EUROPEAN PATENT SPECIFICATION

(54) Rubber compositions for tyre treads, preparation thereof
Gummimischungen für Reifenlaufflächen und deren Herstellung
Compositions de caoutchouc pour bandes de roulement de pneus et leur préparation

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(56) References cited:
EP-A- 0 349 472

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Description

This invention relates generally to compositions for tire treads, and more particularly to compositions for tire treads which contain emulsion polymers blended with 1,4 cis-polyisoprene, either as a synthetic or natural rubber. A particular preferred aim is the provision of emulsion polymer/natural rubber tire tread compositions which have properties comparable to solution polymer/natural rubber tire tread compositions, and superior to those of tire treads formed with emulsion styrene-butadiene/natural rubber blends.

Background

There are many different properties which are desirable in automotive tires, and the designers and builders of tires utilize many different rubber blends for different tire components, such as treads, side walls, etc. in an attempt to optimize the various properties of the tire. One of the component of a tire is the tire tread component and this component itself requires many different properties which designers attempt to optimize. For example, lower energy consumption of vehicles is a continuing goal and one factor in the energy consumption of vehicles is the rolling resistance of the tire which is a function primarily of the tire tread composition. Additionally, it is desirable to have a high wear resistance of the tread to avoid early or premature wear of the tire which takes place due to normal operating and certain abnormal conditions. Additionally, it is not only desirable but essential to have a reasonably good traction of the tire so that it provides the necessary skid resistance to the vehicle. Moreover it is also desirable to have a relatively low $T_{g}$ (i.e. glass transition temperature) of the tire in order that the tires will not fail in extremely cold weather. Moreover, various ingredients of the rubber compositions while improving one property may adversely affect one or more of the other properties. Thus, a primary task of the tire designers and makers is to provide a rubber composition for the tread component of the tire which seeks to optimize these various properties by balancing the selection of relative amounts of these ingredients without causing any one of desired properties to be unduly unfeasible or unacceptable.

In the blending of the compositions for use as a tire tread component, it is conventional to blend natural rubber with different synthetic rubbers formed by various polymerization processes. Some of the original work done in this field provided polymer blends of various butadiene rubbers with emulsion SBR. Emulsion polymerization was developed extensively and there is extensive use of emulsion polymerization because of certain technological advantages as well as economic advantages in using existing equipment. EP-A-0 349 472 discloses a tire having an outer tread including cis 1,4-polyisoprene and SBR prepared by polymerizing styrene, isoprene and butadiene in a non-polar aliphatic solvent. However, emulsion polymerization has some draw backs and limitations as to the type of products it can produce. Specifically, emulsion polymerization generally does not permit much control of the diene microstructure of the produced rubbers, such as the percent of vinyl in the polymerized product. This in turn has posed limitations as to the properties which could be achieved, since microstructure features such as the amount of vinyl groups and other configurations, affect some significant properties of the end product.

These drawbacks, which are limitations in emulsion polymerization, were overcome by the development of solution polymerization of synthetic rubbers. In solution polymerization there is the possibility of using different catalysts and modifiers, different solvents, different temperatures and varying other types of ingredients and conditions to more closely control the resulting microstructure over a much broader range of polydiene microstructures, especially the ability to control the vinyl content over a much broader range than with emulsion polymerisation which generally is limited to the range of about 18 to 24% vinyl. However, solution polymerisation requires new facilities and cannot be accomplished in those facilities which are constructed and utilised for emulsion polymerisation without extensive re-construction. Further, solution polymerisation requires the use of organic solvents and expensive materials as well as requiring complex recovery systems for the waste products.

The aim of the invention is to provide novel rubber compositions, in particular suitable for use in the manufacture of tyre treads, methods of making and using them, and in particular the novel use of a certain type of synthetic polymer rubber in such a composition.

Aspects of the invention are set out in the claims.

In a general aspect, the invention proposes the use of emulsion-polymerised rubber which is a copolymer of isoprene monomer with styrene and/or butadiene monomer(s) as a blend component in a rubber composition, suitable for use in or as a tyre tread composition. A 1,4 cis-polyisoprene component such as natural rubber is blended with the emulsion copolymer rubber in making the rubber composition.

By the use of such an emulsion-copolymer rubber in the blend, we have found that we can prepare rubber compositions providing in combination good wear resistance, rolling resistance, low $T_{g}$ and good traction in corresponding tyre tread properties. Indeed, properties obtained in embodiments are comparable to those previously obtainable only by using solution-polymerised synthetic rubbers in the mixture.

The relative proportions of the emulsion-polymerised copolymer rubber and the polyisoprene/natural rubber may be adjusted in accordance with the desired properties, determinable by the skilled man using standard tests. Typically
the emulsion-polymerised copolymer rubber constitutes at least 30wt% of rubber in the composition. Typically the 1,4 cis-polyisoprene constitutes at least 30wt% of rubber in the composition. Rubber in the composition may consist essentially of (i.e. at least 90wt% and preferably all) said two types of rubber e.g. 30 to 70wt% of each complementarily. The relative weight proportions of the two rubber types may be substantially the same in the composition, or broadly from 4:6 to 6:4, more broadly from 3:7 to 7:3.

The emulsion copolymer rubber desirably comprises at least 9wt% of the non-isoprene (styrene and/or butadiene) monomer(s).

In a further aspect, the invention provides a method comprising the preparation of a rubber composition by blending the rubbers as defined, which method may include the prior preparation of the copolymer rubber by emulsion copolymerisation.

In further aspects, the invention provides a method comprising preparing a vulcanisable tyre tread composition using the rubber composition, and a vulcanisable tyre tread composition obtained thereby.

In a further aspect, the invention provides a vulcanised tyre tread of the above-defined tyre tread composition, in particular a tyre having such a tread.

Description of the Drawings

Figure 1 is a graphical plotting of the values of Tan δ for various compositions of tyre tread material; Figure 2 is a graphical plotting of μ-Wet of various compositions of tyre tread material.

Description of the Preferred Embodiment

The synthetic rubbers used in the tyre tread compositions embodying the new concepts, including styrene-isoprene (E-SIR), isoprene-butadiene (E-IBR), or styrene-isoprene-butadiene rubber (E-SIBR), were prepared by cold emulsion polymerization. E-SIR was prepared according to the recipe in Table I. The cold emulsion polymerizations were accomplished by conventional free radical polymerization techniques well known in the art. See for example, *Synthetic Rubber,* G.S. Whitby, C.C. Davis, and R.E. Dunnbrook, Eds., Pg. 213-219 John Wiley & Sons, Inc. New York, New York.

| TABLE I |
|-----------------|-----------------|
| Ingredient      | Parts by Weight|
| Isoprene        | 82.0            |
| Styrene         | 18.0            |
| Water           | 175.0           |
| Rosin Acid Soap (Dresinate 214) | 5.0 |
| t-Dodecanethiol | 0.14            |
| p-Menthane Hydroperoxide | 0.1 |
| Trisodium Phosphate | 0.5 |
| Ferrous Sulfate | 0.008           |
| Sodium Formaldehyde Sulfoxylate | 0.01 |
| Sodium Hydroxide | 0.006         |
| Sequestrene AA  | 0.015           |
| Tamol SN        | 0.5             |
| Polymerization Temperature (°C) | 5 |
| Polymerization Time (Hrs.) | 15 |
| % Conversion    | 61              |

For comparison purposes, emulsion polymers of styrene/butadiene (E-SBR) were prepared which represent conventional prior art emulsion polymerization rubber compositions, as well as medium-vinyl solution polymers of styrene/butadiene rubber (MVSBR).

The microstructure (as determined by high field proton NMR), glass transition temperature (T_g) and molecular weight are listed for these three compositions in Table II.
The MVSB was prepared in cyclohexane with N-butylithium and tetramethylenediamine. The emulsion styrene-butadiene rubber was prepared using the recipe of Table 1 but with butadiene substituted for isoprene.

Rubber compositions were then prepared according to the formulations shown in Table III. These were prepared with the compounds being mixed on a two roll 254mm (10") mill and then cured at a 160°C to maximum torque as measured by a Monsanto Rheometer. Tread vulcanization properties were determined as follows: Loss tangent delta (Tan δ) was measured by means of an instrumented Yerzley Oscillograph (YO) at room temperature and 5Hz. The Yerzley Oscillograph is a good predictor of twin-roll rolling resistance of tire tread material formulations. The lower the Tan δ value, the lower the rolling resistance; lower rolling resistance is a desirable property. Wet coefficient of friction (μ-Wet) was measured with an instrumented British Portable Skid Tester (IPST) on a smooth concrete surface. This test shows good correlation of μ-Wet with wet tire traction data (peak traction at 96.6 kilometers per hour). The higher the μ-Wet the better the traction performance on a wet concrete road. For comparison purposes this instrument measured a μ-Wet of 0.629 for a 65/35 emulsion SBR/Cis-BR tread formulation used on the ASTM pavement skid resistance test tire.

The comparison of the various tread vulcanizate properties of the three different rubbers blended with natural rubber in a 50:50 ratio is shown in Table IV below. With the styrene content at a level of about 15% by weight, the main variables include the diene microstructure and type of polydiene. As can be seen from the examination of Table II, the Tg of the E-SIR is higher than that of the E-SBR and the Tg of the medium vinyl SBR with 45% vinyl content is intermediate to that of the emulsion polymers. The data in Table IV indicates that the rolling resistance (Tan δ) of E-SIR is
significantly lower than E-SBR and nearly the same as MVSBR. However, the E-SIR has a lower μ-Wet and lower Pico abrasion resistance than a MVSBR. E-SIR can be seen to have slightly better wet traction behavior but lower Pico abrasion resistance than E-SBR. The Pico Abrasion test was run as described in ASTM D 2228. The higher the number, the better the abrasion resistance. In summary, it appears that the emulsion polymer E-SIR has values very comparable to the medium-vinyl solution-polymerized rubber and has much better rolling resistance and better traction than the emulsion styrene-butadiene rubber.

<table>
<thead>
<tr>
<th>TABLE IV</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comparison of Tread Properties</strong> Using E-SBR, E-SIR, and MVSBR</td>
</tr>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>E-SIR</td>
</tr>
<tr>
<td>E-SBR</td>
</tr>
<tr>
<td>MVSBR**</td>
</tr>
</tbody>
</table>

** Tread Compound: Table III, Formulation A
** 45%, 1.2, 15% styrene

To compare the properties of the synthetic rubbers, various tests were performed on the E-SIR, E-SBR and MVSBR in the unfilled condition which test results are shown in Table V. This data in Table V shows that in the absence of carbon black and natural rubber, emulsion polymer SIR is very comparable to the MVSBR and both the E-SIR and the MVSBR have tan δ values significantly better than the E-SBR.

<table>
<thead>
<tr>
<th>TABLE V</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comparison of Yerzley Tan Delta Values of Unfilled Vulcanizes</strong> of E-SIR, Solution MVSBR, and E-SBR</td>
</tr>
<tr>
<td>Polymer**</td>
</tr>
<tr>
<td>E-SIR</td>
</tr>
<tr>
<td>MVSBR</td>
</tr>
<tr>
<td>E-SBR</td>
</tr>
</tbody>
</table>

** Recipe: Table III, Formulation B
** Polymers same as shown in Table II

Table VI below shows certain characteristics of Emulsion IR as compared to Solution IR and natural rubber, including microstructure and key tread property indicators. This includes Tan δ and μ-Wet skid coefficient of friction and Pico abrasion resistance test.

<table>
<thead>
<tr>
<th>TABLE VI</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Comparison of Tread Properties</strong> Using Emulsion and Solution Polysoprenes</td>
</tr>
<tr>
<td>Polymer</td>
</tr>
<tr>
<td>% Microstructure</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Emulsion IR</td>
</tr>
<tr>
<td>Solution IR</td>
</tr>
<tr>
<td>Natural Rubber</td>
</tr>
</tbody>
</table>

** Tread Compound: Table III, Formulation C

Since the cost of butadiene monomer is less than isoprene monomer, various different compositions of polymers which substituted butadiene for some of the isoprene monomer were formulated. The various polymers were then blended at a ratio of 50:50 with natural rubber as shown in Table VII to formulate tire tread compositions. The results of various tests to determine tread vulcanize properties of these formulations are shown in Table VII; specifically, the Yerzley Tan δ, Pico abrasion index and IPST μ-Wet are shown for various blends of these rubbers. The Yerzley tan δ values are also shown graphically in Figure 1 and the μ-Wet properties are also shown graphically in Figure 2.
TABLE VII

<table>
<thead>
<tr>
<th>Example</th>
<th>Polymer Comp**</th>
<th>Bdl/1 St</th>
<th>Yerzley Tan Delta (Rolling Res.)</th>
<th>Pico Abrasion Index (Wear Res.)</th>
<th>IPST,μ-Wet (Traction)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0/91/9</td>
<td>0.188</td>
<td>80</td>
<td>0.628</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>18/78/4</td>
<td>0.160</td>
<td>86</td>
<td>0.619</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8/80/12</td>
<td>0.179</td>
<td>80</td>
<td>0.619</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>30/53/17</td>
<td>0.208</td>
<td>83</td>
<td>0.622</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>43/57/0</td>
<td>0.183</td>
<td>92</td>
<td>0.590</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>36/55/9</td>
<td>0.194</td>
<td>85</td>
<td>0.607</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>36/55/9</td>
<td>0.192</td>
<td>88</td>
<td>0.599</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>62/31/7</td>
<td>0.203</td>
<td>91</td>
<td>0.572</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>59/27/14</td>
<td>0.199</td>
<td>88</td>
<td>0.596</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>85/8/7</td>
<td>0.197</td>
<td>91</td>
<td>0.589</td>
<td></td>
</tr>
</tbody>
</table>

* Compound: Table III, Formula A.
**Composition determined 13C NMR.

As indicated earlier, the lower the value of Yerzley Tan δ, the lower the rolling resistance of the tire; the higher the Pico abrasion index, the better the abrasion resistance of the tire; and the greater the value of the IPST μ-Wet, the better traction properties of the tire. As can be seen from Table VII and Figures 1 and 2, Examples 2, 3 and 5 have the best values for the Yerzley tan δ value and therefore the best performance with respect to rolling resistance. Examples 1, 2, 3 and 4 have the best μ-Wet, thus the best traction. Thus, Compositions 2 and 3 have the best combination of these two values with Example 1 also having a good combination of these values although all of the examples given are acceptable. It should be noted, however, that when the μ-Wet drops below about .600, the traction value becomes less desirable and thus, Compositions 5, 7, 8, 9 and 10 are less desirable than the compositions of Examples 2 and 3 which are the preferred examples. Between Examples 2 and 3, Example 2 has the better abrasion resistance which makes it the preferred composition for tire treads. Thus, broadly, the present invention includes a rubber composition having a mixture of between 30% and 70% of 1,4 cis-polyisoprene, preferably 50% thereof and between 70% and 30% of an emulsion copolymer rubber comprised of an isoprene monomer and a second monomer selected from the group of butadiene and styrene and mixtures thereof, preferably 50% thereof. Further, while neither styrene or butadiene may be used, it is preferred that both styrene and butadiene be present in the ranges of 4-17% and more preferably 4-16% and most preferably 4-14% styrene monomer, and 8-85%, more preferably 8-80% and most preferably 8-30% butadiene monomer.

Finally, compositions were mixed using mixtures of emulsion isoprene-styrene rubber, natural rubber and low-vinyl styrene-butadiene rubber and compared with compositions containing medium-vinyl solution styrene-butadiene rubber (MVSBR), low-vinyl solution styrene-butadiene rubber (LVSBR) and natural rubber. These results are shown in Table VIII. As can be seen in Table VIII good results are obtained when the emulsion isoprene-styrene rubber is substituted for MVSBR with there actually being an improvement in the Yerzley tan δ for rolling resistance and an improvement in wet traction with μ-Wet and essentially no change in abrasion resistance.
### TABLE VIII

*Comparison of Tread Properties* of Blends Containing E-SIR vs. MVSB

<table>
<thead>
<tr>
<th>Polymer Composition (Blend Right)</th>
<th>Tensile Strength (MPa)</th>
<th>Yerzley Tan δ (Rolling Res.)</th>
<th>Abrasion Index (Wear Res.)</th>
<th>IPST, μ-Wet Angle, Pico Abrader***</th>
</tr>
</thead>
<tbody>
<tr>
<td>85-15 Isoprene-Styrene/NR/LVSBR (33/31/36), BS358-95A</td>
<td>16.6</td>
<td>0.362</td>
<td>90</td>
<td>102</td>
</tr>
<tr>
<td>MVSBR/NR/LVSBR</td>
<td>17.2</td>
<td>0.378</td>
<td>91</td>
<td>100</td>
</tr>
</tbody>
</table>

* Compound: Table III, Formulation D

** MVSBR: 15% Styrene, 45% vinyl  
   LVSBR: 21% Styrene, 10% vinyl

*** Modified Goodyear Angle Abrader with a test angle of 11°
be readily apparent to those skilled in the art. For example, natural rubber is used in formulating the tire tread compositions in the examples. However, 1,4 cis-polyisoprene synthetic rubber may also be used to achieve similar results. While the present examples have been described in a certain amount of detail, various adaptations and modifications can be made to the exact compositions.

Claims

1. A rubber composition suitable for use in preparing a tyre tread, comprising
   (a) a first, 1,4 cis-polyisoprene rubber, and
   (b) a second rubber which is an emulsion copolymer of
      (i) isoprene with
      (ii) butadiene, styrene, or butadiene and styrene.

2. A composition according to claim 1 in which the second rubber copolymer comprises at least 9wt% of the butadiene and/or styrene component (ii).

3. A composition according to claim 1 or claim 2 in which the second rubber copolymer includes both butadiene and styrene monomers.

4. A composition according to any one of claims 1 to 3 in which the second rubber copolymer is made from at least 50wt% isoprene monomer.

5. A composition according to any one of the preceding claims in which the second rubber copolymer comprises residues of from 4 to 17wt% styrene monomer and from 8 to 80wt% butadiene monomer.

6. A composition according to claim 5 in which the second rubber copolymer comprises residues of from 4 to 14wt% styrene monomer and from 8 to 30wt% butadiene monomer.

7. A composition according to claim 6 in which the second rubber copolymer comprises residues of about 4wt% styrene monomer and about 15wt% butadiene monomer.

8. A composition according to any one of the preceding claims in which the 1,4 cis-polyisoprene rubber is natural rubber.

9. A composition according to any one of the preceding claims comprising at least 30wt% of each of the first and second rubbers.

10. A composition according to claim 9, consisting essentially of 30 to 70wt% of the first rubber and 70 to 30wt% of the second rubber.

11. A composition according to claim 10, comprising substantially equal weight proportions of the first and second rubbers.

12. A method of preparing a rubber composition suitable for use in preparing a tyre tread, the method comprising
   (a) providing a first, 1,4 cis-polyisoprene rubber;
   (b) preparing a second rubber which is an emulsion copolymer of
      (i) isoprene with
      (ii) butadiene, styrene or butadiene and styrene; and
   (c) combining said first and second rubbers.

13. A method according to claim 12 in which the second rubber copolymer comprises at least 9wt% of the butadiene and/or styrene component (ii).
14. A method according to claim 12 or claim 13 in which the second rubber copolymer includes both butadiene and styrene monomers.

15. A method according to any one of claims 12 to 14 in which the second rubber copolymer is made from at least 50wt% isoprene monomer.

16. A method according to any one of claims 12 to 15 in which the second rubber copolymer comprises residues of from 4 to 17% styrene monomer and from 8 to 80wt% butadiene monomer.

17. A method according to claim 16 in which the second rubber copolymer comprises residues of 4wt% styrene monomer and from 8 to 30wt% butadiene monomer.

18. A method according to claim 17 in which the second rubber copolymer comprises residues of about 4wt% styrene monomer and about 18wt% butadiene monomer.

19. A method according to any one of claims 12 to 18 in which the 1,4 cis-polysoprene rubber is natural rubber.

20. A method according to any one of claims 12 to 19 in which said composition comprises at least 30wt% of each of the first and second rubbers.

21. A method according to claim 20, in which said composition comprises 30 to 70wt% of the first rubber and 70 to 30wt% of the second rubber.

22. A method according to claim 21, in which said composition comprises substantially equal weight proportions of the first and second rubbers.

**Patentansprüche**

1. Gummizusammensetzung, die sich zur Herstellung einer Reifenlauffläche eignet, umfassend
   (a) einen ersten 1,4-cis-Polysoprenkautschuk,
   dadurch gekennzeichnet, daß sie weiters umfaßt:
   (b) einen zweiten Kautschuk, der ein Emulsionscopolymer von

   (i) Isopren mit
   (ii) Butadien, Styrol oder Butadien und Styrol ist.

2. Zusammensetzung nach Anspruch 1, worin das Copolymer des zweiten Kautschuks zumindest 9 Gew.-% der Butadien und/oder Styrol-Komponente (ii) umfaßt.


8. Zusammensetzung nach einem der vorangegangenen Ansprüche, worin der 1,4-cis-Polysoprenkautschuk Naturkautschuk ist.

10. Zusammensetzung nach Anspruch 9, die im wesentlichen aus 30 bis 70 Gew.-% des ersten Kautschuks und aus 70 bis 30 Gew.-% des zweiten Kautschuks besteht.


12. Verfahren zur Herstellung einer Gummizusammensetzung, die sich zur Verwendung bei der Herstellung einer Reifenlaufläche eignet, wobei das Verfahren folgendes umfaßt:

   (a) Bereitstellen eines ersten Kautschuks, nämlich 1,4-cis-Polyisoprenkautschuk;
   (b) Herstellung eines zweiten Kautschuks, der ein Emulsionscopolymer von

   (i) Isopren mit
   (ii) Butadien, Styrol oder Butadien und Styrol ist; und

   (c) Kombinieren des ersten und zweiten Kautschuks.


15. Verfahren nach einem der Ansprüche 12 bis 14, worin das Copolymer des zweiten Kautschuks aus zumindest 50 Gew.-% Isopren-Monomer hergestellt ist.


19. Verfahren nach einem der Ansprüche 12 bis 18, worin der 1,4-cis-Polyisoprenkautschuk Naturkautschuk ist.


Revendications

1. Composition de caoutchouc appropriée à une utilisation dans la préparation d’une bande de roulement de pneumatique, comprenant

   (a) un premier caoutchouc de 1,4 cis-polyisoprène, et

   (b) un second caoutchouc qui est un copolymère en émulsion de
2. Composition selon la revendication 1 dans laquelle le copolymère du second caoutchouc comprend au moins 9% en poids d’un composant de butadiène et/ou styrène (ii).

3. Composition selon la revendication 1 ou 2 dans laquelle le copolymère du second caoutchouc contient à la fois des monomères de butadiène et de styrène.

4. Composition selon l’une quelconque des revendications 1 à 3 dans laquelle le copolymère du second caoutchouc est formé de 50% en poids d’un monomère d’isoprène.

5. Composition selon l’une quelconque des revendications précédentes dans laquelle le copolymère du second caoutchouc comprend des résidus de 4 à 17% en poids du monomère de styrène et 8 à 80% en poids du monomère de butadiène.

6. Composition selon la revendication 5 dans laquelle le copolymère du second caoutchouc comprend des résidus de 4 à 14% en poids du monomère de styrène et de 8 à 30% en poids du monomère de butadiène.

7. Composition selon la revendication 6 dans laquelle le copolymère du second caoutchouc comprend des résidus d’environ 4% en poids du monomère de styrène et d’environ 18% en poids du monomère de butadiène.

8. Composition selon l’une quelconque des revendications précédentes dans laquelle le caoutchouc de 1,4 cis-polyisoprène est du caoutchouc naturel.

9. Composition selon l’une quelconque des revendications précédentes comprenant au moins 30% en poids de chacun des premier et second caoutchoucs.

10. Composition selon la revendication 9 consistant essentiellement en 30 à 70% en poids du premier caoutchouc et 70 à 30% en poids du second caoutchouc.

11. Composition selon la revendication 10, comprenant des proportions pondérales sensiblement égales des premier et second caoutchoucs.

12. Méthode de préparation d’une composition de caoutchouc appropriée à une utilisation dans la préparation d’une bande de roulement de pneumatique, la méthode consistant à

   (a) prévoir un premier caoutchouc de 1,4 cis-polyisoprène;

   (b) préparer un second caoutchouc qui est un copolymère en émulsion de

   (i) isoprène avec

   (ii) butadiène, styrène ou butadiène et styrène; et

   (c) combiner lesdits premier et second caoutchoucs.

13. Méthode selon la revendication 12 dans laquelle le copolymère du second caoutchouc comprend au moins 9% en poids du composant de butadiène et/ou de styrène (ii).

14. Méthode selon la revendication 12 ou la revendication 13 dans laquelle le copolymère du second caoutchouc comprend à la fois des monomères de butadiène et de styrène.

15. Méthode selon l’une quelconque des revendications 12 à 14 dans laquelle le copolymère du second caoutchouc est formé d’au moins 5% en poids de monomère d’isoprène.

16. Méthode selon l’une quelconque des revendications 12 à 15 dans laquelle le copolymère du second caoutchouc
comprend des résidus de 4 à 17% du monomère de styrène et de 8 à 80% en poids du monomère de butadiène.

17. Méthode selon la revendication 16 dans laquelle le copolymère du second caoutchouc comprend des résidus de 4% en poids du monomère de styrène et de 8 à 30% du monomère de butadiène.

18. Méthode selon la revendication 17 dans laquelle le copolymère du second caoutchouc comprend des résidus d'environ 4% en poids du monomère de styrène et d'environ 18% en poids du monomère de butadiène.

19. Méthode selon l'une quelconque des revendications 12 à 18 dans laquelle le caoutchouc de 1,4 cis-polyisoprène est du caoutchouc naturel.

20. Méthode selon l'une quelconque des revendications 12 à 19 dans laquelle ladite composition comprend au moins 30% en poids de chacun des premier et second caoutchoucs.

21. Méthode selon la revendication 20, dans laquelle ladite composition comprend 30 à 70% en poids du premier caoutchouc et 70 à 30% en poids du second caoutchouc.

22. Méthode selon la revendication 21, dans laquelle ladite composition comprend des proportions pondérales sensiblement égales des premier et second caoutchoucs.