Title: MODIFIED PHENOLIC TACKIFYING RESINS FOR RUBBER COMPOUNDING APPLICATIONS

Abstract: This invention is related to modified alkylphenol aldehyde resins and process for preparing them from the reactions of alkylphenols, aldehydes, amines, rosins and fatty acids. When used in rubber compounds, these modified alkylphenol aldehyde resins provide much improved tack properties.
MODIFIED PHENOLIC TACKIFYING RESINS FOR RUBBER COMPOUNDING APPLICATIONS

Technical Field

This invention is related to modified alkylphenol aldehyde resins and process for preparing them from the reactions of alkylphenols, aldehydes, amines, rosins and fatty acids. When used in rubber compounds, these modified alkylphenol aldehyde resins provide much improved tack properties.

Background for the Current Invention

Modern radial and bias/belted passenger car tires are designed to provide good crack and abrasion resistance, low hysteresis, low rolling resistance, and good gas mileage as well as long service life. In order to achieve this, tire industries employ blends of styrene-butadiene (SBR) and butadiene (BR) rubber in the rubber formulations, particularly in tread cap and under tread compounds. Generally, natural rubber has sufficient inherent tack for most applications so that tackifying agents may not be necessary. Styrene-butadiene (SBR) has a relatively low polarity compared to other synthetic rubbers; unlike natural rubber, SBR does not develop surface peroxidal activity upon mastication. Therefore, SBR has relatively poor inherent or processed tack.

The need for improved rubber tack is probably most apparent in the tire industry. Tires are typically constructed by applying layers of rubber-coated fabric one to another, followed by a breaker strip, cushion, and tread. The layers must possess sufficient surface tack to adhere firmly one to another and to maintain the desired relative position of the various parts prior to vulcanization. Absence of tack causes difficulty in the building operation. Thus, the tack of uncured rubber compounds has always been one of the most important properties required for building tires.

Tack of uncured rubber components, particularly treads, is an important property for building rubber articles, such as tires. The term "tack" refers to the ability of two uncured rubber materials or surfaces to resist separation after bringing them into contact for a short time under relatively light pressure. It is important that uncured components, such as those in a tire, especially the tread, exhibit tack so that rubber components can be securely adhered and so that splices resist separation prior to vulcanization.

Lack of sufficient tack in uncured rubber components, especially treads, has been an ongoing problem.

In the tyre industry, tackifiers are often used to provide building tack to rubber compounds. Other than natural rubber, synthetic rubber does not have the sufficient building tack. Therefore
resin must be added to increase tack. Building tack is an important prerequisite to enable tyre building from flat layered materials. This building tack provides the handling strength of green tyres until they are vulcanized. Another important feature is tack retention. Tire segments are premanufactured and then stored. During the storage time the building tack should not change.

Tackifiers, used in the manufacture of tires, should be compatible with synthetic rubbers and exhibit the desired tackifying effects on the synthetic rubbers. Tackifiers have a very low reactivity with the synthetic rubbers. This means that there is no substantial reaction occurs between the synthetic rubber and the tackifiers upon heating.

Tackifying resins can be divided into three groups: hydrocarbon resins, rosin resins and phenolic resins. Generally, there are two different types of tackifier resins used by the rubber industry: hydrocarbon resin tackifiers and phenolic resin tackifiers. Sometimes, blends of hydrocarbon resin and phenolic resin tackifiers are used. Hydrocarbon tackifier resins provide good initial tack, but typically do not provide good long-term tack. Phenolic tackifiers provide good initial and long-term tack, but are typically expensive.

The hydrocarbon resins are less expensive than are the phenolic resins, but require the use of up to three times the amount to give equivalent tack with tack retention being adversely affected. Since tackifiers which remain in the fabricated rubber article can tend to detract from the properties of the rubber, phenolic resins are often advantageously used because of the lower level required.

The hydrocarbon resins include aliphatic, aromatic and alicyclic resins having a number average molecular weight of generally about 500 to about 5,000 and a softening point of at least 70 °C. These resins, in general, are obtained, for example, by polymerizing isoprene, cyclopentadiene or dicyclopentadiene which is a C5 fraction obtained as a by-product in the thermal cracking of petroleum naphtha, or a styrene derivative or indene which is a C9 fraction, also obtained in the thermal cracking of petroleum naphtha.

In the case of phenolic resins, para-tert-octylphenol (PTOP) and para-tert-butylphenol (PTBP) based novolaks are predominantly used by the tire industry. With phenolic novolak resins tack retention of 2 days is achievable, and with a special resin made from para-tert-butylphenol and acetylene (Koresin® - BASF), tack retention of 8 days could be possible. However, the Koresin® price is very high and its availability is limited.

Before the introduction of novolak resins, rosin was used as a tackifying resin. Rosin is mainly a mixture of C20, tricyclic fused-ring, monocarboxylic acids, typified by pimaric and abietic acids, which are commonly referred to as "rosin acids." Rosin resins have a wide span of compatibility with almost all polymers. They are well known for their peel and tack contribution to the adhesive strength.

Phenolic-modified rosin esters are seldom employed as tackifiers.
Based upon the foregoing, even though a number of different kinds of materials are currently available for use as tackifier resins, there is a need in the art for a tackifier for a rubber compound, wherein the tackifier provides good initial and long-term tack. The present invention is directed to such a tackifier and a rubber compound containing the same. The current invention also provides a process for synthesizing or manufacturing modified phenolic tackifying resins and develops rubber compositions containing such resins.

Summary of Invention

According to the current invention, vulcanizable rubber compositions having improved tack properties are obtained by the use of novel and efficient phenolic tackifier resins prepared by the reactions of para-alkylphenols, aldehydes, primary or secondary amines, rosin acids and / or fatty acids. One aspect of the present invention is to provide modified and more efficient phenolic resin tackifier resins for synthetic rubber compositions. Another aspect is to provide a method of synthesizing or manufacturing this tackifier resins from the reactions of alkylphenol resoles containing terminal methylole groups with morpholine, rosin acids and / or fatty acids.

Detailed Description of the Current Invention

The modified phenolic tackifying resins of this invention are prepared by reacting one or more substituted phenolic compounds selected from the group of compounds represented by the general formula (a)

![Formula Image](a)

wherein R is independently selected from the alkyl groups or radicals of 1 to 18 carbon atoms in their various isomeric forms and substituted on the phenolic nucleus in the ortho-, meta- or para-positions; alicyclic groups of 5 to 18 carbon atoms such as cyclohexyl, cyclopentyl, methyl cyclohexyl, or butyl-cyclohexyl; alkyl and alicyclic ketonic groups; alkyl and alicyclic carboxylic groups and aryl substituted alkyl wherein the aryl is phenyl which may contain lower alkyl and/or hydroxyl substituents so that the resulting phenol is for example a bisphenol; with one or more aldehyde or ketone compounds represented by the general formula (b)

![Formula Image](b)

wherein R₁ and R₂ groups can be independently hydrogen; alkyl groups or radicals of 1 to 8 carbon atoms; a cycloalkyl; in the presence of base to obtain the phenolic resole mixture comprising the following general structural formulae (c - f);
In the above formulae, R₁ and R₂ groups can be independently hydrogen; alkyl groups or radicals of 1 to 8 carbon atoms; a cycloalkyl; R₅ and R₆ are independently hydrogen or methylol groups; and x plus y is at least 1.

Then the resole mixtures are modified by reacting first with amine compounds selected from the group comprising the general formula (g)

\[ R₃ - NH - R₄ \]  

wherein R₃ and R₄ are independently selected from the group comprising hydrogen, alkyl group of 1 to 6 carbon atoms; alkenyl group of 2 to 6 carbon atoms; aryl and substituted aryl; hydroxyethyl; hydroxypropyl; carboxyalkyl; and together with nitrogen forming a heterocyclic 5 or 6 membered ring; and then with rosin acid and / or longer chain aliphatic carboxylic acids.

The aliphatic, cycloaliphatic or aromatic mono or polyamine compounds containing at least one amine group can be used in the modifications. Preferably 1, 8-p-methane diamine, ethylene diamine, triethylene tetramine, 1, 3-bis(aminomethyl) cyclohexane, m-xylylenediamine, diethanolamine, and morpholine can be used.

Suitable substituted alklyphenols include the following: para – tertiary- butylphenol (PTBP), para-secondary-butylphenol, para-tert-hexylphenol, para-isooctylphenol; para-tert-octylphenol (PTOP), para-cydocohexylphenol, para-decylphenol, para-dodecylphenol, para-tetradecyl phenol,
para-octadecylphenol, para-nonylphenol, para-methylphenol, para-pentadecylphenol, para-cetylphenol, bisphenols, such as para,para' - isopropylidenediphenol, para,para'-methylene diphenol, a phenol alkylated with oleic acid, as well as the corresponding ortho and meta derivatives of the previously mentioned compounds such as meta- butyl phenol and ortho-buty1 phenol, as well as mixtures thereof. Suitable alkylphenols that can be advantageously used to prepare the tackifying resins are para-tert-butylphenol (PTBP and para-tert-octylphenol (PTOP) or mixtures of these two.

From the above lists, it is apparent that many alkylphenols may be used in practicing the present invention provided the alkylphenol employed has a reactive phenolic hydroxyl group and is capable of reacting with aldehydes, such as formaldehyde, to produce a condensate. The pure refined alkylphenols may be used, but this is not always necessary. For instance, phenols may be alkylated and then may be reacted with an aldehyde as the crude product which may contain some polyalkylated, as well as unalkylated phenols. Mixtures of variously substituted phenols may also be used.

In the preparation of the parent phenol-aldehyde condensates, suitable aldehydes or mixtures of aldehydes capable of reacting with a phenol and having not more than eight carbon atoms are satisfactory provided they do not detrimentally affect the resinification, esterification of oxyalkylation of the resin. The preferred aldehydes are aldehydes having 1 to 8 carbon atoms such as formaldehyde, which may be in aqueous solution or in any of its low polymeric forms such as paraformaldehyde or trioxane, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde, n-valeraldehyde, heptaldehyde and octaldehyde. Other examples of aldehydes include paraaldehyde, furfural, 2-ethylhexenal, ethylbutyraldehyde and glyoxal. Formaldehyde in the form of paraformaldehyde or aqueous formalin/formaldehyde solutions or in the form of any compound generating formaldehyde for chemical reactions can be used. It is possible to use mixtures of aldehydes. The most preferred aldehyde is aqueous formaldehyde or solid paraformaldehyde or a mixture of these two.

The resole for the preparation of modified tackifier resin can be conveniently prepared with a mole ratio of aldehyde, for example formaldehyde, to para-alkylphenol, for example para-tert-buty1phenol, in the range of about 1.0 to 2.5, and particularly in the range of about 1.0 to 1.5.

A resole resin containing a mixture of variously substituted methy1ol groups from the reactions of para-alkylphenol with formaldehyde in the presence of basic catalyst can be conveniently represented by the following general reaction scheme.
The formation of such chemical structures depends on various conditions such as the molar ratios of alkylphenol and formaldehyde, reaction temperatures and times, reaction medium, nature of catalysts and amounts, and so on.

A basic catalyst material such as ammonium hydroxide; tertiary amines such as triethylamine, triethanolamine, diethyl cyclohexyl amine, triisobutyl amine; alkali and alkaline earth metal oxides and hydroxides can be used to form the resoles.

In the preparation of alkylphenol resoles, suitable organic solvents either miscible or immiscible with the reaction medium can be used. Aromatic and aliphatic (including cycloaliphatic) hydrocarbons can be employed as solvents for a given resin, including benzene, toluene, xylene, naphthalene, nonane, octane and petroleum fractions.

The resole resin can also be conveniently prepared from the para-alkylphenol-formaldehyde novolak polymer based on the following reaction scheme.

From the above reaction scheme, alkylphenol and formaldehyde are reacted first in the presence of an acid catalyst to produce novolak type structures. Then, the resoles containing methylol groups are prepared under the basic conditions from the novolak resin.

Suitable acidic catalysts to prepare the alkylphenol novolaks are an alkyl, aryl and aralkyl sulfonic acids, such as ethanesulfonic acid, benzenesulfonic acid, benzenedisulfonic acid, chlorobenzenesulfonic acid, 3,4-dichlorobenzene sulfonic acid, cresolsulfonic acids, phenol
sulfonic acids, toluenesulfonic acids, xylenesulfonic acids, octylphenolsulfonic acid, naphthalenesulfonic acid, 1-naphthol-4-sulfonic acid, dodecylsulfonic acid and an oxalic acid.

The resole product produced by the reaction of alkylphenol with formaldehyde as described can be used to obtain modified phenolic tackifier resins of this invention. As those skilled in the art fully appreciate, the methylolel content and the degree of advancement are readily controllable, so that one can optimize such a resole resin for use in a particular application. For purposes of this invention, a alkylphenol-formaldehyde resole resin can be regarded as being the reaction product of the above-described alkylphenols and formaldehyde under the aqueous base catalyzed conditions as described herein which can be further modified with primary or secondary aliphatic or aromatic amines, rosin acids and / or longer chain aliphatic carboxylic acids.

In the preparation of a rosin-modified alkylphenolic resin by the reaction of a rosel type addition-condensation product with a rosin, the active groups such as a methylolel or methylene ether group of the resole type addition-condensation product and the active groups such as a conjugated double bond of the rosin are consumed partially or completely by the formation of a coumarone ring or by self-condensation in the course of the reaction. Therefore, the rosin-modified phenolic resin may scarcely contain these active groups after the modifications.

Rosin is mainly a mixture of C_{20}, fused-ring, monocarboxylic acids, typified by levopimaric and abietic acids, both of which are susceptible to numerous chemical transformations. The resins to which this invention relates include gum rosin, wood rosin, and tall oil rosin or the rosin acids contained therein as for example, abietic acid, pimamic acid, sapinic acid, etc. There are no specific restrictions with respect to the rosin type that can be employed to develop modified novolak resins of this invention.

In the modification of phenolic tackifying resins of this invention, longer chain aliphatic fatty acids can be employed. The fatty acids may be saturated or unsaturated mono-carboxylic acids having at least 8 carbon atoms in the chain. Preferably, the saturated fatty acids have 8 to 32 carbon atoms can be used. Suitable saturated fatty acids include caprylic, capric, undecylic, lauric and stearic. Suitable unsaturated fatty acids include oleic and undecylic acids. Synthetic fatty acid mixtures obtained by saponification of vegetable oils can also be used in the resin modifications. The most preferred aliphatic acid is stearic acid.

With the combination of a para-alkylphenol, formaldehyde, morpholine and rosin acid, the most probable reaction scheme outlining the preparation of a modified phenolic tackifying resin in the presence of basic conditions is shown below.
In addition, these modified phenolic resins can also be prepared starting from the para-alkylphenol novolak resins. In this case, the resoles are prepared from the para-alkylphenol novolak resins produced in the presence an acid and then modified with morpholine and rosin acids. This reaction scheme is shown below.

Depending upon the reaction conditions such as the type of alkylphenol and aldehyde, reaction temperature and time, reaction pH and nature of solvent, the resole reaction mixture may contain methyol groups of varying structural characteristics. In general, these modified phenolic tackifying resins may be obtained from the reactions of morpholine and rosin acids with para-alkylphenol – aldehyde condensation product having following structure.

where, \( R \) is an alkyl chain, \( R_1 \) and \( R_2 \) are independently hydrogen or alkyl chain; \( R_5 \) and \( R_6 \) are independently hydrogen or methyol groups and \( x + y \) is at least 1.

The inventive modified phenolic tackifying resins can be suitably used in various rubber compositions. In addition to natural rubber (NR) compositions, other synthetic rubber compositions, for example, butadiene rubber (BR), styrene-butadiene rubber (SBR), halogenated isoprene isobutylene rubber (XIIIR), nitrile rubber (NBR), hydrogenated nitrile rubber (HNBR), EPDM and chloroprene rubber (CR) or mixtures also can use this modified phenolic...
resins to achieve improved tack properties. Blends of various rubbers can of course be used in this invention, particularly desirable of which are blends of natural and synthetic rubbers. There are no specific restrictions with respect to the rubber type.

The rubber compositions containing the modified phenolic tackifying resins of this invention may be used in any part of a tyre, for example, side wall compounds, apex, inner liners, under tread cement. However, they are also useful in general for a wide variety of industrial goods, such as rubber based products or goods, or (pressure sensitive) adhesives, hot melts.

Therefore, the object of this invention is to provide rubber compositions or compounds with good building tack and good tack retention properties. Building tack and tack retention should be comparable or even better as for rubber compositions containing conventional tackifiers such as novolak resins based on tert-butylphenol or tert-octylphenol or Koresin®.

The present invention will be illustrated with reference to the following examples, which are only given for the purpose of illustration and are not to be interpreted as limiting.

**Example 1**

**Rosin and Morpholine Modified para-tert-butylphenol (PTBP) – Formaldehyde Resin**

Into a reactor, 50 kilograms of para-tert-butylphenol (PTBP) and 25 kilograms of toluene are charged and heated to 85 to 110 °C to dissolve the phenol. Next, triethylamine (TEA) catalyst was added to take the pH of the reaction mixture to basic conditions. Then, 32 kilograms of aqueous formaldehyde (37 %) solution was added slowly over a period of about 2 to 3 hours under the reflux conditions. Morpholine (5 kilograms) and rosin (5 kilograms) were added into the resole mixtures and then continued the reflux for an additional period of 2 to 3 hours. Finally, the reaction mixture was first dehydrated under the atmospheric conditions and then under vacuum conditions of 180 to 200 °C temperature and 25 to 50 mm Hg vacuum to remove the volatile matters present in the resin product.

**Example 2**

**Rosin, Stearic Acid and Morpholine Modified para-tert-butylphenol (PTBP) – Formaldehyde Resin**

Into a reactor, 150 kilograms of para-tert-butylphenol (PTBP) and 75 kilograms of toluene are charged and heated to 85 to 110 °C to dissolve the phenol. Next, triethylamine (TEA) catalyst was added to take the pH of the reaction mixture to basic conditions. Then, 95 kilograms of aqueous formaldehyde (37 %) solution was added slowly over a period of about 2 to 3 hours under the reflux conditions. Morpholine (14 kilograms), rosin (15 kilograms) and stearic acid (6 kilograms) were added into the resole mixtures and then continued the reflux for an additional period of 2 to 3 hours. Finally, the reaction mixture was first dehydrated under the atmospheric conditions and then under vacuum conditions of 180 to 200 °C temperature and 25 to 50 mm Hg vacuum to remove the volatile matters present in the resin product.
Example 3

Rosin, Stearic Acid and Morpholine Modified para-tert-octylphenol (PTOP) – Formaldehyde Resin

Into a reaction flask, 225 grams of para-tert-octylphenol (PTOP) and 150 grams of toluene are charged and heated to 85 to 110 °C to dissolve the phenol. Next, triethylamine (TEA) catalyst was added to take the pH of the reaction mixture to basic conditions. Then, 104 grams of aqueous formaldehyde (37 %) solution was added slowly over a period of about 2 to 3 hours under the reflux conditions. Morpholine (15 grams), rosin (16 grams) and stearic acid (6 grams) were added into the resole mixtures and then continued the reflux for an additional period of 2 to 3 hours. Finally, the reaction mixture was first dehydrated under the atmospheric conditions and then under vacuum conditions of 180 to 200 °C temperature and 25 to 50 mm Hg vacuum to remove the volatile matters present in the resin product.

Example 4

Rosin and Morpholine Modified para-tert-octylphenol (PTOP) – Formaldehyde Resin

309 Grams of para-tert-octylphenol, 20 grams of distilled water and 3 grams of oxalic acid were taken in a one liter reaction flask equipped with a stirrer, thermometer, reflux condenser and addition funnel and heated to about 90 to 105 °C. Then, 75 grams of aqueous formaldehyde (37 %) solution were gradually added and refluxed for 2 to 4 hours. After the reflux period, the acid catalyst was neutralized and the reaction mixture was changed into basic conditions by the addition of triethylamine. Now, 40.5 grams of aqueous formaldehyde solutions were slowly added again and continued the reaction to produce phenolic resole type product. Once the resole forming reaction was completed, morpholine (28.5 grams) and rosin (18 grams) were added. The resulting reaction mixture was stirred under the reflux conditions for 2 to 3 hours and finally vacuum dehydrated at 180 to 200 °C temperature conditions to obtain resin of this invention.

Example 5

Rosin and Morpholine Modified para-tert-butylphenol (PTBP) – Formaldehyde Resin

225 Grams of para-tert-butylphenol, 200 grams of toluene and 3 grams of oxalic acid were taken in a one liter reaction flask equipped with a stirrer, thermometer, reflux condenser and addition funnel and heated to about 90 to 105 °C. Then, 75 grams of aqueous formaldehyde (37 %) solution were gradually added and refluxed for 2 to 4 hours. After the reflux period, the acid catalyst was neutralized and the reaction mixture was changed into basic conditions by the addition of triethylamine. Now, 40.5 grams of aqueous formaldehyde solutions were slowly added again and continued the reaction to produce phenolic resole type product. Once the resole forming reaction was completed, morpholine (28.5 grams) and rosin (18 grams) were added. The resulting reaction mixture was stirred under the reflux conditions for 2 to 3
hours and finally vacuum dehydrated at 180 to 200 °C temperature conditions to obtain resin of this invention.

**Example 6**

The natural rubber compounds used for testing were prepared in three stages. The basic compound formulation is shown in Table 1.

<table>
<thead>
<tr>
<th>Rubber Compound Used in Testing</th>
<th>Parts by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Rubber</td>
<td>30</td>
</tr>
<tr>
<td>Butadiene Rubber</td>
<td>70</td>
</tr>
<tr>
<td>Carbon Black (N326)</td>
<td>80</td>
</tr>
<tr>
<td>Oil</td>
<td>4</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>3</td>
</tr>
<tr>
<td>Sulfur (80 %) (OT20)</td>
<td>1</td>
</tr>
<tr>
<td>Stearic Acid</td>
<td>2</td>
</tr>
<tr>
<td>Sulfenamide (NS)</td>
<td>2.2</td>
</tr>
<tr>
<td>Polymerized 1,2-Dihydro-2,2,4-Trimethyl Quinoline (TMQ)</td>
<td>1.5</td>
</tr>
<tr>
<td>N-(1,2-Dimethylbutyl)-N'-Phenyl-p-Phenylene Diamine (6PPD (4020))</td>
<td>1.6</td>
</tr>
<tr>
<td>Tackifying Resin</td>
<td>4</td>
</tr>
</tbody>
</table>

The resin prepared according to Examples 1 and 2 were evaluated in a natural and butadiene rubber compound to assess and compare their performance against commercially available tackifying resins.

The rubber master batch, containing natural rubber, butadiene rubber, carbon black, oil, zinc oxide and stearic acid, was mixed in the first stage to about 150 °C in a Banbury mixer. In a second stage, tackifying resins prepared according to the methods of Examples 1 and 2, 6PPD and TMQ were then mixed into an appropriate amount of the master batch on the Banbury mixer at about 140 °C. The insoluble sulfur and sulfonamide accelerator were mixed in the third stage open mill mixer at about 100 °C and sheeted. The test compounds were conditioned overnight in a constant temperature room at about 23 °C and 50% relative humidity. The compounds were then tested for rheometer cure, shaped and optimum cured at 150 °C for the evaluation of mechanical properties.

Cure properties were measured with an Alpha Technology MDR 2000 Rheometer at 151 °C, 1° arc and 1.67 Hz according to ASTM D 5289 and ISO 6502 test methods. In such an oscillating disc rheometer, compounded rubber samples are subjected to an oscillating shearing action of constant amplitude. The torque of the oscillating disc embedded in the stock that is being tested that is required to oscillate the rotor at the vulcanization temperature is measured. The test data are given in Table 2.
Table 2

<table>
<thead>
<tr>
<th>Resins</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Koresin®</th>
<th>SL - 1801</th>
<th>SP-1068®</th>
</tr>
</thead>
<tbody>
<tr>
<td>ML</td>
<td>3.27</td>
<td>3.56</td>
<td>3.53</td>
<td>3.41</td>
<td>3.57</td>
</tr>
<tr>
<td>MH</td>
<td>20.62</td>
<td>20.97</td>
<td>22.38</td>
<td>20.34</td>
<td>21.46</td>
</tr>
<tr>
<td>TS1</td>
<td>4.3</td>
<td>4.28</td>
<td>3.18</td>
<td>4.27</td>
<td>3.59</td>
</tr>
<tr>
<td>TS2</td>
<td>5.25</td>
<td>5.18</td>
<td>4.51</td>
<td>5.18</td>
<td>5.09</td>
</tr>
<tr>
<td>T10</td>
<td>5.17</td>
<td>5.09</td>
<td>4.46</td>
<td>5.08</td>
<td>5.01</td>
</tr>
<tr>
<td>T50</td>
<td>6.53</td>
<td>6.41</td>
<td>6.29</td>
<td>6.47</td>
<td>6.39</td>
</tr>
<tr>
<td>T90</td>
<td>10.08</td>
<td>9.49</td>
<td>10.16</td>
<td>9.59</td>
<td>9.49</td>
</tr>
</tbody>
</table>

Koresin® is a Trademark from BASF  
SL-1081 is a Commercial Product from Sino Legend Chemical Company, China  
SP-1068® is a Commercial Product from Schenectady International, USA

From the Table 2 results, the resins of this showed similar cure properties compared to well commercially available tackifier resins.

Table 3 shows the scorch properties determined on rubber compounds containing the phenolic tackifying resins.

<table>
<thead>
<tr>
<th>Resins</th>
<th>Mooney Scorch Property (127 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Example 1</td>
</tr>
<tr>
<td>Initial</td>
<td>130.39</td>
</tr>
<tr>
<td>Ts5</td>
<td>20.33</td>
</tr>
<tr>
<td>Ts10</td>
<td>21.35</td>
</tr>
<tr>
<td>Ts18</td>
<td>22.22</td>
</tr>
<tr>
<td>Ts35</td>
<td>23.08</td>
</tr>
</tbody>
</table>

Koresin® is a Trademark from BASF  
SL-1081 is a Commercial Product from Sino Legend Chemical Company, China  
SP-1068® is a Commercial Product from Schenectady International, USA

From the Table 3 results, the resins of this invention showed scorch properties comparable to the commercial tackifier resins.

The unaged and aged tensile properties of rubber compounds containing resins of this invention are shown in Table 4.
### Table 4

<table>
<thead>
<tr>
<th>Resins</th>
<th>Example 1</th>
<th>Example 2</th>
<th>Koresin®</th>
<th>SL-1801</th>
<th>SP-1068®</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unaged Properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% Modulus, Mpa</td>
<td>2.2</td>
<td>2.3</td>
<td>2.4</td>
<td>2.7</td>
<td>2.4</td>
</tr>
<tr>
<td>100% Modulus, Mpa</td>
<td>3.8</td>
<td>3.9</td>
<td>4.0</td>
<td>3.8</td>
<td>3.9</td>
</tr>
<tr>
<td>300% Modulus, Mpa</td>
<td>18.2</td>
<td>18.7</td>
<td>18.8</td>
<td>18.4</td>
<td>18.3</td>
</tr>
<tr>
<td>Tensile Strength, Mpa</td>
<td>20</td>
<td>21</td>
<td>20.2</td>
<td>21.2</td>
<td>20</td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>325</td>
<td>333</td>
<td>321</td>
<td>353</td>
<td>325</td>
</tr>
<tr>
<td>Hardness, Shore A</td>
<td>78</td>
<td>77</td>
<td>78</td>
<td>77</td>
<td>78</td>
</tr>
<tr>
<td><strong>After Heat Ageing, 100 °C for 24 Hours</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>50% Modulus, Mpa</td>
<td>2.9</td>
<td>2.9</td>
<td>2.9</td>
<td>2.7</td>
<td>3.2</td>
</tr>
<tr>
<td>100% Modulus, Mpa</td>
<td>5.1</td>
<td>5.0</td>
<td>4.9</td>
<td>4.8</td>
<td>5.7</td>
</tr>
<tr>
<td>Tensile Strength, Mpa</td>
<td>19.3</td>
<td>18.4</td>
<td>17.2</td>
<td>18.7</td>
<td>17.8</td>
</tr>
<tr>
<td>Elongation at Break, %</td>
<td>282</td>
<td>262</td>
<td>254</td>
<td>270</td>
<td>237</td>
</tr>
<tr>
<td>Hardness, Shore A</td>
<td>80</td>
<td>80</td>
<td>80</td>
<td>79</td>
<td>81</td>
</tr>
</tbody>
</table>

Koresin® is a Trademark from BASF
SL-1081 is a Commercial Product from Sino Legend Chemical Company, China
SP-1068® is a Commercial Product from Schenectady International, USA

When compared Koresin®, the resins of the current invention showed much improved heat aged tensile strength properties.

In order to determine the tack properties, two pieces of rubber sheets (140mm×20mm) were cut from the sheeted rubber compounds. The test pieces were separately retained for 16 hours, avoiding any moisture and dust contamination and then pressed together under a pressure of 0.2 MPa for 60 seconds. These samples were then tested for their tack properties using standard test procedures. The results are summarized in Table 5.

### Table 5

<table>
<thead>
<tr>
<th>Storage Time (Hours)</th>
<th>16</th>
<th>24</th>
<th>40</th>
<th>48</th>
<th>64</th>
<th>72</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Tackifying Resin</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Example 1</td>
<td>25.36</td>
<td>23.54</td>
<td>29.97</td>
<td>27.64</td>
<td>21.42</td>
<td>23.07</td>
</tr>
<tr>
<td>Example 2</td>
<td>24.2</td>
<td>23.08</td>
<td>23.31</td>
<td>22.61</td>
<td>22.56</td>
<td>21.15</td>
</tr>
<tr>
<td>Koresin®</td>
<td>35.47</td>
<td>30.14</td>
<td>31.93</td>
<td>22.08</td>
<td>22.83</td>
<td>25.19</td>
</tr>
<tr>
<td>SP-1068®</td>
<td>13.57</td>
<td>14.02</td>
<td>15.71</td>
<td>12.41</td>
<td>9.95</td>
<td>8.16</td>
</tr>
</tbody>
</table>

Koresin® is a Trademark from BASF
SL-1081 is a Commercial Product from Sino Legend Chemical Company, China
SP-1068® is a Commercial Product from Schenectady International, USA
As can be seen from Table 5 results, the tack properties of resins of this invention, Examples 1 and 2, show much improved performance over the conventional para-tert-octylphenol - formaldehyde type novolak resins.

It would be appreciated that, in the above teaching of invention, the skilled in the art could make certain changes or modifications to the invention, and these equivalents would still be within the scope of the invention defined by the appended claims of the application.
Claims

1. Rubber compositions having improved tack properties comprising a natural rubber or synthetic rubber or a mixture of natural and synthetic rubbers and a modified phenolic tackifier resin prepared from the reactions of primary or secondary amine, rosin, fatty acid and an alkylphenol aldehyde resole type mixtures comprising the following structure:

   \[
   \begin{array}{c}
   \text{R}_6 \quad \text{R}_1 \quad \text{R}_2 \quad \text{R}_3 \\
   \text{R} \quad \text{O} \quad \text{C} \quad \text{C} \\
   \text{R}_4 \quad \text{R}_5 \quad \text{R}_6
   \end{array}
   \]

   wherein,
   
   \( \text{R} \) is independently selected from the alkyl groups or radicals of 1 to 18 carbon atoms in their various isomeric forms and substituted on the phenolic nucleus in the ortho-, meta- or para-positions; alicyclic groups of 5 to 18 carbon atoms such as cyclohexyl, cyclopentyl, methyl cyclohexyl, or butyl-cyclohexyl; alkyl and alicyclic ketonic groups; alkyl and alicyclic carbonylic groups and aryl substituted alkyl wherein the aryl is phenyl which may contain lower alkyl and/or hydroxyl substituents so that the resulting phenol is for example a bisphenol;

   \( \text{R}_1 \) and \( \text{R}_2 \) are independently hydrogen; alkyl groups or radicals of 1 to 8 carbon atoms; or cycloalkyls;

   \( \text{R}_3 \) and \( \text{R}_6 \) are independently hydrogen or methylol groups;

   and \( x \) plus \( y \) is at least 1.

2. The rubber composition of Claim 1, wherein the alkylphenol resole type mixtures are modified by reacting with an amine compound selected from the group comprising the general formula

   \[
   \begin{array}{c}
   \text{R}_3 \quad \text{NH} \quad \text{R}_4
   \end{array}
   \]

   wherein \( \text{R}_3 \) and \( \text{R}_4 \) are independently selected from the group consisting of hydrogen, alkyl group of 1 to 6 carbon atoms; alkenyl group of 2 to 6 carbon atoms; aryl and substituted aryl; hydroxyethyl; hydroxypropyl; carboxyalkyl; and together with nitrogen forming a heterocyclic 5 or 6 membered ring;

3. The rubber composition of Claim 1, wherein the alkylphenol resole type mixtures are modified by reacting with amine compounds and rosins selected from the group
comprising a mixture of C_{20}, fused-ring, monocarboxylic acids, typified by levopimaric and abietic acid; gum rosin, wood rosin and tall oil rosin.

4. The rubber composition of Claim 1, wherein the alkylphenol resole type mixtures are modified by reacting with amine compounds, rosins and fatty acids selected from the group comprising saturated or unsaturated mono-carboxylic acids having at least 8 carbon atoms in the chain.

5. The rubber composition of Claim 1, wherein the alkylphenol aldehyde reaction mixtures before the modification with amines, rosins and fatty acids contain resole type products comprising the following structures:

\[ \text{\includegraphics[width=0.5\textwidth]{image.png}} \]

wherein R is independently selected from the alkyl groups or radicals of 1 to 18 carbon atoms; R1 and R2 groups can be independently hydrogen; alkyl groups or radicals of 1 to 8 carbon atoms; a cycloalkyl; and the sum of x and y is at least one.

6. The rubber composition of Claim 5, wherein the alkylphenol is selected from the group comprising para – tertiary- butylphenol (PTBP), para-secondary-butylphenol, para-tert-hexylphenol, para-isoctylphenol; para-tert-
octylphenol (PTOP), para-cylohexylphenol, para-decylphenol, para-dodecylphenol, para-tetradecyl phenol, para-octadecylphenol, para-nonylphenol, para-methylphenol, para-pentadecylphenol and para-cetylphenol.

7. The rubber composition of Claim 2, wherein the amine compounds is selected from the group comprising 1, 8-p-methane diamine, ethylene diamine, triethylene tetramine, 1, 3-bis(aminomethyl) cyclohexane, m-xylylenediamine, monoethanolamine, diethanolamine and morpholine.

8. The rubber composition of Claim 3, wherein the rosin is selected from the group comprising gum rosin, wood rosin, and tall oil rosin or the rosin acids contained therein as for example, abietic acid, pimic acid and sapinic acid.

9. The rubber composition of Claim 1, wherein the fatty acid is selected from the group consisting of caprylic, capric, undecylic, lauric, stearic, and oleic.

10. A process for preparing the modified phenolic tackifying resins comprising the steps of:

   (i) first preparing an alkylphenol-aldehyde resin of resoles type mixtures comprising the following structure:

   ![Chemical Structure](image)

   wherein

   R is independently selected from the alkyl groups or radicals of 1 to 18 carbon atoms in their various isomeric forms and substituted on the phenolic nucleus in the ortho-, meta- or para-positions; alicyclic groups of 5 to 18 carbon atoms such as cyclohexyl, cyclopentyl, methyl cyclohexyl, or butyl-cyclohexyl; alkyl and alicyclic ketonic groups; alkyl and alicyclic carboxylic groups andaryl substituted alkyl wherein the aryl is phenyl which may contain lower alkyl and/or hydroxyl substituents so that the resulting phenol is for example a bisphenol;
R₁ and R₂ are independently hydrogen; alkyl groups or radicals of 1 to 8 carbon atoms; or cycloalkyls;

R₃ and R₄ are independently hydrogen or methylol groups;

and x plus y is at least 1;

(ii) then the resulting resole is first reacted with a primary or secondary aliphatic or aromatic amine having the following general structure:

\[ R_3 - \text{NH} - R_4 \]

wherein R₃ and R₄ are independently selected from the group comprising hydrogen, alkyl group of 1 to 6 carbon atoms; alkenyl group of 2 to 6 carbon atoms; aryl and substituted aryl; hydroxyethyl; hydroxypropyl; carboxyalkyl; and together with nitrogen forming a heterocyclic 5 or 6 membered ring; and

(iii) then the resulting resole and amine reaction mixture is modified with rosin and or fatty acids.

11. The process for preparing the modified phenolic tackifying resins according to Claim 10, wherein the alkylphenol-aldehyde resin of resole type can be directly prepared from the reaction of an alkylphenol with an aldehyde in the presence of base catalysts.

12. The process for preparing the modified phenolic tackifying resins according to Claim 10, wherein the alkylphenol-aldehyde resin of resole type can be prepared from the reaction of an alkylphenol novolak resin with an aldehyde in the presence of base catalysts.

13. The process for preparing the modified phenolic tackifying resins according to Claim 12, wherein the alkylphenol novolak resin can be prepared from the reaction of an alkylphenol with an aldehyde in the presence of acid catalysts.

14. The process for preparing the modified phenolic tackifying resins according to Claim 10, wherein the alkylphenol can be selected from the group comprising para – tertiary-butylphenol (PTBP), para-secondary-butylphenol, para-tert-hexylphenol, para-isoctylphenol; para-tert-octylphenol (PTOP), para-cydohexylphenol, para-decylphenol,
para-dodecylphenol, para-tetradecyl phenol, para-octadecylphenol, para-nonylphenol, para-methylphenol, para-pentadecylphenol and para-cetylphenol.

15. The process for preparing the modified phenolic tackifying resins according to Claim 11, wherein the base catalysts can be selected from the group comprising ammonium hydroxide; tertiary amines such as triethylamine, triethanolamine, diethyl cyclohexyl amine, triisobutyl amine; alkali and alkaline earth metal oxides and hydroxides.

16. The process for preparing the modified phenolic tackifying resins according to Claim 13 wherein the acid catalysts can be selected from the group comprising ethanesulfonic acid, benzenesulfonic acid, benzenedisulfonic acid, chlorobenzenesulfonic acid, 3,4-dichlorobenzene sulfonic acid, cresolsulfonic acids, phenol sulfonic acids, tolenesulfonic acids, xylenesulfonic acids, octylphenolsulfonic acid, naphthalenesulfonic acid, 1-naphthol-4-sulfonic acid, dodecylsulfonic acid and oxalic acid.

17. The process for preparing the modified phenolic tackifying resins according to Claim 10 wherein the rosin is selected from the group comprising gum rosin, wood rosin, and tall oil rosin or the rosin acids contained therein as for example, abietic acid, pimaric acid and sapinic acid.

18. The process for preparing the modified phenolic tackifying resins according to Claim 10 wherein the fatty acid can be selected from the group comprising caprylic, capric, undecylic, lauric, stearic, and oleic.

19. The process for preparing the modified phenolic tackifying resins according to Claim 10, wherein the aldehyde is selected from the group consisting of aqueous formaldehyde, paraformaldehyde, trioxane, acetaldehyde, propionaldehyde, n-butyaldehyde, isobutyraldehyde, n-valeraldehyde, heptaldehyde, octaldehyde, paraldehyde, furfural, 2-ethylhexanal, ethylbutyaldehyde and glyoxal.

20. The process for preparing the modified phenolic tackifying resins according to Claim 10, wherein the primary or secondary amine can be selected from the group consisting of 1, 8-p-menthane diamine, ethylene diamine, triethylene tetramine, 1, 3-bis-
(aminomethyl) cyclohexane, m-xylylenediamine, monoethanolamine, diethanolamine and morpholine.

21. The improved rubber compositions according to Claim 1 and their use, wherein the synthetic rubbers can be selected from the group consisting of butadiene rubber (BR), styrene-butadiene rubber (SBR), halogenated isoprene isobutylene rubber (XITIR), nitrile rubber (NBR), hydrogenated nitrile rubber (HNBR), EPDM and chloroprene rubber (CR).

22. The use of the improved rubber compositions according to Claim 1, wherein the rubber compositions can be used for any part of a tyre, for example, side wall compounds, apex, inner liners, under tread cement and, are also useful in general for a wide variety of industrial goods, such as rubber based products or goods, or pressure sensitive adhesives and hot melts.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C08L21/; C08L7/; C08L9/; C08L11/; C08L13/; C08L15/; C08L17/; C08L19/; C08L61/00; C08L61/06; C08L61/08, C08L61/10; C08L61/12; C08L61/14; C08G8/28; C08G8/32; C08G8/34; C09J121/; B60C1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI; EPODOC; PAJ; CNKI; CPRS; resol, resole, +amino+, resin, +morpholin?, +amine?, acid, rubber, fatty, aliphatic, oil, stearic, oleic, capric, caprylic, lauric

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
</table>

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
  “A” document defining the general state of the art which is not considered to be of particular relevance
  “E” earlier application or patent but published on or after the international filing date
  “L” document which may throw doubts on priority claim (S) or which is cited to establish the publication date of another citation or other special reason (as specified)
  “O” document referring to an oral disclosure, use, exhibition or other means
  “P” document published prior to the international filing date but later than the priority date claimed
  “T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
  “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
  “Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
  “&” document member of the same patent family

Date of the actual completion of the international search 23 March 2009 (23.03.2009)

Date of mailing of the international search report 02 Apr. 2009 (02.04.2009)

Name and mailing address of the ISA/CN
The State Intellectual Property Office, the P.R.China
6 Xitucheng Rd., Jinnen Bridge, Haidian District, Beijing, China 100088
Facsimile No. 86-10-62019451

Authorized officer LI, Kaiyang
Telephone No. (86-10)62084429

Form PCT/ISA/210 (second sheet) (April 2007)
<table>
<thead>
<tr>
<th>Patent Documents referred in the Report</th>
<th>Publication Date</th>
<th>Patent Family</th>
<th>Publication Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>EP1902864A1</td>
<td>26.03.2008</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>JP8302159A</td>
<td>19.11.1996</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP0361103A</td>
<td>04.04.1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BRP8904615A</td>
<td>26.06.1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP2175771A</td>
<td>09.07.1990</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP0361103B1</td>
<td>11.01.1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE58908875G</td>
<td>23.02.1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ES2066814T3</td>
<td>16.03.1995</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP57002319A</td>
<td>07.01.1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP57061017A</td>
<td>13.04.1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP57061071A</td>
<td>13.04.1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP57061072A</td>
<td>13.04.1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US4398016A</td>
<td>09.08.1983</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP0041838B</td>
<td>05.02.1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td>DE3173701G</td>
<td>20.03.1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP62005469B</td>
<td>05.02.1987</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP62005470B</td>
<td>05.02.1987</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP63062523B</td>
<td>02.12.1988</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP1034278B</td>
<td>18.07.1989</td>
</tr>
</tbody>
</table>

Form PCT/ISA/210 (patent family annex) (April 2007)
INTERNATIONAL SEARCH REPORT

CLASSIFICATION OF SUBJECT MATTER

C08L21/00 (2006.01) i
C08L61/14 (2006.01) i
C08G8/32 (2006.01) i
C08G8/34 (2006.01) i
C09J121/00 (2006.01) i
B60C1/00 (2006.01) i
C08G8/28 (2006.01) n

International application No.
PCT/CN2008/071450

Form PCT/ISA/210 (extra sheet) (April 2007)