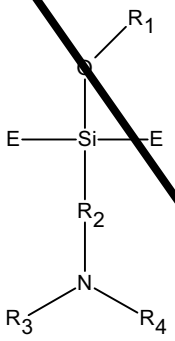
CLAIMS

1. Modified diene elastomer comprising predominantly the entity functionalized in the middle of the chain by an alkoxysilane group, optionally partially or completely hydrolysed to give silanol, bearing a tertiary amine functional group and the silicon atom of which bonds the two pieces of the chain, the chain ends of the modified diene elastomer being functionalized to at least 70 mol%, with respect to the number of moles of chain end, by an amine functional group.

2. Modified diene elastomer according to Claim 1, characterized in that the entity functionalized in the middle of the chain by the alkoxysilane group, optionally partially or completely hydrolysed to give silanol, bearing a tertiary amine functional group, the silicon atom of which bonds the two pieces of the chain, the chain ends being functionalized to at least 70 mol% by an amine functional group, corresponds to the following formula (I):



Formula (I)

in which:

- the symbol E denotes a diene elastomer functionalized to at least 70 mol% at the chain end by an amine functional group,
- R_1 denotes, as a function of the degree of hydrolysis, a hydrogen atom or a linear or branched C_1 – C_{10}, preferably C_1-C_8, alkyl radical, more preferably a C_1-C_4 alkyl group,

- R_2 is a saturated or unsaturated, cyclic or non-cyclic, divalent C_1-C_{18} aliphatic hydrocarbon group or C_6-C_{18} aromatic hydrocarbon group,

- R_3 and R_4, which are identical or different, represent a linear or branched C_1-C_{18}, preferably C_1-C_{10} and more preferably C_1-C_4 alkyl radical, or else R_3 and R_4 form, with N to which they are bonded, a heterocycle comprising a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms.

3. Modified diene elastomer according to Claim 2, characterized in that R_1 represents a hydrogen atom or a methyl or ethyl radical.

4. Modified diene elastomer according to Claim 2 or 3, characterized in that R_1 represents a hydrogen atom.

5. Modified diene elastomer according to any one of Claims 2 to 4, characterized in that R_2 represents the saturated linear divalent C_3 aliphatic hydrocarbon radical.

6. Modified diene elastomer according to one of Claims 2 to 5, characterized in that R_3 and R_4, which are identical or different, preferably identical, represent a methyl or ethyl radical, preferably a methyl radical.

7. Modified diene elastomer according to one of Claims 1 to 6, characterized in that the modified diene elastomer is a copolymer of butadiene and of a vinylaromatic monomer, in particular an SBR.

8. Modified diene elastomer according to one of Claims 1 to 7, characterized in that it comprises at least 70% by weight, with respect to the modified diene elastomer, of the entity functionalized in the middle of the chain by the alkoxysilane group, optionally partially or completely hydrolysed to give silanol, bearing a tertiary amine functional group, the silicon atom of which bonds the two pieces of

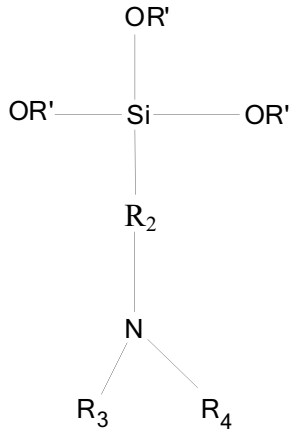
the chain, the chain ends being functionalized to at least 70 mol% by an amine functional group.

9. Process for the preparation of a modified diene elastomer as defined in any one of Claims 1 to 8, characterized in that it comprises:

- anionic polymerization of at least one conjugated diene monomer in the presence of a polymerization initiator having an amine functional group,
- modification of the living diene elastomer bearing an active site obtained in the preceding stage by a functionalization agent, capable of coupling the elastomer chains, bearing at least one tertiary amine functional group and an alkoxysilane functional group, which can be hydrolysed to give silanol, with a molar ratio of the functionalization agent to the polymerization initiator with a value ranging from 0.35 to 0.65.

10. Preparation process according to Claim 9, characterized in that the polymerization initiator comprising an amine functional group is chosen from lithium amides obtained from a secondary amine, preferably a cyclic secondary amine, and from an organolithium compound.

11. Preparation process according to Claim 9 or 10, characterized in that the functionalization agent corresponds to the formula:



Formula (II)

in which:

- R_2 is a saturated or unsaturated, cyclic or non-cyclic, divalent C_1-C_{18} aliphatic hydrocarbon group or C_6-C_{18} aromatic hydrocarbon group,

- R_3 and R_4, which are identical or different, represent a linear or branched C_1-C_{18}, preferably C_1-C_{10} and more preferably C_1-C_4 alkyl radical, or else R_3 and R_4 form, with N to which they are bonded, a heterocycle comprising a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms,

- the linear or branched R' radicals, which are identical to or different from one another, represent a C_1-C_{10}, preferably C_1-C_8, alkyl group, better still a C_1-C_4 alkyl group.

12. Reinforced rubber composition based on at least one reinforcing filler and an elastomer matrix comprising at least one modified diene elastomer as defined in any one of Claims 1 to 8.

13. Rubber composition according to Claim 12, characterized in that the elastomer matrix predominantly comprises the modified diene elastomer as defined in any one of Claims 1 to 8.

14. Rubber composition according to either of Claims 12 and 13, characterized in that said reinforcing filler comprises a reinforcing inorganic filler of siliceous type according to a fraction by weight of greater than 50% and ranging up to 100%.

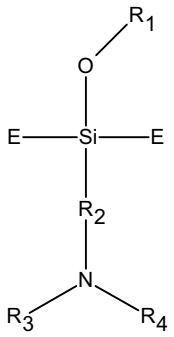
15. Semi-finished article made of rubber for a tyre, characterized in that it comprises a crosslinkable or crosslinked rubber composition according to any one of Claims 12 to 14.

16. Tyre, characterized in that it comprises a semi-finished article as defined in Claim 15.

CLAIMS

1. Modified diene elastomer comprising a mixture of modified entities, of which the predominant entity is functionalized in the middle of the chain by an alkoxysilane group, optionally partially or completely hydrolysed to give a silanol, bearing a tertiary amine functional group and the silicon atom of which bonds respective portions of the chain, the chain ends of the modified diene elastomer being functionalized to at least 70 mol%, with respect to the number of moles of chain end, by an amine functional group.

2. Modified diene elastomer according to Claim 1, characterized in that the predominant entity functionalized in the middle of the chain by the alkoxysilane group, optionally partially or completely hydrolysed to give the silanol, bearing a tertiary amine functional group, the silicon atom of which bonds the respective portions of the chain, the chain ends being functionalized to at least 70 mol% by an amine functional group, corresponds to the following formula (I):



Formula (I)

in which:

- the symbol E denotes a diene elastomer functionalized to at least 70 mol% at the chain end by an amine functional group,
- R_1 denotes, as a function of the degree of hydrolysis, a hydrogen atom or a linear or branched C_1 – C_{10}, preferably C_1-C_8, alkyl radical, more preferably a C_1-C_4 alkyl group,

- R_2 is a saturated or unsaturated, cyclic or non-cyclic, divalent C_1-C_{18} aliphatic hydrocarbon group or C_6-C_{18} aromatic hydrocarbon group,

- R_3 and R_4, which are identical or different, represent a linear or branched C_1-C_{18}, preferably C_1-C_{10} and more preferably C_1-C_4 alkyl radical, or else R_3 and R_4 form, with N to which they are bonded, a heterocycle comprising a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms.

3. Modified diene elastomer according to Claim 2, characterized in that R_1 represents a hydrogen atom or a methyl or ethyl radical.

4. Modified diene elastomer according to Claim 2 or 3, characterized in that R_1 represents a hydrogen atom.

5. Modified diene elastomer according to any one of Claims 2 to 4, characterized in that R_2 represents the saturated linear divalent C_3 aliphatic hydrocarbon radical.

6. Modified diene elastomer according to one of Claims 2 to 5, characterized in that R_3 and R_4, which are identical or different, preferably identical, represent a methyl or ethyl radical, preferably a methyl radical.

7. Modified diene elastomer according to one of Claims 1 to 6, characterized in that the modified diene elastomer is a copolymer of butadiene and of a vinylaromatic monomer, in particular an SBR.

8. Modified diene elastomer according to one of Claims 1 to 7, characterized in that it comprises at least 70% by weight, with respect to the modified diene elastomer, of the entity functionalized in the middle of the chain by the alkoxysilane group, optionally partially or completely hydrolysed to give silanol, bearing a tertiary amine functional group, the silicon atom of which bonds the two pieces of

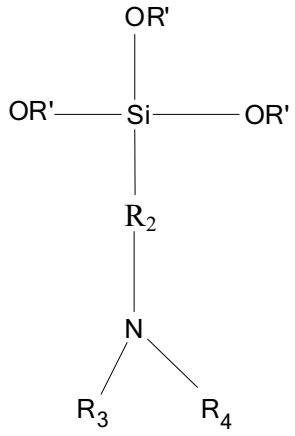
the chain, the chain ends being functionalized to at least 70 mol% by an amine functional group.

9. Process for the preparation of a modified diene elastomer as defined in any one of Claims 1 to 8, characterized in that it comprises:

- anionic polymerization of at least one conjugated diene monomer in the presence of a polymerization initiator having an amine functional group,
- modification of the living diene elastomer bearing an active site obtained in the preceding stage by a functionalization agent, capable of coupling the elastomer chains, bearing at least one tertiary amine functional group and an alkoxysilane functional group, which can be hydrolysed to give silanol, with a molar ratio of the functionalization agent to the polymerization initiator with a value ranging from 0.35 to 0.65.

10. Preparation process according to Claim 9, characterized in that the polymerization initiator comprising an amine functional group is chosen from lithium amides obtained from a secondary amine, preferably a cyclic secondary amine, and from an organolithium compound.

11. Preparation process according to Claim 9 or 10, characterized in that the functionalization agent corresponds to the formula:



Formula (II)

in which:

- R_2 is a saturated or unsaturated, cyclic or non-cyclic, divalent C_1-C_{18} aliphatic hydrocarbon group or C_6-C_{18} aromatic hydrocarbon group,

- R_3 and R_4, which are identical or different, represent a linear or branched C_1-C_{18}, preferably C_1-C_{10} and more preferably C_1-C_4 alkyl radical, or else R_3 and R_4 form, with N to which they are bonded, a heterocycle comprising a nitrogen atom and at least one carbon atom, preferably from 2 to 6 carbon atoms,

- the linear or branched R' radicals, which are identical to or different from one another, represent a C_1-C_{10}, preferably C_1-C_8, alkyl group, better still a C_1-C_4 alkyl group.

12. Reinforced rubber composition based on at least one reinforcing filler and an elastomer matrix comprising at least one modified diene elastomer as defined in any one of Claims 1 to 8.

13. Reinforced rubber composition according to Claim 12, characterized in that the elastomer matrix predominantly comprises the modified diene elastomer as defined in any one of Claims 1 to 8.

14. Reinforced rubber composition according to either of Claims 12 and 13, characterized in that said reinforcing filler comprises a reinforcing inorganic filler of siliceous type according to a fraction by weight of greater than 50% and ranging up to 100%.

15. Semi-finished article made of rubber for a tyre, characterized in that it comprises a reinforced rubber composition according to any one of Claims 12 to 14 which is crosslinkable or crosslinked.

16. Tyre, characterized in that it comprises a semi-finished article as defined in Claim 15.