US 20020000280A1

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0000280 A1**

**Scholl** (43) **Pub. Date: Jan. 3, 2002**

# (54) RUBBER MIXTURES FOR PRODUCING HIGHLY REINFORCED VULCANISATES WITH LOW DAMPING BEHAVIOUR

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(21) Appl. No.: **09/862,149**

(22) Filed: **May 22, 2001**

(30) **Foreign Application Priority Data**

May 24, 2000 (DE) ........................................ 10025625.2

**Publication Classification**

(51) **Int. Cl.**$^{7}$ ........................................ **C10L 1/00**
(52) **U.S. Cl.** ........................................ **152/519**; 585/5

(57) **ABSTRACT**

The rubber mixtures according to the invention consisting of a rubber, a filler and a specific sulphurized mineral oil are suitable for producing shaped vulcanizates, in particular for producing tires with reduced rolling resistance and high resistance to wet skidding, and tires with particularly reinforced side walls ("run flat tires").

# RUBBER MIXTURES FOR PRODUCING HIGHLY REINFORCED VULCANISATES WITH LOW DAMPING BEHAVIOUR

[**0001**] The present patent application relates to rubber mixtures consisting of rubber, filler and a specific sulphurised mineral oil. Vulcanisates with surprisingly good reinforcement- and temperature-dependent dynamic damping behaviour which are particularly suitable for producing tires with low-damping treads with a high resistance to wet skidding and for producing tires with low-damping highly reinforced lateral walls can be produced from the rubber mixtures according to the invention.

[**0002**] Mineral oils are often added to rubbers and rubber mixtures to improve the processing properties. The differing content of paraffinic, naphthenic and aromatic contents in the mineral oils is known to have a corresponding effect on the damping properties of the rubber vulcanisates produced, wherein, disadvantageously, it is not possible to improve both the rolling resistance and the resistance to wet skidding together in tires by altering the mineral oil composition, but only one of the two properties at the cost of the other. In this regard, see Kautschuk, Gummi, Kunststoffe 44, 1991, page 528 to 536.

[**0003**] Therefore, it was an object of the present invention to provide rubber mixtures containing a specific mineral oil which do not have these disadvantages in the damping behaviour of the vulcanisates.

[**0004**] Many methods of producing vehicle tires with low-damping tire treads and low-damping highly reinforced lateral walls have been investigated. U.S. Pat. No. 5,227,425 thus describes the production of tire treads with low rolling resistance and with high resistance to wet skidding made of solution SBR rubber, silica, conventional aromatic mineral oil and a polysulphide-containing silyl ether. The mineral oil certainly improves the flowability and processibility of the rubber mixtures, but simultaneously reduces the reinforcement level. To obtain acceptable reinforcement properties, large quantities of an expensive polysulphide-containing silyl ether are therefore required.

[**0005**] Therefore, a further object of the present invention was to provide mineral oil-containing rubber mixtures and vulcanisates with improved reinforcement behaviour.

[**0006**] JP-B 47 008 135 describes reaction products of aromatic mineral oils with sulphur monochloride for improving the processing behaviour of rubber mixtures. The modified mineral oils are produced by a method which predominantly leads to mono- and disulphide bridges due to the chemical nature of sulphur monochloride. Moreover, the sulphur monochloride used leads to an undesirable residue of bound chlorine in the end product.

[**0007**] It has now been found that rubber vulcanisates with exceptionally favourable dynamic damping behaviour and an exceptionally high reinforcement level can be obtained from rubber mixtures containing certain sulphurised mineral oils and that rubber mixtures of this type are suitable, in particular, for producing tires which are resistant to wet skidding with particularly low rolling resistance and for producing tires with low damping with highly reinforced lateral walls (“run flat tires”).

[**0008**] The present invention therefore relates to rubber mixtures consisting of a rubber, a fillet and optionally further rubber auxiliaries and cross-linking agents and 0.1 to 75 parts by weight, based on 100 parts by weight of rubber, of a specific sulphurised mineral oil, the sulphurised mineral oil having been obtained by reacting an aromatic-containing mineral oil with sulphur.

[**0009**] The sulphurised mineral oil used was produced according to the invention in that an aromatic-containing mineral oil with an aromatic content according to ASTM D 2140 of 5 to 50 wt. % and a viscosity-density constant VDK of 0.82 to 1.05 was reacted with 2.5 to 40 parts by weight of sulphur per 100 parts by weight of mineral oil at temperatures of 130 to 250° C., optionally in the presence of catalysts.

[**0010**] The sulphurised mineral oils according to the invention have a bound sulphur content of 2.5 to 12.5 wt. %, preferably 4 to 10 wt. %, and a glass transition temperature (determined by DSC) of −25 to −65° C., preferably −35 to −55° C., and a density of 0.85 to 1.1 g/cm$^3$, preferably 0.92 to 1.03 g/cm$^3$ (at 20° C.).

[**0011**] The viscosities are 0.3 to 100 Pa.sec, particularly preferably 0.8 to 20 Pa.sec at 20° C. (plate and cone viscometer, 20 rpm).

[**0012**] The starting products for producing the sulphurised mineral oils used according to the invention are aromatic-containing mineral oils with an aromatic content (according to ASTM D 2140) of 5 to 50%, preferably 15 to 40%, a viscosity-density constant VDK (according to ASTM D 2501) of 0.82 to 1.05, preferably 0.84 to 1.0. Preferred aromatic-containing mineral oils moreover have a density of 0.85 to 1.03 g/cm$^3$ (at 15° C.), preferably 0.9 to 1.0 g/cm$^3$ and a pour point (according to ASTM D 97) between −20° C. and +30° C., particularly preferably between −15° C. and +20° C., and contain less than 0.1 wt. %, preferably less than 0.005 wt. %, of polycyclic aromatic hydrocarbons and/or a DMSO-extract according to IP 346<3 wt. %. Mineral oil products of this type are commercially available; suitable products are, for example, Enerthene® 1849-1 (BP) and Catenex Oil SNR® (Shell). In this regard see Kautschuk, Gummi, Kunststoffe, 45 (1992), pages 24-29.

[**0013**] The reaction of aromatic-containing mineral oils with sulphur is preferably carried out with 5 to 20 parts by weight of sulphur per 100 parts by weight of aromatic-containing mineral oils at temperatures of preferably 160 to 220° C., particularly preferably 180 to 210° C., for a time period of a few minutes (5 min) up to several hours (10 hours), optionally in the presence of catalysts. Suitable catalysts are acidic or basic catalysts, such as zinc chloride, aluminium chloride, tin chloride, hydrogen sulphide and/or alkyl amines, such as dodecylamine or octadecylamine. Suitable quantities of catalysts are 0.01 to 3 parts by weight based on aromatic-containing mineral oil. However, the reaction is preferably carried out without a catalyst.

[**0014**] Following the reaction, residues of hydrogen sulphide and volatile mercaptans can be removed, for example, by applying a vacuum or blowing out with nitrogen or by chemical methods, such as oxidising agents (for example atmospheric oxygen or peroxides). Unreacted sulphur can be removed by filtering off, for example.

[**0015**] In addition to natural rubbers, synthetic rubbers are also suitable for producing the rubber mixtures and vulcanisates according to the invention. Preferred synthetic rubbers are described, for example, in W. Hofmann, Kautschuktechnologie, Gentner Verlag, Stuttgart 1980 and I. Franta, Elastomers and Rubber Coumpounding Materials, Elsevier, Amsterdam 1989. They include inter alia

**[0016]** BR—polybutadiene

**[0017]** ABR—butadiene acrylic acid-C1-4-alkyl ester copolymers

**[0018]** CR—polychloroprene

**[0019]** IR—polyisoprene

**[0020]** SBR—styrene/butadiene copolymers with styrene contents of 1-60, preferably 20-50 wt. %

**[0021]** IIR—isobutylene isoprene copolymers

**[0022]** NBR—butadiene acrylonitrile copolymers with acrylonitrile contents of 5-60, preferably 10-40 wt. %

**[0023]** HNBR—partially or completely hydrogenated NBR rubber

**[0024]** EPDM—ethylene propylene diene copolymers

**[0025]** and mixtures of these rubbers. Of interest for the production of car tires, are, in particular, natural rubber, emulsion SBR and solution SBR rubbers with a glass transition temperature above −50° C. which can optionally be modified with silyl ethers or other functional groups according to EP-A 447 066, polybutadiene rubber with a high 1.4-cis-content (>90%) produced by catalysts based on Ni, Co, Ti or Nd, and polybutadiene rubber with a vinyl content of up to 75% and mixtures thereof. Most particularly preferred are the so-called solution SBR and polybutadiene rubbers.

**[0026]** The rubber mixtures according to the invention contain the fillers known and used in the rubber industry; these include both the active and the inactive fillers, notably:

**[0027]** fine-particled silicas, produced, for example, by precipitation of solutions of silicates or flame hydrolysis of silicon halides with specific surface areas of 5 -1000, preferably 20-400 $m^2/g$ (BET surface area) and with primary particle sizes of 10-400 nm. The silicas can optionally be present as mixed oxides with other metal oxides, such as Al, Mg, Ca, Ba, Zn, Zr, Ti oxides;

**[0028]** synthetic silicates, such as aluminium silicate, alkaline-earth silicate such as magnesium silicate or calcium silicate, with BET surface areas of 20-400 $m^2/g$ and primary particle diameters of 10-400 nm;

**[0029]** natural silicates such as kaolin and other naturally occurring silicas;

**[0030]** glass-fibres and glass-fibre products (mats, strands) or glass microbeads;

**[0031]** metal oxides, such as zinc oxide, calcium oxide, magnesium oxide, aluminium oxide;

**[0032]** metal carbonates, such as magnesium carbonate, calcium carbonate, zinc carbonate;

**[0033]** metal hydroxides, such as for example, aluminium hydroxide, magnesium hydroxide;

**[0034]** carbon blacks. The carbon blacks to be used in this process are produced by the lamp black, furnace or gas black process and have BET surface areas of 20-200 $m^2/g$, for example, SAF, ISAF, HAF, FEF or GPF carbon blacks;

**[0035]** rubber gels

**[0036]** rubber powder, obtained, for example, by size-reduction of rubber vulcanisates. Preferred particle sizes are between 0.001 to 0.5 mm.

**[0037]** Fine-particle silicas and carbon blacks, optionally together with rubber powder, are preferably used as fillers.

**[0038]** The fillers mentioned can be used alone or in a mix, specifically in quantities of 1 to 300 parts by weight, preferably 10 to 150 parts by weight based on 100 parts by weight of rubber. In a particularly preferred embodiment, the rubber mixtures contain as fillers, a mixture of light fillers, such as fine-particled silicas, and carbon blacks, the mixing ratio of light filler to carbon blacks being 1:0.05 to 20, preferably 1:0.1 to 10.

**[0039]** The rubber mixtures according to the invention can obviously also contain other rubber auxiliaries and cross-linking agents. Sulphur or sulphur-supplying compounds or peroxides are used as cross-linking agents. Particularly preferred are sulphur or sulphur-supplying compounds in quantities of 0.01 to 3 parts by weight based on rubber.

**[0040]** Furthermore, as mentioned, the rubber mixtures according to the invention can contain further auxiliary agents, such as the known reaction accelerators, anti-ageing agents, heat stabilisers, light protection agents, ozone protection agents, process aids, reinforcing resins, for example phenolic resins, steel cord bonding agents, such as, for example, silica/resorcinol/hexamethylenetetramine or cobalt-naphthenate, plasticisers, tackifiers, blowing agents, dyes, pigments, waxes, extenders, organic acids, retarding agents, metal oxides and activators.

**[0041]** The rubber auxiliaries are used in the usual, known quantities, the quantity used depending on the subsequent intended purpose of the rubber mixtures. For example, normal quantities of rubber auxiliaries are in the range of 2 to 70 parts by weight, based on 100 parts by weight of rubber.

**[0042]** The use of additional filler activators is particularly advantageous for the rubber mixtures according to the invention which are filled with highly active silicas. Preferred filler activators are sulphur-containing silyl ethers, in particular bis-(trialkoxysilyl-alkyl)-polysulphides as described in DE-A 2 141 159 and DE-A 2 255 577. Further possibilities are oligomeric and/or polymeric sulphur-containing silyl ethers according to the description in DE-A 4 435 311 and EP-A 670 347. Mercapto-alkyltrialkoxysilanes, in particular mercaptopropyltriethoxysilane and thiocyanatoalkylsilylethers (see DE-A 19 544 469), amino group-containing silyl ethers, such as for example 3-amino-propyltriethoxysilane and N-oleyl-N-propyl-trimethoxysilane and trimethylolpropane. The filler activators are used in the usual quantities, i.e. in quantities of 0.1 to 15 parts by weight, based on 100 parts by weight of rubber.

**[0043]** The rubber mixtures according to the invention can be produced, for example, by mixing the rubbers with the fillers, rubber auxiliaries and the sulphurised mineral oils in suitable mixing apparatuses, such as kneaders, rollers or extruders, or by mixing the rubber solutions with fillers and the sulphurised mineral oils and removing the solvent, for example by steam distillation.

[**0044**] The present invention also relates to the use of the rubber mixtures according to the invention for producing vulcanisates which, in turn, are used for the production of highly reinforced rubber shaped articles, in particular for the production of tires.

[**0045**] Particularly preferred is the use of the rubber mixtures for producing tire treads with low rolling resistance and resistance to wet skidding and for producing particularly reinforced lateral walls for tires with emergency running properties ("run flat tires"), as described, for example, in U.S. Pat. No. 5,368,082, EP-A 475 258, U.S. Pat. No. 5,427,166, U.S. Pat. No. 5,511,599 and EP-A 943 466.

## EXAMPLES

### Example 1

### Sulphurised Mineral Oil with 5.3 wt. % of Bound Sulphur

[**0046**] 100 g sulphur were added to 1,000 g Enerthene 1849-1 (solvent-refined mineral oil from BP, aromatics content according to ASTM D 2140: 24%, density 0.945 g/cm$^3$, S content 0.9%, pour point 0° C., VDK 0.884, polycyclic aromatic compound content <50 ppm), DMSO-extract (according to IP 346): 2.2 wt.%) and heated for 2 hours to 200° C., hydrogen sulphide being released. A vacuum was then applied for 10 minutes at 110° C. to remove the released hydrogen sulphide. 1,045 g of a black oil were obtained with a sulphur content of 5.3 wt.%, viscosity 5 Pa.sec (plate and cone, 20 rpm, 20° C.), glass transition temperature of −50° C. (according to DSC) and density 0.97g/cm$^3$.

### Example 2

### Rubber Mixtures and Vulcanisates

[**0047**] The following rubber mixtures were produced in a 1.51 kneader. (Mixing time: 5 minutes, speed 60 rpm). The sulphur and accelerators were finally added on a roller at 50° C.:

| | Comparison 2.1 | Example 2.A | Example 2.B |
|---|---|---|---|
| Mixed in the kneader: | | | |
| L-SBR Buna VSL 5025-0 (Bayer AG) | 70 | 70 | 70 |
| Polybutadiene Buna CB 25 (Bayer AG) | 30 | 30 | 30 |
| Silica Vulkasil 5 (Bayer AG) | 70 | 70 | 70 |
| Aromatic mineral oil Enerthene 1849-1 (BP) | 37.5 | 17.5 | 0 |
| Sulphurised mineral oil, Example 1 | 0 | 20 | 37.5 |
| Zinc oxide | 2.5 | 2.5 | 2.5 |
| Stearic acid | 1 | 1 | 1 |
| Antioxidant Vulkanox 4020 (Bayer AG) | 1 | 1 | 1 |
| Silane Si 69 (Degussa Hüls) | 5.6 | 5.6 | 5.6 |
| Mixed on the roller: | | | |
| Sulphur | 1.5 | 1.5 | 1.5 |
| Accelerator Vulkacit CZ (Bayer AG) | 1.8 | 1.8 | 1.8 |
| Accelerator Vulkacit D (Bayer AG) | 2 | 2 | 2 |
| Mooney-Viscosity ML 1 + 4 (100° C.) | 41 | 43 | 45 |

[**0048**] The mixtures were then vulcanised for 15 minutes at 170° C. The following vulcanisate properties were found:

| | Comparison 2.1 | Example 2.A | Example 2.B |
|---|---|---|---|
| Tensile modulus 100% elongation (MPa) | 2.2 | 2.8 | 3.3 |
| Tensile modulus 300% elongation (MPa) | 8.4 | 10.8 | 12.5 |
| Tensile strength (MPa) | 15.7 | 16.1 | 17 |
| Rebound at 23° C. (%) | 34 | 33 | 32 |
| Rebound at 70° C. (%) | 53 | 59 | 60 |
| Shore A hardness (23° C.) | 60 | 63 | 66 |
| Abrasion DIN 53.516 (mm$^3$) | 109 | 92 | 93 |

[**0049**] The test results show that vulcanisates with improved dynamic damping properties (low rebound at 23° C. correlated with high resistance to wet skidding in tires, high rebound at 70° C. correlated with low rolling resistance in tires) and low abrasion at a significantly higher reinforcement level can be produced from the rubber mixtures with the content according to the invention of sulphurised mineral oils (I).

**1**. Rubber mixtures consisting of a rubber, a filler and 0.1 to 75 parts by weight, based on 100 parts by weight of rubber, of a sulphurised mineral oil, wherein the sulphurised mineral oil is obtained by reacting an aromatic-containing mineral oil with sulphur.

**2**. Rubber mixtures according to claim 1, characterised in that the sulphurised mineral oil has a bound sulphur content of 2.5 to 12.5 wt. %, a glass transition temperature of −25 to −65° C. and a density of 0.85 to 1.1 g/cm$^3$.

**3**. Use of the rubber mixtures according to the invention and according to claim 1 for producing shaped vulcanisates, in particular for producing tires with reduced rolling resistance and high resistance to wet skidding and tires with particularly reinforced lateral walls ("run flat tires").

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