Claims

1. Vulcanizable rubber mixtures comprising at least the following components:

I.) 100 parts by weight of an oil-free rubber matrix consisting of

a) 15 to 79 parts by weight, preferably 20 to 70 parts by weight, of at least one solution SBR (S-SBR) (oil-free) having a glass transition temperature ($Tg_{(S\text{-}SBR)}$) between -70°C and -10°C,

b) 20 to 75 parts by weight, preferably 25 to 70 parts by weight, of at least one 1,4-cis-polybutadiene (BR) (oil-free) having a glass transition temperature ($Tg_{(BR)}$) between -95°C and -115°C,

c) 1 to 37.5 parts by weight, preferably 5 to 35 parts by weight, of natural rubber (NR) (oil-free) and/or at least one synthetic polyisoprene (IR) (oil-free) having a glass transition temperature ($Tg_{(NR)}$) between -50°C and -75°C,

II.) at least one hydroxyl-containing microgel based on polybutadiene,

III.) at least one hydroxyl-containing, oxidic filler,

IV.) at least one polysulphide-containing alkoxysilane,

V.) at least one vulcanizing agent,

VI.) optionally at least one rubber additive.

2. Vulcanizable rubber mixtures according to Claim 1, characterized in that the oil-free rubber matrix I.) has a glass transition temperature ($Tg_{(matrix)}$) between -70°C and -90°C, the $Tg_{(Matrix)}$ being calculated by the general equation

$$\mathbf{Tg_{(matrix)} = X_{(BR)} \times Tg_{(BR)} + X_{(S\text{-}SBR)} \times Tg_{(S\text{-}SBR)} + X_{(NR)} \times Tg_{(NR)}}$$

where

glass transition temperature of the rubber matrix (oil-free)	$Tg_{(matrix)}$
parts by weight of 1,4-cis-polybutadiene (oil-free)	$X_{(BR)}$
parts by weight of S-SBR (oil-free)	$X_{(S\text{-}SBR)}$
parts by weight of NR or IR (oil-free)	$X_{(NR)}$

glass transition temperature of 1,4-cis-polybutadiene (oil-free) $Tg_{(BR)}$

glass transition temperature of S-SBR (oil-free) $Tg_{(S\text{-}SBR)}$

glass transition temperature of NR or IR (oil-free) $Tg_{(NR)}$.

3. Vulcanizable rubber mixtures according to Claim 2, characterized in that the solution SBR has a Mooney viscosity (ML 1+4 at 100°C) of 20 to 150 Mooney units, preferably of 30 to 100 Mooney units.

4. Vulcanizable rubber mixtures according to Claim 2, characterized in that the 1,4-cis-polybutadiene has a 1,4-cis content of at least 90 mol%.

5. Vulcanizable rubber mixtures according to Claim 4, characterized in that the 1,4-cis-polybutadiene is Ti-BR, Co-BR, Ni-BR or Nd-BR.

6. Vulcanizable rubber mixtures according to Claim 2, characterized in that the polyisoprene has a 1,4-cis content of at least 70 mol%.

7. Vulcanizable rubber mixtures according to Claim 2, characterized in that the hydroxyl-containing microgel II.) has a glass transition temperature ($Tg_{(MICROGEL)}$) between -82°C and -60°C, preferably – 65°C and -82°C, especially preferably -70°C and -80°C.

8. Vulcanizable rubber mixtures according to Claim 2, characterized in that 1 to 50 parts by weight, preferably 2.5 to 30 parts by weight, more preferably 5 to 20 parts by weight, based on 100 parts by weight of oil-free rubber matrix, of the hydroxyl-containing microgel II.) are used.

9. Vulcanizable rubber mixtures according to Claim 8, characterized in that the hydroxyl-containing microgel has a gel content of more than 70% by weight, preferably more than 75% by weight, especially preferably more than 80% by weight.

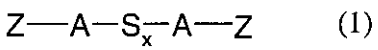
10. Vulcanizable rubber mixtures according to Claim 9, characterized in that the hydroxyl-containing microgel has a swelling index (Qi) in toluene of less than 30, preferably less than 25, especially preferably less than 20.

11. Vulcanizable rubber mixtures according to Claim 10, characterized in that the hydroxyl-containing microgel has a particle size of 10 to 100 nm.

12. Vulcanizable rubber mixtures according to Claim 2, characterized in that the hydroxyl-containing, oxidic filler III.) is silica, the content thereof being in the range of 10 up to 150

parts by weight, preferably in the range of 20 to 120 parts by weight, and more preferably 25 to 100 parts by weight, based on 100 parts by weight of oil-free rubber matrix.

13. Vulcanizable rubber mixtures according to Claim 2, characterized in that the polysulphide-containing alkoxysilane is of the general formula (1) or (2)



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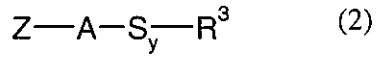


(2)

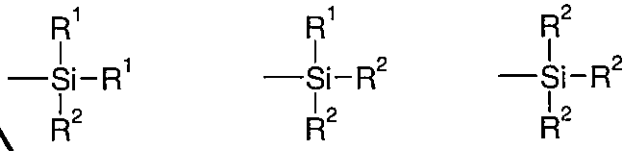
in which

x is an integer of 2 to 8,

y is an integer of 1 to 8,

A are the same or different and are each a divalent hydrocarbon group ("spacer")

Z are the same or different and have one of the following formulae:



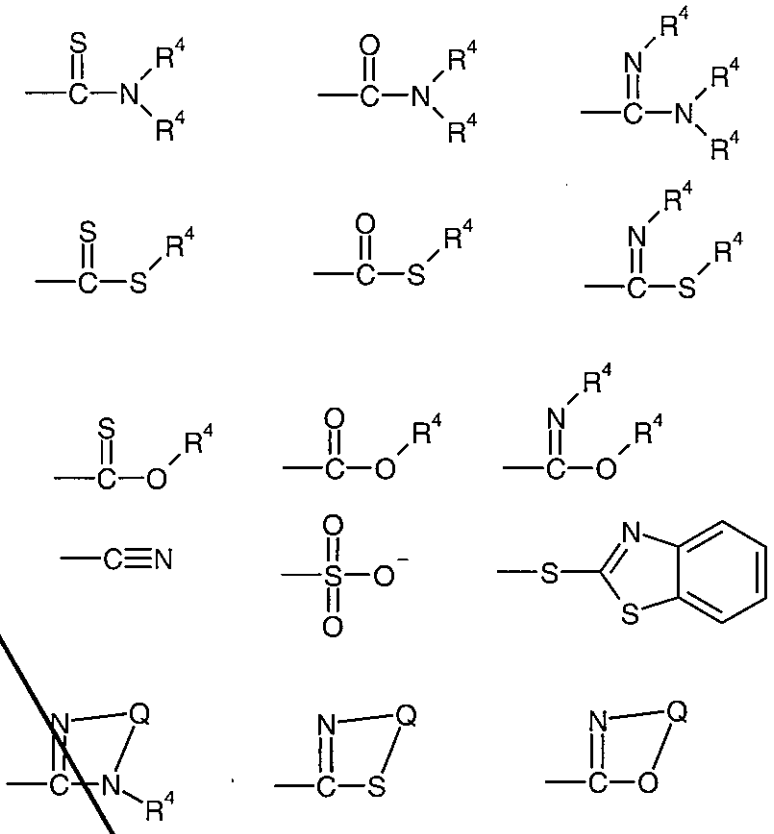
in which

R^1 are the same or different, may be substituted or unsubstituted and are each a C_1-C_{18} alkyl group, a C_5-C_{18} cycloalkyl group or C_6-C_{18} aryl group and

R^2 are the same or different, may be substituted or unsubstituted and are each a C_1-C_{18} alkoxy group, a C_5-C_{18} cycloalkoxy group or C_6-C_{18} aryloxy group

and

R^3 is hydrogen, straight-chain or branched alkyl, where the alkyl chain may optionally be interrupted by one or more, preferably up to five heteroatoms, especially oxygen, sulphur or N(H), aryl, preferably C_6-C_{20}-aryl and/or a radical having the following structures:



in which R^4 is an aliphatic, heteroaliphatic, cycloaliphatic, aromatic or heteroaromatic radical having 1 to 20, preferably 1 to 10, carbon atoms and having optionally 1 to 3 heteroatoms, preferably oxygen, nitrogen or sulphur.

14. Vulcanizable rubber mixtures according to Claim 13, characterized in that 0.2 to 12 parts by weight, preferably 1 to 10 parts by weight, based on 100 parts by weight of oil-free rubber matrix, of polysulphide-containing alkoxysilane are used.

15. Vulcanizable rubber mixtures according to any of the preceding claims, characterized in that they do not comprise any polythiophosphorus compounds.

16. Process for producing vulcanizable rubber mixtures according to any of Claims 1 to 15, characterized in that components I.) to VI.) are mixed with one another in one or more stages, preferably by a three-stage mixing operation with two mixing stages in an internal mixer and a final mixing stage on a roller, or by a two-stage mixing operation in which the 1st mixing stage is effected in an internal mixer and the 2nd mixing stage on a roller, or by a two-stage mixing operation in which both mixing stages are effected in an internal mixer, the mixture being cooled prior to addition of those components which are added on the roller in the three-stage mixing operation to temperatures of < 120°C, preferably < 110°C.

17. Process for producing vulcanizates, characterized in that vulcanizable rubber mixtures according to any of Claims 1 to 15 are subjected to a crosslinking reaction, preferably at a temperature in the range of 100 to 250°C, especially 130 to 180°C, under a pressure in the range of 1 to 200 bar.

18. Process according to Claim 17, characterized in that the crosslinking takes place in the course of a shaping operation.

19. Vulcanizates obtainable by the process according to Claim 17 or 18.

20. Use of vulcanizable rubber mixtures according to any of Claims 1 to 15 for production of pneumatic tyres, especially winter tyres, tyre components, especially tyre treads, especially treads of winter tyres, subtreads, carcasses, sidewalls, reinforced sidewalls for runflat tyres and apex mixtures, and for the production of industrial rubber articles, preferably damping elements, roll coverings, conveyor belt coverings, drive belts, spinning cops, seals, golfball cores and shoe soles.

Claims

1. Vulcanizable rubber mixtures comprising at least the following components:

I.) 100 parts by weight of an oil-free rubber matrix consisting of

a) 15 to 79 parts by weight, preferably 20 to 70 parts by weight, of at least one solution SBR (S-SBR) (oil-free) having a glass transition temperature ($Tg_{(S\text{-}SBR)}$) between -70°C and -10°C,

b) 20 to 75 parts by weight, preferably 25 to 70 parts by weight, of at least one 1,4-cis-polybutadiene (BR) (oil-free) having a glass transition temperature ($Tg_{(BR)}$) between -95°C and -115°C,

c) 1 to 37.5 parts by weight, preferably 5 to 35 parts by weight, of natural rubber (NR) (oil-free) and/or at least one synthetic polyisoprene (IR) (oil-free) having a glass transition temperature ($Tg_{(NR)}$) between -50°C and -75°C,

II.) at least one hydroxyl-containing microgel based on polybutadiene,

III.) at least one hydroxyl-containing, oxidic filler,

IV.) at least one polysulphide-containing alkoxysilane,

V.) at least one vulcanizing agent,

VI.) optionally at least one rubber additive,

characterized in that the oil-free rubber matrix I.) has a glass transition temperature ($Tg_{(matrix)}$) between -70°C and -90°C, the $Tg_{(Matrix)}$ being calculated by the general equation

$$\mathbf{Tg_{(matrix)} = X_{(BR)} \times Tg_{(BR)} + X_{(S\text{-}SBR)} \times Tg_{(S\text{-}SBR)} + X_{(NR)} \times Tg_{(NR)}}$$

where

glass transition temperature of the rubber matrix (oil-free)	$Tg_{(matrix)}$
parts by weight of 1,4-cis-polybutadiene (oil-free)	$X_{(BR)}$
parts by weight of S-SBR (oil-free)	$X_{(S\text{-}SBR)}$
parts by weight of NR or IR (oil-free)	$X_{(NR)}$

glass transition temperature of 1,4-cis-polybutadiene (oil-free) $Tg_{(BR)}$

glass transition temperature of S-SBR (oil-free) $Tg_{(S\text{-}SBR)}$

glass transition temperature of NR or IR (oil-free) $Tg_{(NR)}$.

2. Vulcanizable rubber mixtures according to Claim 1, characterized in that the solution SBR has a Mooney viscosity (ML 1+4 at 100°C) of 20 to 150 Mooney units, preferably of 30 to 100 Mooney units.

3. Vulcanizable rubber mixtures according to Claim 1, characterized in that the 1,4-cis-polybutadiene has a 1,4-cis content of at least 90 mol%.

4. Vulcanizable rubber mixtures according to Claim 3, characterized in that the 1,4-cis-polybutadiene is Ti-BR, Co-BR, Ni-BR or Nd-BR.

5. Vulcanizable rubber mixtures according to Claim 1, characterized in that the polyisoprene has a 1,4-cis content of at least 70 mol%.

6. Vulcanizable rubber mixtures according to Claim 1, characterized in that the hydroxyl-containing microgel II.) has a glass transition temperature ($Tg_{(MICROGEL)}$) between -82°C and -60°C, preferably – 65°C and -82°C, especially preferably -70°C and -80°C.

7. Vulcanizable rubber mixtures according to Claim 1, characterized in that 1 to 50 parts by weight, preferably 2.5 to 30 parts by weight, more preferably 5 to 20 parts by weight, based on 100 parts by weight of oil-free rubber matrix, of the hydroxyl-containing microgel II.) are used.

8. Vulcanizable rubber mixtures according to Claim 7, characterized in that the hydroxyl-containing microgel has a gel content of more than 70% by weight, preferably more than 75% by weight, especially preferably more than 80% by weight.

9. Vulcanizable rubber mixtures according to Claim 8, characterized in that the hydroxyl-containing microgel has a swelling index (Qi) in toluene of less than 30, preferably less than 25, especially preferably less than 20.

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parts by weight, preferably in the range of 20 to 120 parts by weight, and more preferably 25 to 100 parts by weight, based on 100 parts by weight of oil-free rubber matrix.

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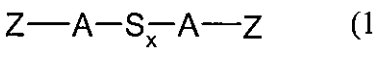
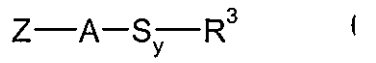


(1)



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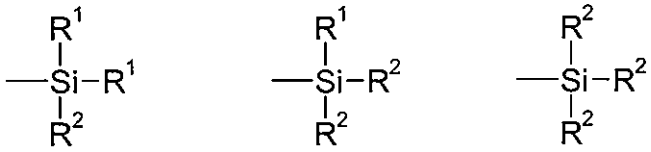


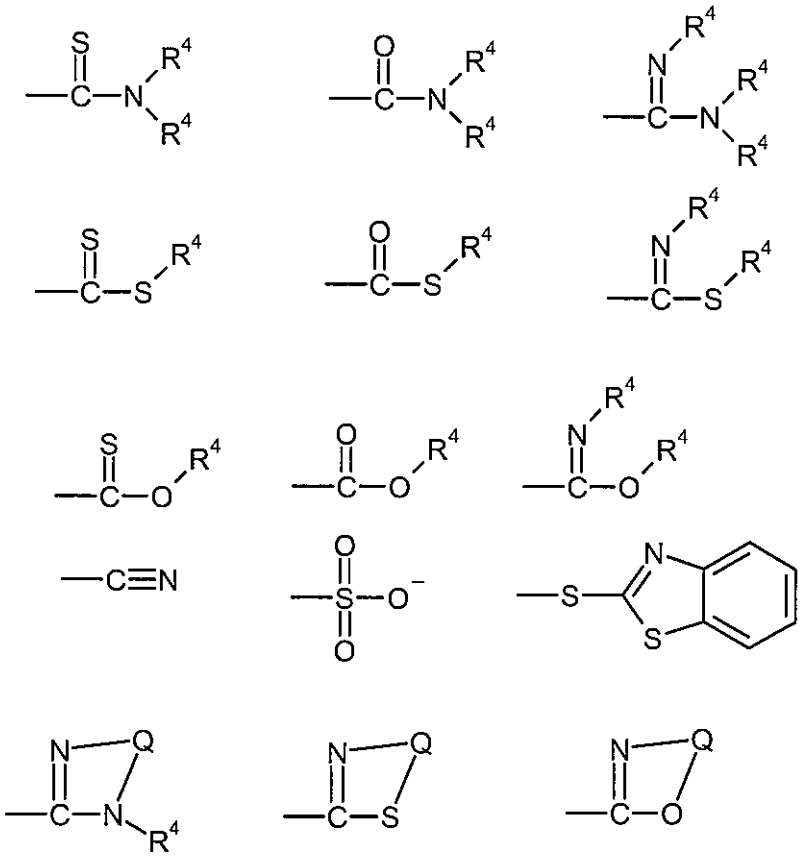
in which

R^1 are the same or different, may be substituted or unsubstituted and are each a C_1-C_{18} alkyl group, a C_5-C_{18} cycloalkyl group or C_6-C_{18} aryl group and

R^2 are the same or different, may be substituted or unsubstituted and are each a C_1-C_{18} alkoxy group, a C_5-C_{18} cycloalkoxy group or C_6-C_{18} aryloxy group

and

R^3 is hydrogen, straight-chain or branched alkyl, where the alkyl chain may optionally be interrupted by one or more, preferably up to five heteroatoms, especially oxygen, sulphur or N(H), aryl, preferably C_6-C_{20}-aryl and/or a radical having the following structures:



in which R^4 is an aliphatic, heteroaliphatic, cycloaliphatic, aromatic or heteroaromatic radical having 1 to 20, preferably 1 to 10, carbon atoms and having optionally 1 to 3 heteroatoms, preferably oxygen, nitrogen or sulphur.

13. Vulcanizable rubber mixtures according to Claim 12, characterized in that 0.2 to 12 parts by weight, preferably 1 to 10 parts by weight, based on 100 parts by weight of oil-free rubber matrix, of polysulphide-containing alkoxysilane are used.

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15. Process for producing vulcanizable rubber mixtures according to any of Claims 1 to 14, characterized in that components I.) to VI.) are mixed with one another in one or more stages, preferably by a three-stage mixing operation with two mixing stages in an internal mixer and a final mixing stage on a roller, or by a two-stage mixing operation in which the 1st mixing stage is effected in an internal mixer and the 2nd mixing stage on a roller, or by a two-stage mixing operation in which both mixing stages are effected in an internal mixer, the mixture being cooled prior to addition of those components which are added on the roller in the three-stage mixing operation to temperatures of < 120°C, preferably < 110°C.

16. Process for producing vulcanizates, characterized in that vulcanizable rubber mixtures according to any of Claims 1 to 14 are subjected to a crosslinking reaction, preferably at a temperature in the range of 100 to 250°C, especially 130 to 180°C, under a pressure in the range of 1 to 200 bar.

17. Process according to Claim 16, characterized in that the crosslinking takes place in the course of a shaping operation.

18. Vulcanizates obtainable by the process according to Claim 16 or 17.

19. Use of vulcanizable rubber mixtures according to any of Claims 1 to 14 for production of pneumatic tyres, especially winter tyres, tyre components, especially tyre treads, especially treads of winter tyres, subtreads, carcasses, sidewalls, reinforced sidewalls for runflat tyres and apex mixtures, and for the production of industrial rubber articles, preferably damping elements, roll coverings, conveyor belt coverings, drive belts, spinning cops, seals, golfball cores and shoe soles.