CLAIMS

1. A process for the preparation of cements comprising aliphatic medium and at least one brominated butyl rubber comprising at least the steps of:

a) providing a butyl rubber cement comprising

A) 5 to 30 wt-%, preferably 8 to 25 wt-%, more preferably 10 to 22 wt.-% of at least one, preferably one butyl rubber

B) 0 to 5 wt-%, preferably 0 to 0.9 wt-%, more preferably 0 to 0.6 wt.-% and more preferably 0 to 0.4 wt.-% of water

C) and an amount of an aliphatic medium comprising at least 50 wt.-% of one or more aliphatic hydrocarbons having a boiling point in the range of 45.0°C to 80.0°C at a pressure of 1013 hPa, selected in such a manner that the sum of A), B) and C) adds up to from 96 to 100 wt-%, preferably to from 98 to 100 wt.-% and more preferably from 99 to 100 wt.-% and even more preferably 100 wt.-% of the total amount of butyl rubber cement

b) brominating the butyl rubber or the butyl rubbers contained in the butyl rubber cement provided in step a) with elemental bromine in the presence of an added aqueous oxidizing agent in order to obtain a heterophasic mixture at least comprising

- a cement comprising aliphatic medium and brominated butyl rubber and
- an aqueous phase

whereby step b) is carried out continuously and the mechanical power input is 0.5 W/l or more to agitate the butyl rubber cement, the added aqueous oxidizing agent and the bromine or the bromine precursor in step b)

and either

c) adjusting the pH-value of the aqueous phase, preferably within the heterophasic mixture obtained according to step b), to 6 to 13, preferably 8 to 12, more preferably 8 to 11 and even more preferably 9 to 10 using a base

d1) separating the cement comprising aliphatic medium and brominated butyl rubber from the aqueous phase

or

d2) separating the heterophasic mixture obtained according to step b) to obtain the cement comprising aliphatic medium and brominated butyl rubber and an aqueous phase and

d3) washing the cement comprising aliphatic medium and brominated butyl rubber with an aqueous mixture, preferably an aqueous solution of a base.

2. The process according to claim 1, wherein the butyl rubber cement is prepared in process comprising at least the steps of

pre-a1) providing a reaction medium comprising

- an aliphatic medium comprising at least 50 wt.-% of one or more aliphatic hydrocarbons having a boiling point in the range of 45°C to 80°C at a pressure of 1013 hPa, and
- a monomer mixture comprising at least one C_4 to C_7 isoolefin, at least one C_4 to C_{14} conjugated diene and either no one or more than one further co-polymerizable monomers

in a mass ratio of monomer mixture to aliphatic medium of from 35:65 to 99:1, preferably from 50:50 to 85:15 and even more preferably from 61:39 to 80:20;

pre-a2) polymerizing the monomer mixture within the reaction medium to form a butyl rubber solution comprising a butyl rubber which is at least substantially dissolved in the medium comprising the aliphatic medium and residual monomers of the monomer mixture;

pre-a3) separating residual monomers of the monomer mixture from the butyl rubber solution to form the butyl rubber cement, whereby the separation is preferably performed by distillation.

3. The process according to claim 1 or 2, wherein the butyl rubber comprises repeating units derived from 92.0 to 99.5, preferably 92.0 to 99.0 and more preferably 97.5 to 98.5 or 94.0 to 96.6 mol-% of at least one, preferably one C_4 to C_7 isoolefin; preferably isobutene and 0.5 to 8.0, preferably 1.0 to 8.0 and more preferably 1.5 to 2.5 or 3.5 to 6.0 mol-% at least one,

preferably one C_4 to C_{14} conjugated diene, preferably isoprene or wherein the butyl rubber comprises repeating units derived from

i) at least one, preferably one C_4 to C_7 isoolefin; preferably isobutene

ii) 0.5 to 8.0, preferably 1.0 to 8.0 and more preferably 1.5 to 2.5 or 3.5 to 6.0 mol-% at least one, preferably one C_4 to C_{14} conjugated diene, preferably isoprene and

iii) 0.1 to 20, preferably 1 to 20 wt-% of further co-polymerizable monomers

whereby the repeating units derived from i), ii) and iii) add up to 100 mol-% of the repeating units contained in the butyl rubber.

4. The process according to anyone of claims 1 to 3, wherein the butyl rubber is a copolymer of isobutene and isoprene comprising 1.5 to 2.5 mol-% repeating units derived from isoprene.

5. The process according to anyone of claims 1 to 4, wherein the aliphatic medium has a content of cyclic aliphatic hydrocarbons of less than 25 wt.-%, preferably less than 20 wt.-%, more preferably of from 0.01 to 20 wt.-%, even more preferably of from 5 to 20 wt.-% .

6. The process according to anyone of claims 1 to 5, wherein the aliphatic medium has a content of cyclohexane of less than 5 wt.-%, preferably less than 2.5 wt.-%.

7. The process according to anyone of claims 1 to 6, wherein the elemental bromine necessary to perform step b) is either added to the butyl rubber cement either in substance or as solution of elemental bromine in the aliphatic medium, preferably in substance or either additionally or alternatively formed by reaction of hydrogen bromide or metal bromides or mixtures of hydrogen bromide or metal bromides as bromine precursors with the aqueous oxidizing agent in situ.

8. The process according to anyone of claims 1 to 7, wherein elemental bromine and an aqueous oxidizing agent are added to the butyl rubber cement in step b).

9. The process according to anyone of claims 1 to 8, wherein the aqueous oxidizing agent is added to the butyl rubber cement prior to, concurrently with or subsequent to the addition of elemental bromine or the bromine precursors.

10. The process according to anyone of claims 1 to 9, wherein the aqueous oxidizing agent is an aqueous solution of hydrogen peroxide comprising 25 to 60 wt.-%, preferably 28 to 38 wt.-%, more preferably 32 to 37 wt.-%, even more preferably 34 to 36 wt.-% of hydrogen peroxide.

11. The process according to anyone of claims 1 to 10, wherein the weight ratio of water soluble peroxides, in particular hydrogen peroxide, to water within the reaction mixture formed by adding the aqueous oxidation agent to the butyl rubber cement is initially higher than 0.05, more preferably higher than 0.12, more preferably higher than 0.14.

12. The process according to anyone of claims 1 to 11, wherein the quantity of bromine atoms employed in form of elemental bromine or bromine precursor or bromine and bromine precursor, preferably only elemental bromine in step b) is 0.2 to 1.2 times the molar quantity of double bonds contained in the butyl rubber, preferably 0.3 to 1.0, more preferably 0.6 to 1.0 times the molar quantity.

13. The process according to anyone of claims 1 to 12, wherein no surfactants are added.

14. The process according to anyone of claims 1 to 13, wherein 0.6 to 5 mol of aqueous oxidizing agent calculated on hydrogen peroxide per mol of elemental bromine are used, preferably from 0.8 to 3 mol and more preferably from 0.8 to 1.2 mol and even more preferably from 1.0 to 1.2 mol or if hydrogen bromide or metal bromides as bromine precursors are used from 1 to 5 mol of aqueous oxidizing agent calculated on hydrogen peroxide per mol of bromide contained in the bromine precursors, preferably from 1.5 to 3 mol and more preferably from 1.5 to 2.4 mol and even more preferably from 1.8 to 2.1 mol.

15. The process according to anyone of claims 1 to 14, wherein step b) is operated at a temperature of from 0°C to 90°C, preferably from 20°C to 80°C and even more preferably 40 to 70°C.

16. The process according to anyone of claims 1 to 15, wherein in step b) the reaction time is from 1 minute to 1 hour , preferably from 10 to 30 minutes.

17. The process according to anyone of claims 1 to 16, wherein the bases employed in step c) or d3) are aqueous solutions or slurries of alkaline or earth alkaline metal hydroxides or

carbonates, preferably with aqueous solutions of alkaline metal hydroxides such as sodium and potassium hydroxide, whereby sodium hydroxide is preferred.

18. The process according to anyone of claims 1 to 17, wherein step d1) or d2) is effected continuously in a separating apparatus comprising a settling section whereby the separation is preferably supported by means of a coalescer.

19. The process according to anyone of claims 1 to 18, wherein the process further comprises a step e) wherein volatile components having a boiling point below 250°C at 1013 hPa are removed from the brominated butyl rubber to obtain the brominated butyl rubber in solid form, whereby the residual content of such volatile components is preferably below 2000 ppm more preferably below 1000 ppm and even more preferably below 500 ppm.

20. The process according to claim 19, wherein the removal is effected by a process using an extruder, preferably a twin screw extruder.

21. The process according to anyone of claims 1 to 20, wherein the brominated butyl rubber is cured in a further step, preferably using a sulphur, resin and peroxide curing systems.

22. The process according to anyone of claims 1 to 21, wherein the brominated butyl rubber comprises a share of bromine atoms being in allylic position to exo-double bonds as measured by 1H-NMR exceeding 40 %, preferably 50 % with respect to the total bromine content of the brominated butyl rubber as measured by XRF.

23. Brominated rubbers or cured brominated rubbers obtainable according to claim 22 as tyre inner liners, treads, sidewalls, adhesives, blends with thermoplastic elastomers, footwear, storage membranes, protective clothing, pharmaceutical stoppers, linings, and barrier coatings or in a process for the preparation thereof.

Claims

1. A process for the preparation of cements comprising aliphatic medium and at least one brominated butyl rubber comprising at least the steps of:

a) providing a butyl rubber cement comprising

A) 5 to 30 wt-%, preferably 8 to 25 wt-%, more preferably 10 to 22 wt.-% of at least one, preferably one butyl rubber

B) 0 to 5 wt-%, preferably 0 to 0.9 wt-%, more preferably 0 to 0.6 wt.-% and more preferably 0 to 0.4 wt.-% of water

C) and an amount of an aliphatic medium comprising at least 50 wt.-% of one or more aliphatic hydrocarbons having a boiling point in the range of 45.0°C to 80.0°C at a pressure of 1013 hPa, selected in such a manner that the sum of A), B) and C) adds up to from 96 to 100 wt-%, preferably to from 98 to 100 wt.-% and more preferably from 99 to 100 wt.-% and even more preferably 100 wt.-% of the total amount of butyl rubber cement

b) brominating the butyl rubber or the butyl rubbers contained in the butyl rubber cement provided in step a) with elemental bromine in the presence of an added aqueous oxidizing agent in order to obtain a heterophasic mixture at least comprising

- a cement comprising aliphatic medium and brominated butyl rubber and
- an aqueous phase

whereby step b) is carried out continuously

and whereby the elemental bromine necessary to perform step b) is either

- added to the butyl rubber cement either in substance or as solution of elemental bromine in the aliphatic medium, preferably in substance or additionally or alternatively

- formed by reaction of hydrogen bromide or metal bromides or mixtures of hydrogen bromide or metal bromides as bromine precursors with the aqueous oxidizing agent in situ

and either

c) adjusting the pH-value of the aqueous phase, preferably within the heterophasic mixture obtained according to step b), to 6 to 13, preferably 8 to 12, more preferably 8 to 11 and even more preferably 9 to 10 using a base

d1) separating the cement comprising aliphatic medium and brominated butyl rubber from the aqueous phase

or

d2) separating the heterophasic mixture obtained according to step b) to obtain the cement comprising aliphatic medium and brominated butyl rubber and an aqueous phase and

d3) washing the cement comprising aliphatic medium and brominated butyl rubber with an aqueous mixture, preferably an aqueous solution of a base.

2. The process according to claim 1, wherein the butyl rubber cement is prepared in process comprising at least the steps of

pre-a1) providing a reaction medium comprising

- an aliphatic medium comprising at least 50 wt.-% of one or more aliphatic hydrocarbons having a boiling point in the range of 45°C to 80°C at a pressure of 1013 hPa, and
- a monomer mixture comprising at least one C_4 to C_7 isoolefin, at least one C_4 to C_{14} conjugated diene and either no one or more than one further co-polymerizable monomers.

in a mass ratio of monomer mixture to aliphatic medium of from 35:65 to 99:1, preferably from 50:50 to 85:15 and even more preferably from 61:39 to 80:20;

pre-a2) polymerizing the monomer mixture within the reaction medium to form a butyl rubber solution comprising a butyl rubber which is at least substantially dissolved in the medium comprising the aliphatic medium and residual monomers of the monomer mixture;

pre-a3) separating residual monomers of the monomer mixture from the butyl rubber solution to form the butyl rubber cement, whereby the separation is preferably performed by distillation.

3. The process according to claim 1 or 2, wherein the butyl rubber comprises repeating units derived from 92.0 to 99.5, preferably 92.0 to 99.0 and more preferably 97.5 to 98.5 or 94.0 to 96.6 mol-% of at least one, preferably one C_4 to C_7 isoolefin; preferably isobutene and 0.5 to 8.0, preferably 1.0 to 8.0 and more preferably 1.5 to 2.5 or 3.5 to 6.0 mol-% at least one, preferably one C_4 to C_{14} conjugated diene, preferably isoprene or wherein the butyl rubber comprises repeating units derived from

i) at least one, preferably one C_4 to C_7 isoolefin; preferably isobutene

ii) 0.5 to 8.0, preferably 1.0 to 8.0 and more preferably 1.5 to 2.5 or 3.5 to 6.0 mol-% at least one, preferably one C_4 to C_{14} conjugated diene, preferably isoprene and

iii) 0.1 to 20, preferably 1 to 20 wt-% of further co-polymerizable monomers

whereby the repeating units derived from i), ii) and iii) add up to 100 mol-% of the repeating units contained in the butyl rubber.

4. The process according to anyone of claims 1 to 3, wherein the butyl rubber is a copolymer of isobutene and isoprene comprising 1.5 to 2.5 mol-% repeating units derived from isoprene.

5. The process according to anyone of claims 1 to 4, wherein the aliphatic medium has a content of cyclic aliphatic hydrocarbons of less than 25 wt.-%, preferably less than 20 wt.-%, more preferably of from 0.01 to 20 wt.-%, even more preferably of from 5 to 20 wt.-% .

6. The process according to anyone of claims 1 to 5, wherein the aliphatic medium has a content of cyclohexane of less than 5 wt.-%, preferably less than 2.5 wt.-%.

7. The process according to anyone of claims 1 to 6, wherein elemental bromine and an aqueous oxidizing agent are added to the butyl rubber cement in step b).

8. The process according to anyone of claims 1 to 7, wherein the aqueous oxidizing agent is added to the butyl rubber cement prior to, concurrently with or subsequent to the addition of elemental bromine.

9. The process according to anyone of claims 1 to 8, wherein the aqueous oxidizing agent is an aqueous solution of hydrogen peroxide comprising 25 to 60 wt.-%, preferably 28 to 38

wt.-%, more preferably 32 to 37 wt.-%, even more preferably 34 to 36 wt.-% of hydrogen peroxide.

10. The process according to anyone of claims 1 to 9, wherein the weight ratio of water soluble peroxides, in particular hydrogen peroxide, to water within the reaction mixture formed by adding the aqueous oxidation agent to the butyl rubber cement is initially higher than 0.05, more preferably higher than 0.12, more preferably higher than 0.14.

11. The process according to anyone of claims 1 to 10, wherein the quantity of bromine atoms employed in form of elemental bromine or bromine precursor or bromine and bromine precursor, preferably only elemental bromine in step b) is 0.2 to 1.2 times the molar quantity of double bonds contained in the butyl rubber, preferably 0.3 to 1.0, more preferably 0.6 to 1.0 times the molar quantity.

12. The process according to anyone of claims 1 to 11, wherein no surfactants are added.

13. The process according to anyone of claims 1 to 12, wherein 0.6 to 5 mol of aqueous oxidizing agent calculated on hydrogen peroxide per mol of elemental bromine are used, preferably from 0.8 to 3 mol and more preferably from 0.8 to 1.2 mol and even more preferably from 1.0 to 1.2 mol or if hydrogen bromide or metal bromides as bromine precursors are used from 1 to 5 mol of aqueous oxidizing agent calculated on hydrogen peroxide per mol of bromide contained in the bromine precursors, preferably from 1.5 to 3 mol and more preferably from 1.5 to 2.4 mol and even more preferably from 1.8 to 2.1 mol.

14. The process according to anyone of claims 1 to 13, wherein step b) is operated at a temperature of from 0°C to 90°C, preferably from 20°C to 80°C and even more preferably 40 to 70°C.

15. The process according to anyone of claims 1 to 14, wherein in step b) the reaction time is from 1 minute to 1 hour , preferably from 10 to 30 minutes.

16. The process according to anyone of claims 1 to 15, wherein the bases employed in step c) or d3) are aqueous solutions or slurries of alkaline or earth alkaline metal hydroxides or carbonates, preferably with aqueous solutions of alkaline metal hydroxides such as sodium and potassium hydroxide, whereby sodium hydroxide is preferred.

17. The process according to anyone of claims 1 to 16, wherein step d1) or d2) is effected continuously in a separating apparatus comprising a settling section whereby the separation is preferably supported by means of a coalescer.

18. The process according to anyone of claims 1 to 17, wherein the process further comprises a step e) wherein volatile components having a boiling point below 250°C at 1013 hPa are removed from the brominated butyl rubber to obtain the brominated butyl rubber in solid form, whereby the residual content of such volatile components is preferably below 2000 ppm more preferably below 1000 ppm and even more preferably below 500 ppm.

19. The process according to claim 18, wherein the removal is effected by a process using an extruder, preferably a twin screw extruder

20. The process according to anyone of claims 1 to 19, wherein the brominated butyl rubber is cured in a further step, preferably using a sulphur, resin and peroxide curing systems.

21. The process according to anyone of claims 1 to 20, wherein the brominated butyl rubber comprises a share of bromine atoms being in allylic position to exo-double bonds as measured by 1H-NMR exceeding 40 %, preferably 50 % with respect to the total bromine content of the brominated butyl rubber as measured by XRF.