkyl radicals having from 5 to 8 carbon atoms and substituted or unsubstituted aryl radicals having from 6 to 12 carbon atoms, and wherein \(A\) is selected from the group consisting of chlorine, bromine and iodine.

The amount of esterification of course depends on the molar ratios and steric hindrance of the materials used. Preferably, the polyphenolic material is treated with from 0.1 mole to 1.0 mole of ester forming compound for each functional hydroxyl group. More preferably, at least one functional hydroxyl group per polyphenolic molecule is esterified.

When the polyphenolics and ester forming compounds described herein are reacted in a 1:1 molar ratio, a near theoretical reaction takes place. Compounds having the formula (I) wherein \(n\) is 0 and \(X\) is a divalent radical selected from \(-S-\) and \(-\text{CH}_2-\), and wherein \(R^2\) is a hydrocarbon radical of at least 4 carbon atoms (preferably tertiary) and ortho to the hydroxyl group; have only one readily reactive hydroxyl group. Upon esterification of one hydroxyl group, steric hindrance operates to decrease the reaction at the second hydroxyl site. For example, if one mole of methacryloyl chloride is reacted with one mole of 2,2-methylenebis-(4-methyl-6-tert.butylyphenol), a near theoretical amount of 2-(2-hydroxy-3-tert.butyly-5-methylbenzyl)-4-methylphenyl methacrylate is obtained.

When an polyphenolic according to structure (I) wherein \(R^2\) (preferably tertiary) is ortho to the hydroxyl group and is reacted with \(n + 2\) moles of an ester forming compound having structure (II), less than \(n + 2\) moles of compound (II) will react. Normally the number of ester groups reacting with the polyphenolic
reactant is not more than n plus 1.5 or less than n minus 0.75. When n is 0 the number of ester groups reacting with the polyphenolic is usually not more than 1.5 or less than 0.25.

The esterification reaction may easily take place at elevated pressure and temperatures or from 0 °C to the boiling point of the reactants. Preferably temperatures from 0 °C to 60 °C are preferred.

Representative of the esters of polyphenolics that are useful in this invention are listed below:

2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert.butylphenyl acrylate
2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert.butyl phenylmethacrylate
2-(3,5-ditert.butyl-4-hydroxybenzyl)-4-methyl-phenyl methacrylate
2-(3,5-ditert.butyl-4-hydroxybenzyl)-4-methyl-phenyl acrylate
4-(3,5-ditert.butyl-4-hydroxybenzyl) phenyl acrylate
2-(2-hydroxy-3-tert.butyl-5-methylphenylthio)-4-methyl-6-tert.butyl phenyl methacrylate
2-(3,5-ditert.butyl-4-hydroxybenzyl) phenyl methacrylate
2,6-bis(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methylphenyl methacrylate

As used herein the term auto-synergistic phenolic reaction product means the reaction mixture disclosed in U.S. Patent 4,707,300. The auto-synergistic phenolic reaction product is derived from the process comprising:

(1) admixing one mole of a mono-alkylated phenol or a 2,4-dialkylated phenol or a mixture thereof, wherein the alkyl radical may be straight or branched and may contain from 1 to 20 carbon atoms; with
20 (a) from 0.5 to 1.5 moles of a primary mercaptan of 3 to 20 carbon atoms; and
(b) from 0 to 50% molar excess of aqueous formaldehyde based on moles of primary mercaptan
when the molar ratio of mercaptan to phenol is 1.0 or greater or 0 to 100% excess of aqueous formaldehyde when the ratio of mercaptan to phenol is less than 1.0; and
(c) from 0.04 to 20 percent by weight based on the weight of alkylated phenol of an acid catalyst; and
25 (d) an adequate amount of an azeotropic solvent;
(2) heating the admixture from ambient up to 180 °C, while azeotropically removing water until the production of the waters of reaction ceases; and
(3) neutralize the catalyst and isolate the products.

More specifically, the auto-synergistic phenolic reaction product can be derived from the process comprising:

(1) admixing one mole of an alkylated phenol selected from the group consisting of p-cresol, m-cresol, o-cresol, 2,4-dimethylphenol, 2-tert.butyl-p-cresol, p-ethylphenol, 3-ethylphenol, p-monomonylophenol, p-isopropylphenol, p-sec-butylphenol, o-sec-butylphenol, p-tert.butylphenol, 3-tert.butylphenol, p-tert.octylphenol, 2,4-dinonylphenol, and dodecylphenol; with
25 (a) from 0.5 to 1.5 moles of a mercaptan of 6 to 14 carbon atoms; and
(b) from 0.5 to 2.25 moles of aqueous formaldehyde; and
(c) from 0.1 to 10 percent by weight based on the weight of the alkylated phenol of an acid selected from the group consisting of toluene sulfonic acid, methanesulfonic acid, xylenesulfonic acid, sulfuric acid, glacial acetic acid, boron trifluoride, and Amberlyst 15; and
(d) an adequate amount of a solvent that will azeotrope with water;
(2) heating the admixture from ambient to 150 °C while azeotropically removing water until the production of the water of reaction ceases;
(3) neutralization of the acid and isolation of the reaction product mixture.

Thus, there is disclosed a process for the prevention or reduction of gel formation in elastomers as defined in the appended claims.

Elastomers to be used in the instant invention are: natural rubber, and synthetic polymers containing carbon to carbon double bonds such as rubbery diene polymers both conjugated and non-conjugated. Representative examples of the synthetic polymers that will benefit through the use of this invention are polychloroprene and homopolymers of conjugated 1,3-dienes such as isoprene and butadiene. Copolymers of conjugated 1,3-dienes such as isoprene and butadiene with up to 50 percent by weight of at least one copolymerizable monomer including ethylenically unsaturated monomers such as styrene and acrylonitrile are included. Butyl rubbers and polyurethanes which contain carbon to carbon double bonds can also benefit from the instant invention. In general, any organic material that is subject to gel formation or undesired crosslinking during preparation and/or processing will benefit from this invention.

The gel inhibiting mixture of this invention may be used with or without antioxidants, antiozonants, vulcanizing agents, synergists, accelerators or other compounding ingredients known in the art. The amount of the gel inhibiting mixture may vary somewhat depending on the type and requirement of the elastomer to be protected.
The method of addition of the gel inhibiting composition to the material to be protected is not critical. It may be added by any of the conventional means such as by adding to a polymer latex, milling on an open mill or by internal mixing. When the composition of this invention is used to protect rubbers such as styrene/butadiene rubber or polybutadiene, a convenient method of incorporation consists of adding the stabilizer to the polymer while it is in latex or cement forms. This is preferably done after the polymerization of the monomers is essentially complete.

Normally from about 0.01 part to about 5.0 parts of the gel inhibiting composition by weight based on the weight of the polymer can be used; however, the precise amount to be employed will depend on the nature of the polymer and the processing conditions to which the elastomer will be exposed. It has been found that an effective amount of the composition will generally range from about 0.01 to about 3.0 parts by weight although it is commonly preferred to use from about 0.25 to about 2.0 parts by weight based on 100 parts by weight of the elastomer. The above limits are merely guidelines and those skilled in this art will readily appreciate the proper amount of the composition that will be required to lessen or eliminate the formation of gel.

Example 1

Preparation of Methacrylate

One hundred grams of 2,2-methylene-bis-4-methyl-6-tert.butylphenol) and 50 grams of triethylamine were dissolved in 150 milliliters of tetrahydrofuran. Thirty-one grams of methacryloyl chloride were added over a 10 minute period. The reaction product was stirred at 65 °C to 75 °C for 1 hour and then filtered. The volatiles were removed under a vacuum. The product was recrystallized from petroleum ether yielding nearly pure 2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert.butyl phenylmethacrylate having a melting point between 141 °C and 142 °C.

Example 2

Preparation of Acrylate

This example was carried out in the same manner as Example 1 except that equal molar amounts of acryloyl chloride was used in place of methacryloyl chloride.

Example 3

Preparation of Autosynergistic Reaction Product

The autosynergistic phenolic antioxidant reaction product used herein was prepared in a production scale reaction vessel equipped with the appropriate controls.

To the empty reactor was rapidly charged 121 kgs of p-nonyl phenol, 111 kgs of dodecylmercaptan, 6.4 kgs of aqueous toluene sulfonic acid (a 70% TSA/30% water by weight solution) and 53.5 kgs of toluene. 56 kgs of formalin (a 37% formaldehyde, 15% methanol, 48% water by weight solution) was then added to the reactor as fast as possible with cooling to limit the temperature rise since the addition of the formaldehyde initiates an exothermic reaction. The addition of the formalin took about 35 minutes while the temperature of the reaction rose from ambient to about 45 °C. The mixture was then reacted for about 1 hour at 60 °C.

The water of solution and production and the toluene were then distilled off at a final pot temperature of 140 °C. The mixture was then cooled to less than 98 °C and the toluene sulfonic acid was then neutralized with an appropriate amount of sodium carbonate. The water layer was removed and the product was again washed with water. The mixture was then vacuum distilled to remove the remaining toluene at 160 °C and 25 mm of Hg. The product was filtered to remove traces of residual salts.

The antigelling composition of this invention which consists of the ester of a polyphenolic and the autosynergistic phenolic reaction product can easily be added to the polymer in the form of a solution. Useful solvents for the antigelling composition include hexane and the like. Usually the solution of the antigelling agents is added to the polymeric cement or latex prior to the quenching system which utilizes the addition of water to form a crumb. The crumb is then dewatered and dried through mechanical means such as screws.

In the evaluations, 10 grams of the selected material (controls) or combination of materials (ester plus reaction product at different ratios) were dissolved in 90 grams of an appropriate solvent such as hexane.
These solutions were then added to the rubber cements at the indicated levels. During the isolation and storage of the elastomers, soft gel or microgel forms within the polymer which results in an undesirable product that is difficult to process. In order to simulate the formation of gel during the processing, a test was developed to evaluate the formation of gel in the polymer during the extrusion drying step. The following examples and discussion will be based upon the use of polybutadiene; however, it must be understood that other elastomers, subject to gel formation, will benefit from the invention described herein.

The mastication test has been found to correlate well with the gel formation experienced in the commercial processing of polybutadiene. The lab test used to evaluate the instant invention uses a Haake mastication apparatus at temperatures and times near the commercially encountered conditions of 100-250 °C and a few seconds of residence time to about 15 minutes. It was determined through experimentation that the developed test correlates far better than a 70 °C oven agings with the conditions encountered in the commercial production of polybutadiene.

The mastication test uses a Haake Brabender with a #750 mixing head and banbury rotors. A computer is used to control temperature, rotor speed and run times. The mixing head temperature was 200 °C and the banbury rotor speed was 70 rpm. The test times were varied from 4 to 20 minutes.

The test samples were prepared by adding the appropriate amount of the antigel solution to a sufficient amount of polymer cement containing 100 grams of dry rubber. The stabilized polymer is then placed in a laboratory hood and dried for about 24 hours. After drying the stabilized polymer is ready for testing.

The mastication test device after reaching temperature equilibrium was started and 50 grams of stabilized polymer was loaded into the mixing chamber and the ram with 5 kgs of weight was lowered into position. After the specified time, the ram was raised and a 2-4 gram sample was removed from the mixing chamber. The ram was then again lowered into position and the test continued. In similar fashion, a number of samples are removed from the device at specified intervals of time.

The samples removed for gel testing were allowed to cool to room temperature and then placed in plastic bags to prevent contamination awaiting analysis for percent gel.

In general the gel test consists of treating the sample with a solvent such as MEK or toluene. The amount of gel is determined from the weight of the polymer not dissolved in the solvent as a percentage of the total polymer weight. Percent gel values are related to the amount of crosslinking present in a polymer.

Specifically the percent is determined by weighing out approximately 0.2 grams of the sample (cut into small pieces) to the nearest 0.0001 grams into a sealable bottle. It is very important that all measurements be made at constant temperature. Thus, the solvent and samples should be at a constant temperature before gel measurement is initiated.

One hundred ml of the solvent is then added to the bottle containing the polymer sample. The bottle is then sealed and placed on a wrist shaker for 16 hours followed by centrifugation at 2000-2500 rpm for at least one hour or until turbidity is no longer observable. The bottle is removed from the centrifuge and a 20 ml aliquot from the upper half of the solution is transferred to a clean tared aluminum pan.

Approximately 35-40 ml of the remaining solution is poured into a pressure filtration apparatus containing a membrane filter compatible with the solvent. The solution is pressure filtered using pressurized nitrogen into a clean and dry bottle. Filtration should be stopped as soon as the filtration rate cannot be maintained. The total volume filtered should be recorded. One aliquot (2-20 ml) of the filtered solution is transferred to a clean tared aluminum pan, covered and placed in a cool vented place for evaporation of the solvent. After all the solvent was evaporated the pans are placed in an oven at about 70 °C until a constant weight is realized. Using the weight of the initial sample W1, the weight of the dried residues from the unfiltered-W2 and the filtered W-3 solutions and the aliquot size of the filtered solution used divided into 100-Y; the percent normal macrogel, %GN, microgel %GM and total gel %GT is calculated using the following expressions:

\[
%GN = \frac{W_1 - (W_2 \times 5) \times 100}{W_1}
\]

\[
%GT = \frac{W_1 - (W_3 \times Y) \times 100}{W_1}
\]
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Antioxidant System</th>
<th>4 min.</th>
<th>6 min.</th>
<th>8 min.</th>
<th>10 min.</th>
<th>20 min.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.75 phr butylated hydroxytoluene (Control)</td>
<td>5.2</td>
<td>13.7</td>
<td>26.9</td>
<td>32.3</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.5 phr A0451/0.25 phr butylated hydroxytoluene (Control)</td>
<td>0.6</td>
<td>7.0</td>
<td>28.4</td>
<td>26.1</td>
<td>46.0</td>
</tr>
<tr>
<td>3</td>
<td>0.5 phr A0451 (Control)</td>
<td>1.8</td>
<td>7.0</td>
<td>15.4</td>
<td>24.7</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>0.5 phr A0451/0.25 phr butylated hydroxytoluene/0.25 phr product of Ex. 2 (Control)</td>
<td>2.1</td>
<td>4.3</td>
<td>7.4</td>
<td>21.3</td>
<td>31.2</td>
</tr>
<tr>
<td>5</td>
<td>0.5 phr product from Ex. 3</td>
<td>5.8</td>
<td>20.4</td>
<td>29.0</td>
<td>33.8</td>
<td>47.2</td>
</tr>
<tr>
<td>6</td>
<td>0.75 phr product from Ex. 3</td>
<td>-</td>
<td>3.0</td>
<td>19.7</td>
<td>24.1</td>
<td>-</td>
</tr>
<tr>
<td>7</td>
<td>0.5 phr product from Ex. 3/0.25 phr product of Ex. 2</td>
<td>3.1</td>
<td>7.1</td>
<td>18.6</td>
<td>21.3</td>
<td>36.3</td>
</tr>
<tr>
<td>8</td>
<td>0.75 phr product from Ex. 3/0.2 phr of product from Ex. 2</td>
<td>-</td>
<td>3.0</td>
<td>7.4</td>
<td>7.2</td>
<td>-</td>
</tr>
<tr>
<td>9</td>
<td>1.0 phr product from Ex. 3/0.2 phr of product from Ex. 2</td>
<td>-</td>
<td>1.3</td>
<td>4.5</td>
<td>13.3</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>0.88 phr product from Ex. 3/0.08 phr of product from Ex. 2</td>
<td>-</td>
<td>-</td>
<td>12.3</td>
<td>23.6</td>
<td>-</td>
</tr>
<tr>
<td>11</td>
<td>0.88 phr product from Ex. 3/0.08 phr of product from Ex. 1</td>
<td>-</td>
<td>-</td>
<td>14.1</td>
<td>23.2</td>
<td>-</td>
</tr>
</tbody>
</table>

- = no sample taken

* A0451 is a reaction product of one mole of hydroquinone with at least two moles of an alpha-olefin containing at least 12 carbon atoms. See U.S. Patent No. 3,772,393.

Different gel prevention systems were evaluated in the mastication test and samples were taken at various times and analyzed for gel content. The results are listed in Table 1.
From the information contained in Table I, it is quite evident that the phenolic reaction product when used alone (Sample No. 5) did not prevent gel formation as well as the commercially accepted butylated hydroxytoluene/alkylated hydroquinone system (Sample No. 2). However, combinations of the ester of a polyphenolic and the phenolic reaction product slowed gel formation longer than any other system tested. One unexpected result of the instant invention is evidenced in samples 8 and 9 which contained the ester of a polyphenolic in combination with the phenolic reaction product demonstrated gel levels below 20% after 10 minutes of mastication.

Example 4

Varying Levels

A designed experiment was conducted to determine the optimum levels of the phenolic reaction product and the ester of a polyphenolic. The levels of antigelling composition were varied from 0.05 to 0.20 phr of the ester and from 0.2 to 1.0 phr of the phenolic reaction product. The gel results at 8 minutes mastication for the designed experiment are shown in Table II together with controls.
TABLE II

Various Levels of Components
Z Levels of Gel after 8 Minutes on Haake Test

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>phr of R.P. from Ex. 3</th>
<th>phr of Ester from Ex. 2</th>
<th>phr of A0451</th>
<th>Z Total Gel</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 Control</td>
<td>-</td>
<td>0.05</td>
<td>0.6</td>
<td>28.8</td>
</tr>
<tr>
<td>13 Control</td>
<td>-</td>
<td>0.075</td>
<td>0.3</td>
<td>43.7</td>
</tr>
<tr>
<td>14 Control</td>
<td>-</td>
<td>0.125</td>
<td>0.2</td>
<td>53.6</td>
</tr>
<tr>
<td>15 Control</td>
<td>-</td>
<td>0.125</td>
<td>0.6</td>
<td>31.7</td>
</tr>
<tr>
<td>16 Control</td>
<td>-</td>
<td>0.125</td>
<td>1.0</td>
<td>6.7</td>
</tr>
<tr>
<td>17 Control</td>
<td>-</td>
<td>0.175</td>
<td>0.3</td>
<td>42.4</td>
</tr>
<tr>
<td>18 Control</td>
<td>-</td>
<td>0.175</td>
<td>0.9</td>
<td>21.4</td>
</tr>
<tr>
<td>19 Control</td>
<td>-</td>
<td>0.075</td>
<td>0.9</td>
<td>22.2</td>
</tr>
<tr>
<td>20 Control</td>
<td>0.5</td>
<td>0.0</td>
<td>-</td>
<td>29.0</td>
</tr>
<tr>
<td>21 Control</td>
<td>0.75</td>
<td>0.0</td>
<td>-</td>
<td>19.7</td>
</tr>
<tr>
<td>22</td>
<td>1.0</td>
<td>0.0</td>
<td>-</td>
<td>23.8</td>
</tr>
<tr>
<td>23</td>
<td>0.6</td>
<td>0.05</td>
<td>-</td>
<td>20.3</td>
</tr>
<tr>
<td>24</td>
<td>0.3</td>
<td>0.08</td>
<td>-</td>
<td>28.3</td>
</tr>
<tr>
<td>25</td>
<td>0.88</td>
<td>0.08</td>
<td>-</td>
<td>5.4</td>
</tr>
<tr>
<td>26</td>
<td>0.75</td>
<td>0.1</td>
<td>-</td>
<td>12.4</td>
</tr>
<tr>
<td>27</td>
<td>1.0</td>
<td>0.1</td>
<td>-</td>
<td>9.4</td>
</tr>
<tr>
<td>28</td>
<td>0.2</td>
<td>0.125</td>
<td>-</td>
<td>39.1</td>
</tr>
<tr>
<td>29</td>
<td>0.6</td>
<td>0.125</td>
<td>-</td>
<td>25.2</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>0.125</td>
<td>-</td>
<td>5.9</td>
</tr>
<tr>
<td>31</td>
<td>0.3</td>
<td>0.175</td>
<td>-</td>
<td>25.2</td>
</tr>
<tr>
<td>32</td>
<td>0.88</td>
<td>0.175</td>
<td>-</td>
<td>4.9</td>
</tr>
<tr>
<td>33</td>
<td>0.6</td>
<td>0.2</td>
<td>-</td>
<td>16.5</td>
</tr>
<tr>
<td>34</td>
<td>0.75</td>
<td>0.2</td>
<td>-</td>
<td>7.4</td>
</tr>
<tr>
<td>35</td>
<td>1.0</td>
<td>0.2</td>
<td>-</td>
<td>4.5</td>
</tr>
</tbody>
</table>
phenolic reaction product did not affect the cure rate or scorch adversely when compared with the system conventionally used in the art. An aging study was conducted and it was determined that the compounds age in a manner similar to compounds containing conventional antigelling compositions.

Example 5

The ester of a polyphenolic [also known as 2,2'-methylenebis(6-t- butyl-p-phenyl) methacrylate] prepared in Example 1 was evaluated with the autosynergistic phenolic reaction product from Example 3. Samples with various levels of the ester and the reaction product were analyzed for percent gel after 6, 8, and 10 minutes on the Haake tester at 200 °C. Table III sets forth the data.
<table>
<thead>
<tr>
<th>Components</th>
<th>Control</th>
<th>36 (Control)</th>
<th>37</th>
<th>38</th>
<th>39</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Budene</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>R.P. of Ex. 3</td>
<td>1.0</td>
<td>1.5</td>
<td>0.7</td>
<td>0.6</td>
<td>0.5</td>
<td>0.4</td>
</tr>
<tr>
<td>Product of Ex. 1</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
<td>0.4</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Product of Ex. 2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

% GEL

<table>
<thead>
<tr>
<th></th>
<th>Control</th>
<th>36 (Control)</th>
<th>37</th>
<th>38</th>
<th>39</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 min. at 200°C</td>
<td>21.9</td>
<td>21.9</td>
<td>13.5</td>
<td>7.3</td>
<td>18.5</td>
<td>8.5</td>
</tr>
<tr>
<td>8 min. at 200°C</td>
<td>31.3</td>
<td>33.2</td>
<td>24.8</td>
<td>17.4</td>
<td>24.2</td>
<td>19.4</td>
</tr>
<tr>
<td>10 min. at 200°C</td>
<td>42.2</td>
<td>34.7</td>
<td>29.5</td>
<td>24.7</td>
<td>30.5</td>
<td>29.2</td>
</tr>
</tbody>
</table>
TABLE III (Cont.)

<table>
<thead>
<tr>
<th>Components</th>
<th>R. P. of Ex. 3</th>
<th>Product of Ex. 1</th>
<th>Product of Ex. 2</th>
<th>6 min. at 200°C</th>
<th>8 min. at 200°C</th>
<th>10 min. at 200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>41</td>
<td>1.2</td>
<td>0.3</td>
<td>1.7</td>
<td>55.0</td>
<td>16.2</td>
<td>22.9</td>
</tr>
<tr>
<td>42(s-c)</td>
<td>100.0</td>
<td>0.25</td>
<td>0.50</td>
<td>1.0</td>
<td>36.2</td>
<td>36.4</td>
</tr>
<tr>
<td>43(s-c)</td>
<td>100.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>44(s-c)</td>
<td>100.0</td>
<td></td>
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</tr>
<tr>
<td>45(s-c)</td>
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<td></td>
</tr>
<tr>
<td>46(s-c)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>47(Cont. C)</td>
<td>100.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Industrial Applicability

The results from the tests conducted herein amply demonstrate that the combination of a ester of a polyphenolic with the autosynergistic phenolic reaction product is very useful in the prevention of gel
formation in synthetic elastomers. The instant invention provides a system that is low in cost, easy to manufacture without attendant pollution problems and provides unexpectedly superior antigelling protection. The antigelling composition of this invention will have utility in the industry since it alleviates problems that have heretofore been tolerated in the manufacture and storage of elastomers.

While certain representative embodiments and details have been shown for the purpose of illustrating the invention, it will be apparent to those skilled in the art that various changes and modifications may be made therein without departing from the scope of the invention.

**Claims**

1. A process for the prevention or reduction of gel formation in elastomers, said process characterized by adding to an elastomer in solid, latex or solution form from 0.01 to 5.0 parts per hundred by weight of solid elastomer of a gel inhibiting composition wherein said elastomer is selected from the group consisting of natural rubber and synthetic polymers containing carbon to carbon double bonds, said gel inhibiting composition comprising a 1:15 to 15:1 mixture by weight of (A) an ester of a polyphenolic compound obtainable by reacting a polyphenolic compound of the structural formula:

   \[
   \begin{align*}
   &\text{R}^1 \quad \text{OH} \\
   &\text{R}^2 \\
   &\text{X} \\
   &\text{OH} \\
   &\text{R}^1 \\
   &\text{R}^2
   \end{align*}
   \]

   wherein \( \text{R}^1 \) and \( \text{R}^2 \) are the same or different radicals selected from the group consisting of hydrogen, alkyl radicals of 1 to 16 carbon atoms, cycloalkyl radicals of from 5 to 9 carbon atoms, aralkyl radicals of 7 to 12 carbon atoms, and substituted and unsubstituted aryl radicals of 6 to 12 carbon atoms; \( \text{X} \) is the same or different radical selected from the group consisting of (1) cyclic dienes with non-adjacent carbon to carbon double bonds within the ring structure containing from 5 to 20 carbon atoms from which the divalent radicals are prepared and (2) a bivalent radical selected from the group consisting of: \(-\text{S}-, -\text{O}-,\)

   \[
   \text{-CH}_2- \quad \text{and} \quad -\text{S-S-}; \text{and wherein the } n \text{ is selected from the group consisting of 0 and real numbers from 1 to 5; with a compound having the general formula:}
   \]

   \[
   \begin{align*}
   &\text{O} \\
   &\text{H} \\
   &\text{-C-} \\
   &\text{A-C-} \\
   &\text{R}^3 \\
   &\text{H} \\
   &\text{A-C-C-C-R}^4
   \end{align*}
   \]

   wherein \( \text{R}^3 \) is selected from the group consisting of hydrogen and alkyl radicals having from 1 to 4 carbon atoms, \( \text{R}^4 \) is selected from the group consisting of hydrogen, alkyl radicals having from 1 to 4 carbon atoms, aralkyl radicals having from 7 to 12 carbon atoms, cycloalkyl radicals having from 5 to 8 carbon atoms and substituted or unsubstituted aryl radicals having from 6 to 12 carbon atoms, and wherein \( \text{A} \) is selected from the group consisting of chlorine, bromine and iodine; and (B) an autosynergistic phenolic reaction product, said autosynergistic phenolic antioxidant reaction product being obtainable by a process comprising:
(1) admixing one mole of a mono-alkylated phenol or a 2,4-dialkylated phenol or a mixture thereof, wherein the alkyl radical may be straight or branched and may contain from 1 to 20 carbon atoms; with

(a) from 0.5 to 1.5 moles of a primary mercaptan of 3 to 20 carbon atoms; and
(b) from 0 to 50% molar excess of aqueous formaldehyde based on moles of primary mercaptan when the molar ratio of mercaptan to phenol is 1.0 or greater or 0 to 100% excess of aqueous formaldehyde when the ratio of mercaptan to phenol is less than 1.0; and
(c) from 0.04 to 20 percent by weight based on the weight of alkylated phenol of an acid catalyst; and
(d) an adequate amount of an azeotroping solvent;
(2) heating the admixture from ambient up to 180 °C, while azeotropically removing water until the production of the waters of reaction ceases; and
(3) neutralizing the catalyst and isolating the products.

2. The process according to claim 1 characterized in that the gel inhibiting composition concentration is from 0.01 to 3.0 parts per hundred by weight of solid elastomer.

3. The process according to claim 1 characterized in that said composition comprises a 1:10 to 10:1 mixture by weight of (A) an ester of a polyphenolic and (B) an autosynergistic phenolic reaction product.

4. The process according to claim 1 characterized in that said composition comprises a 1:5 to 5:1 mixture by weight of (A) an ester of a polyphenolic and (B) an autosynergistic phenolic reaction product.

5. The process according to claim 1 characterized in that (A) the ester of a polyphenolic is selected from 2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert.butyl phenylmethacrylate and 2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert butyl phenylacrylate.

6. The process according to claim 1 characterized in that the elastomer is selected from natural rubber, polybutadiene and SBR.

7. A process for the prevention or reduction of gel formation in polymeric elastomers, said process characterized by adding to the elastomer from 0.01 to 5.0 parts per hundred by weight of solid elastomer of a gel inhibiting composition, wherein said elastomer is selected from the group consisting of natural rubber and synthetic polymers containing carbon to carbon double bonds, said gel inhibiting composition comprising a 1:10 to 15:1 mixture by weight of (1) a compound selected from the group consisting of 2-(2-hydroxy-3-tert.butyl-5-ethylbenzyl)-4-ethyl-6-tert.butyl phenylmethacrylate; 2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert.butyl phenylmethacrylate; 2,6-bis-(2-hydroxy-3-tert butyl-5-methylbenzyl)-4-methylphenylmethacrylate and 2-(2-hydroxy-3-tert butyl-5-methylbenzyl)-4-methyl-6-tert butyl phenylacrylate; and (2) an autosynergistic phenolic antioxidant reaction product, said autosynergistic phenolic antioxidant reaction product being obtainable by a process comprising:

(a) admixing one mole of a mono-alkylated phenol or a 2,4-dialkylated phenol or a mixture thereof, wherein the alkyl radical may be straight or branched and may contain from 1 to 20 carbon atoms; with

(b) from 0.5 to 1.5 moles of a primary mercaptan of 3 to 20 carbon atoms; and
(c) from 0 to 50% molar excess of aqueous formaldehyde based on moles of primary mercaptan when the molar ratio of mercaptan to phenol is 1.0 or greater or 0 to 100% excess of aqueous formaldehyde when the ratio of mercaptan to phenol is less than 1.0; and
(d) from 0.04 to 20 percent by weight based on the weight of alkylated phenol of an acid catalyst; and
(e) an adequate amount of an azeotroping solvent;
(2) heating the admixture from ambient up to 180 °C while azeotropically removing water until the production of the waters of reaction ceases; and
(3) neutralizing the catalyst and isolating the products.

8. A process according to claim 6 characterized in that the gel inhibiting composition is present at from 0.01 to 3.0 parts per hundred by weight of solid elastomer.
9. A process according to claim 7 characterized in that the ratio of compound (1) to compound (2) is from 1:10 to 10:1.

10. A process according to claim 7 characterized in that the ratio of compound (1) to compound (2) is from 1:5 to 5:1.

11. A process according to claim 7 characterized in that the elastomer is selected from natural rubber, polybutadiene and SBR.

12. A process according to claim 7 characterized in that (A) the ester of a polyphenolic is selected from 2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert.butyl phenylmethacrylate and 2-(2-hydroxy-3-tert.butyl-5-methylbenzyl)-4-methyl-6-tert.butyl phenylacrylate.

**Patentansprüche**

1. Verfahren zur Verhinderung oder Reduktion von Gelbildung in Elastomeren, wobei das Verfahren gekennzeichnet ist durch Zugabe von 0,01 bis 5,0 Gewichtsteilen pro Hundert eines festen Elastomers einer Gel-inhibierenden Zusammensetzung zu einem Elastomer in fester, Latex- oder Lösungsform, worin das Elastomer ausgewählt ist aus der Gruppe, die aus Naturkautschuk und synthetischen Polymeren, die Kohlenstoff-Kohlenstoff-Doppelbindungen enthalten, besteht, worin die Gel-inhibierende Zusammensetzung eine 1:15 bis 15:1-Gewichtsmischung umfaßt von (A) einem Ester einer polyphenolischen Verbindung, der erhältlich ist durch Umsetzen einer polyphenolischen Verbindung der Strukturformel:

![strukturformel](image)

worin R¹ und R² gleiche oder verschiedene Reste sind, die aus der Gruppe, die aus Wasserstoff, Alkylresten mit 1 bis 16 Kohlenstoffatomen, Cycloalkylresten mit 5 bis 9 Kohlenstoffatomen, Arylalkylresten mit 7 bis 12 Kohlenstoffatomen und substituierten und unsubstituierten Arylresten mit 6 bis 12 Kohlenstoffatomen besteht, ausgewählt sind; X ein gleicher oder verschiedener Rest ist, der ausgewählt ist aus der Gruppe, die aus (1) cyclischen Dienen mit nicht-benachbarten Kohlenstoff-Kohlenstoff-Doppelbindungen innerhalb der Ringstruktur, die 5 bis 20 Kohlenstoffatome enthalten, aus denen die zweiwertigen Reste hergestellt werden, und (2) einem zweiwertigen Rest, der aus der Gruppe, die aus -S-, -O-, -C(=O), -CH₂- und -S-S- besteht, ausgewählt ist; und worin das n aus der Gruppe, die aus 0 und reellen Zahlen von 1 bis 5 besteht, ausgewählt ist; mit einer Verbindung mit der allgemeinen Formel:

![strukturformel](image)

worin R³ aus der Gruppe, die aus Wasserstoff und Alkylresten mit 1 bis 4 Kohlenstoffatomen besteht, ausgewählt ist, R⁴ aus der Gruppe, die aus Wasserstoff, Alkylresten mit 1 bis 4 Kohlenstoffatomen, Arylalkylresten mit 7 bis 12 Kohlenstoffatomen, Cycloalkylresten mit 5 bis 8 Kohlenstoffatomen und substituierten oder unsubstituierten Arylresten mit 6 bis 12 Kohlenstoffatomen besteht, ausgewählt ist, und worin A aus der Gruppe, die aus Chlor, Brom und Iod besteht, ausgewählt ist; und
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(B) einem autosynergistischen phenolischen Reaktionsprodukt, wobei das autosynergistische pheno-
lische Antioxidans-Reaktionsprodukt erhältlich ist durch ein Verfahren, das umfaßt:

1. Mischen von 1 Mol eines mono-alkylierten Phenols oder eines 2,4-dialkylierten Phenols oder
einer Mischung davon, worin der Alkylrest gerade oder verzweigt sein kann und 1 bis 20
Kohlenstoffatome enthalten kann, mit
   (a) 0,5 bis 1,5 Mol eines primären Mercaptans mit 3 bis 20 Kohlenstoffatomen; und
   (b) 0 bis 50% molarem Überschuß von wäßrigem Formaldehyd, bezogen auf die Mol des
primären Mercaptans, wenn das Molverhältnis von Mercaptan zu Phenol 1,0 oder größer ist,
oder 0 bis 100% Überschuß wäßriger Formaldehyds, wenn das Verhältnis von Mercaptan zu
Phenol weniger als 1,0 ist; und
   (c) 0,04 bis 20 Gewichtsprozent, bezogen auf das Gewicht von alkyliertem Phenol, eines
Säurekatalysators; und
   (d) einer adäquaten Menge eines azeotropierenden Lösungsmittels;
2. Erwärmen der Mischung von Umgebungstemperatur auf bis hinauf zu 180 °C, während
   Wasser azeotrop entfernt wird, bis die Erzeugung der Reaktionswasser aufhört; und
   (3) Neutralisieren des Katalysators und Isolieren des Produkts.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Konzentration der Gel-inhibierende
   Zusammensetzung 0,01 bis 3,0 Gewichtsteile pro Hundert des festen Elastomers ist.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung eine 1:10 bis 10:1
   Gewichtsmischung von (A) einem Ester eines Polyphenols und (B) einem autosynergistischen phenoli-
schen Reaktionsprodukt umfaßt.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung eine 1:5 bis 5:1
   Gewichtsmischung von (A) einem Ester eines Polyphenols und (B) einem autosynergistischen phenoli-
schen Reaktionsprodukt umfaßt.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß (A) der Ester eines Polyphenols aus 2-(2-
   Hydroxy-3-tert-butyl-5-methylbenzyl)-4-methyl-6-tert-butylphenylmethacrylat und 2-(2-Hydroxy-3-tert-
   butyl-5-methylbenzyl)-4-methyl-6-tert-butylphenylacrylat ausgewählt ist.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Elastomer aus Naturkautschuk, Polybu-
tadien und SBR ausgewählt ist.

7. Verfahren zur Verhinderung oder Verminderung von Gelbildung in polymeren Elastomeren, wobei das
   Verfahren gekennzeichnet ist durch Zugabe zu dem Elastomer von 0,01 bis 5,0 Gewichtsteilen pro
   Hundert eines festen Elastomers einer Gel-inhibierenden Zusammensetzung, worin das Elastomer
   ausgewählt ist aus der Gruppe, die aus Naturkautschuk und synthetischen Polymeren, die Kohlenstoff-
   Kohlenstoff-Doppelbindungen enthalten, besteht, wobei die Gel-inhibierende Zusammensetzung eine
   1:15 bis 15:1-Gewichtsmischung umfaßt von (1) einer Verbindung, die aus der Gruppe, die aus 2-(2-
   Hydroxy-3-tert-butyl-5-ethylbenzyl)-4-ethyl-6-tert-butylphenylmethacrylat, 2-(2-Hydroxy-3-tert-butyl-5-
   methylbenzyl)-4-methyl-6-tert-butylphenylmethacrylat, 2,6-Bis(2-hydroxy-3-tert-butyl-5-methylbenzyl)-4-
   methylphenylmethacrylat und 2-(2-Hydroxy-3-tert-butyl-5-methylbenzyl)-4-methyl-6-tert-butylphenylacry-
   lat besteht, ausgewählt ist; und (2) einem autosynergistischen phenolischen Antioxidans-Reaktionspro-
   dukt, wobei das autosynergistische phenolische Antioxidans-Reaktionsprodukt erhältlich ist durch ein
   Verfahren, das umfaßt:
   (1) Mischen von 1 Mol eines mono-alkylierten Phenols oder eines 2,4-dialkylierten Phenols oder
   einer Mischung davon, worin der Alkylrest gerade oder verzweigt sein kann und 1 bis 20 Kohlen-
   stoffatome enthalten kann, mit
      (a) 0,5 bis 1,5 Mol eines primären Mercaptans mit 3 bis 20 Kohlenstoffatomen; und
      (b) 1 bis 50% molarem Überschuß von wäßrigem Formaldehyd, bezogen auf die Mol des
primären Mercaptans, wenn das Molverhältnis von Mercaptan zu Phenol 1,0 oder größer ist, oder
0 bis 100% Überschuß wäßriger Formaldehyds, wenn das Verhältnis von Mercaptan zu Phenol
weniger als 1,0 ist; und
      (c) 0,04 bis 20 Gewichtsprozent, bezogen auf das Gewicht des alkylierten Phenols, eines
Säurekatalysators; und
      (d) einer adäquaten Menge eines azeotropierenden Lösungsmittels;

8. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß die Gel-inhibierende Zusammensetzung zu 0,01 bis 3,0 Gewichtsteilen pro Hundert des festen Elastomers anwesend ist.

9. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Verhältnis von Verbindung (1) zu Verbindung (2) 1:10 bis 10:1 beträgt.

10. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Verhältnis von Verbindung (1) zu Verbindung (2) 1:5 bis 5:1 beträgt.

11. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Elastomer aus Naturkautschuk, Polybutadien und SBR ausgewählt ist.

12. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß (A) der Ester eines Polyphenols aus 2-(2-Hydroxy-3-tert-butyl-5-methylbenzyl)-4-methyl-6-tert-butylphenylacrylat und 2-(2-Hydroxy-3-tert-butyl-5-methylbenzyl)-4-methyl-6-tert-butylphenylacrylat ausgewählt ist.

**Revendications**

1. Procédé pour la prévention ou la réduction de formation de gel dans des élastomères, ledit procédé étant caractérisé par l'addition à un élastomère sous forme solide, de latex ou en solution, de 0,01 à 5,0 parties par cent parties en poids de l'élastomère solide d'une composition d'inhibition de gel, dans lequel ledit élastomère est choisi parmi le groupe constitué par le caoutchouc naturel et par des polymères synthétiques contenant des doubles liaisons carbone-carbone, ladite composition d'inhibition de gel comprenant un mélange en poids de 1:15 à 15:1 de (A) un ester d'un composé polyphénolique que l'on obtient en faisant réagir un composé polyphénolique répondant à la structure développée :

   ![Structure](image)

   dans laquelle R² et R² représentent des radicaux identiques ou différents choisis parmi le groupe constitué par un atome d'hydrogène, par des radicaux alkyle contenant de 1 à 16 atomes de carbone, par des radicaux cycloalkyle contenant de 5 à 9 atomes de carbone, par des radicaux aralkyle contenant de 7 à 12 atomes de carbone, ainsi que par des radicaux aryle substitués et non substitués contenant de 6 à 12 atomes de carbone; X représente un radical identique ou différent choisi parmi le groupe constitué par (1) des diènes cycliques contenant des doubles liaisons carbone-carbone non adjacentes à l'intérieur de la structure cyclique contenant de 5 à 20 atomes de carbone à partir desquels on prépare les radicaux divalents et (2) un radical bivalent choisi parmi le groupe constitué par : -S-, -O-, -CH₂- et -S-S-; et dans laquelle n est choisi parmi le groupe constitué par 0 et par les entiers de 1 à 5; avec un composé répondant à la formule générale :

   ![Structure](image)
dans laquelle $R^3$ est choisi parmi le groupe constitué par un atome d'hydrogène et par des radicaux alkyle contenant de 1 à 4 atomes de carbone, $R^4$ est choisi parmi le groupe constitué par un atome d'hydrogène, par des radicaux alkyle contenant de 1 à 4 atomes de carbone, par des radicaux aralkyle contenant de 7 à 12 atomes de carbone, par des radicaux cycloalkyle contenant de 5 à 8 atomes de carbone, ainsi que par des radicaux aryle substitués ou non substitués contenant de 6 à 12 atomes de carbone, et dans laquelle A est choisi parmi le groupe constitué par un atome de chlore, par un atome de brome et par un atome d'iode; et (B) un produit réactionnel phénolique autosynergique, ledit produit réactionnel phénolique antioxydant autosynergique pouvant être obtenu par un procédé comprenant le fait de :

(1) mélanger une mole d'un phénol mono-alkylé ou d'un phénol 2,4-dialkylé ou encore d'un mélange de ces derniers, dans lequel le radical alkyle peut être à chaîne droite ou ramifiée et peut contenir de 1 à 20 atomes de carbone, avec
(a) de 0,5 à 1,5 mole d'un mercaptan primaire contenant de 3 à 20 atomes de carbone, et
(b) un excès molaire de 0 à 50% d'un formaldéhyde aqueux basé sur les moles du mercaptan primaire lorsque le rapport molaire entre le mercaptan et le phénol est égal à 1,0 ou plus, ou bien un excès de 0 à 100% de formaldéhyde aqueux lorsque le rapport entre le mercaptan et le phénol est inférieur à 1,0, et
(c) de 0,04 à 20 pour cent en poids, basés sur le poids du phénol alkylé, d'un catalyseur acide, et
(d) une quantité adéquate d'un solvant azéotrope;
(2) chauffer le mélange de la température ambiante à 180 °C tout en éliminant l'eau par voie azéotrope jusqu'à ce que la production d'eau réactionnelle cesse; et
(3) neutraliser le catalyseur et isoler les produits.

2. Procédé selon la revendication 1, caractérisé en ce que la concentration de la composition inhibitrice de gel est de 0,01 à 3,0 parties par cent parties en poids de l'élastomère solide.

3. Procédé selon la revendication 1, caractérisé en ce que ladite composition comprend un mélange 1:10 à 10:1 en poids de (A) un ester d'un composé polyphénolique et de (B) un produit réactionnel phénolique autosynergique.

4. Procédé selon la revendication 1, caractérisé en ce que ladite composition comprend un mélange 1:5 à 5:1 en poids de (A) un ester d'un composé polyphénolique et de (B) un produit réactionnel phénolique autosynergique.

5. Procédé selon la revendication 1, caractérisé en ce que l'ester (A) du composé polyphénolique est choisi parmi le pényl méthacrylate de 2-(2-hydroxy-3-tert.-butyl-5-méthylbenzyl)-4-méthyl-6-tert.-butyle et le pényl acrylate de 2-(2-hydroxy-3-tert.-butyl-5-méthylbenzyl)-4-méthyl-6-tert.-butyle.

6. Procédé selon la revendication 1, caractérisé en ce que l'élastomère est choisi parmi le caoutchouc naturel, le polybutadiène et le SBR.

7. Procédé pour la prévention ou la réduction de formation de gel dans des élastomères polymères, ledit procédé étant caractérisé par l'addition à l'élastomère de 0,01 à 5,0 parties par cent parties en poids de l'élastomère solide d'une composition d'inhibition de gel, dans lequel ledit élastomère est choisi parmi le groupe constitué par le caoutchouc naturel et par des polymères synthétiques contenant des doubles liaisons carbone-carbone, ladite composition d'inhibition de gel comprenant un mélange en poids de 1:15 à 15:1 de (1) un composé choisi parmi le pénylacrylate de 2-(2-hydroxy-3-tert.-butyl-5-éthylbenzyl)-4-éthyl-6-tert.-butyle, le pénylméthacrylate de 2-(2-hydroxy-3-tert.-butyl-5-méthylbenzyl)-4-méthyl-6-tert.-butyle, le pényléméthacrylate de 2,6-bis(2-hydroxy-3-tert.-butyl-5-méthylbenzyl)-4-méthyle et le pénylacrylate de 2-(2-hydroxy-3-tert.-butyl-5-méthylbenzyl)-4-méthyl-6-tert.-butyle et (2) un produit réactionnel phénolique antioxydant autosynergique, ledit produit réactionnel phénolique antioxy-
dant autosynergique pouvant être obtenu par un procédé comprenant le fait de :
(1) mélanger une mole d’un phénol mono-alkylé ou d’un phénol 2,4-dialkyié ou encore d’un mélange
de ces derniers, dans lequel le radical alkylé peut être à chaîne droite ou ramifiée et peut contenir
de 1 à 20 atomes de carbone, avec
   (a) de 0,5 à 1,5 mole d’un mercaptan primaire contenant de 3 à 20 atomes de carbone, et
   (b) un excès molaire de 1 à 50% d’un formaldéhyde aqueux basé sur les moles du mercaptan
   primaire lorsque le rapport molaire entre le mercaptan et le phénol est égal à 1,0 ou plus, ou bien
   un excès de 0 à 100% de formaldéhyde aqueux lorsque le rapport entre le mercaptan et le
   phénol est inférieur à 1,0, et
   (c) de 0,04 à 20 pour cent en poids, basés sur le poids du phénol alkylé d’un catalyseur acide, et
   (d) une quantité adéquate d’un solvant azéotrope;
(2) chauffer le mélange de la température ambiante à 180 °C tout en éliminant l’eau par voie
   azéotrope jusqu’à ce que la production d’eau réactionnelle cesse; et
(3) neutraliser le catalyseur et isoler les produits.

8. Procédé selon la revendication 6, caractérisé en ce que la composition inhibitrice de gel est présente
   en une quantité de 0,01 à 3,0 parties par cent parties en poids de l’élastomère solide.

9. Procédé selon la revendication 7, caractérisé en ce que le rapport entre le composé (1) et le composé
   (2) est de 1:10 à 10:1.

10. Procédé selon la revendication 7, caractérisé en ce que le rapport entre le composé (1) et le composé
    (2) est de 1:5 à 5:1.

11. Procédé selon la revendication 7, caractérisé en ce que l’élastomère est choisi parmi le caoutchouc
    naturel, le polybutadiène et le SBR.

12. Procédé selon la revendication 7, caractérisé en ce que l’ester (A) du composé polyphénolique est
    choisi parmi le phénylméthacrylate de 2-(2-hydroxy-3-tert.-butyl-5-méthylbenzyl)-4-méthyl-6-tert.-butyle
    et le phénylacrylate de 2-(2-hydroxy-3-tert.-butyl-5-méthylbenzyl)-4-méthyl-6-tert.-butyle.