CLAIMS

1. A silane sulfide modifier represented by the following Formula 1:

$$((R^1O)_x(R^2)_ySi\text{-}R^3\text{-}S)_sM(R^4)_t(X)_u$$

Formula 1

wherein:

M is silicon or tin;

x is an integer selected from 1, 2 and 3;

y is an integer selected from 0, 1, and 2; wherein x + y = 3;

s is an integer selected from 2, 3 and 4;

t is an integer selected from 0, 1 and 2;

u is an integer selected from 0, 1 and 2; wherein s + t + u = 4;

R^1 is independently selected from hydrogen and (C_1-C_6) alkyl;

R^2 is independently selected from (C_1-C_{16}) alkyl, (C_7-C_{16}) alkylaryl and (C_7-C_{16}) arylalkyl;

R^3 is at least divalent and is independently selected from (C_1-C_{16}) alkyl, (C_8-C_{16}) alkylarylalkyl, (C_7-C_{16}) arylalkyl and (C_7-C_{16}) alkylaryl, and each group may be substituted with one or more of the following groups: tertiary amine group, silyl group, (C_7-C_{18}) aralkyl group and (C_6-C_{18}) aryl group;

R^4 is independently selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) alkylaryl;

X is independently selected from chloride, bromide and $-OR^5$; wherein R^5 is selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) arylalkyl.

2. The silane sulfide modifier according to Claim 1, wherein R^3 is divalent (C_1-C_{16}) alkyl.

3. The silane sulfide modifier according to Claim 1 or 2, wherein X is selected from chloride, bromide and -OR^5, wherein R^5 is selected from (C_1-C_{16}) alkyl.

4. The silane sulfide modifier according to any one of Claims 1 to 3, wherein R^2 and R^4 are independently selected from (C_1-C_{16}) alkyl.

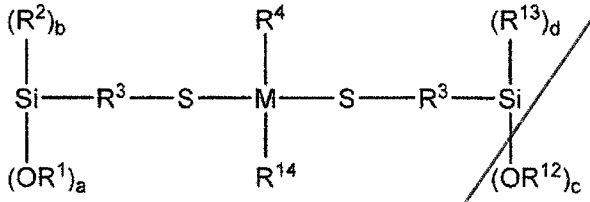
5. The silane sulfide modifier according to any one of Claims 1 to 4, wherein R^1, R^2, R^4 and R^5 are independently selected from (C_1-C_4) alkyl.

6. The silane sulfide modifier according to any one of Claims 1 to 5, wherein s and t are

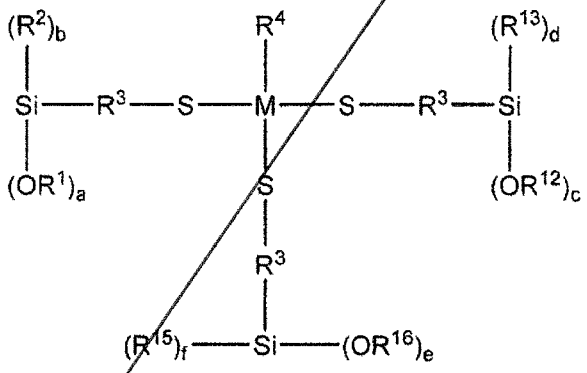
each 2 and u is 0; or s is 3, t is 1 and u is 0.

7. The silane sulfide modifier according to any one of Claims 1 to 6, wherein x is 2 and y is 1; or x is 1 and y is 2.

8. The silane sulfide modifier according to Claim 1, which has the following Formula 5 or Formula 6:



Formula 5



Formula 6

wherein

M is a silicon atom or a tin atom;

R^3 is at least divalent and is (C_8-C_{16}) alkylarylalkyl, (C_7-C_{16}) arylalkyl, (C_7-C_{16}) alkylaryl, or (C_1-C_{16}) alkyl, and each group may be substituted with one or more of the following groups: tertiary amine group, silyl group, (C_7-C_{18}) aralkyl group and (C_6-C_{18}) aryl group;

R^1, R^{12} and R^{16} are each independently selected from a hydrogen atom and (C_1-C_4) alkyl;

R^2, R^{13} and R^{15} are each independently selected from (C_1-C_{16}) alkyl, (C_7-C_{16}) alkylaryl and (C_7-C_{16}) arylalkyl;

R^4 and R^{14} are each independently selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) alkylaryl;

b, d and f are each independently selected from an integer of 0, 1 and 2; a, c and e are each independently selected from an integer of 1, 2 and 3; a + b = 3; c + d = 3; and e+f=3.

9. The silane sulfide modifier according to Claim 8, wherein R^3 is a (C_1-C_{16}) divalent alkyl group or (C_8-C_{16}) divalent alkylarylalkyl group.

10. The silane sulfide modifier according to Claim 8 or 9, wherein R^3 is selected from $-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CH_2-C_6H_4-CH_2-$ and $-C_6H_4-C(CH_3)_2-C_6H_4-$.

11. The silane sulfide modifier according to any one of Claims 8 to 10, wherein R^2, R^4, R^{13} and R^{15} are each independently selected from (C_1-C_{16}) alkyl.

12. The silane sulfide modifier according to any one of Claims 8 to 11, wherein M is a silicon atom; a, c and e are each an integer selected from 2 and 3; and b, d and e are each an integer selected from 0 and 1.

13. A method of making the silane sulfide modifier of Formula 1, Formula 5 or Formula 6 as defined in any one of Claims 1 to 12, said method comprising the steps of

(i) combining

(ia) a compound of the following Formula 2

$$(R^1O)_x(R^2)_ySi\text{-}R^3\text{-}SH$$

Formula 2,

wherein R^1, R^2, R^3, x and y are as defined in Claim 1; and

(ib) an amine compound selected from the following Formula 3a and Formula 3b

$R^5R^6R^7N$ $R^8R^9N\text{-}(CR^{10}R^{11})_v\text{-}NR^8R^9$

Formula 3a Formula 3b

wherein R^5, R^6 R^7, R^8, R^9, R^{10} and R^{11} are each independently selected from hydrogen, (C_1-C_{16}) alkyl, (C_7-C_{16}) alkylaryl; (C_7-C_{16}) arylalkyl and (C_6-C_{16}) aryl; and v is an integer selected from 1 to 10;

(ii) reacting the mixture resulting from step (i) with a compound of the following Formula 4

$$M(R^4)_t(X)_u$$

Formula 4,

wherein M is silicon or tin, u is an integer selected from 2, 3 and 4; R^4, X and t are as defined in Claim 1; and $t + u = 4$;

in a solvent; and

(iii) optionally isolating the silane sulfide modifier of Formula 1, Formula 5 or Formula 6 obtained in step (ii).

14. A method of making the silane sulfide modifier of Formula 1, Formula 5 or Formula 6 as defined in any one of Claims 1 to 12, said method comprising the steps of

(i) reacting a compound of Formula 2 as defined above and an alkali metal hydride in a solvent,

(ii) reacting the reaction product resulting from step (i) with a compound of Formula 4 as defined above in a solvent; and

(iii) optionally isolating the silane sulfide modifier of Formula 1, Formula 5 or Formula 6 obtained in step (ii).

15. The method according to Claim 13 or 14, wherein the silane sulfide modifier of Formula 1, Formula 5 or Formula 6 obtained in step (ii) is isolated in step (iii) by filtration, evaporation of the solvent or distillation.

16. A silane sulfide modified elastomeric macromolecular compound obtainable by reacting

i) a living anionic elastomeric polymer and

ii) a silane sulfide modifier represented by Formula 1, Formula 5 or Formula 6 as defined in any one of Claims 1 to 12.

17. The silane sulfide modified elastomeric macromolecular compound according to Claim 16, which is represented by the following Formula P1

$$((P)_r(R^1O)_{x-r}(R^2)_ySi\text{-}R^3\text{-}S)_sM(R^4)_t(X)_u$$

(Formula P1),

wherein

P is a polymer chain comprising monomer units derived from at least one of the following monomer groups: butadiene, isoprene, styrene and alpha-methylstyrene, the number of monomer units per macromolecule ranging from 10 to 50.000, preferably from 20 to 40.000;

M is a silicon atom or a tin atom;

x is an integer selected from 1, 2 and 3; y is an integer selected from 0, 1, and 2; r is an integer selected from 1, 2 and 3; wherein $x + y + r = 3$;

s is an integer selected from 2, 3 and 4; t is an integer selected from 0, 1 and 2; u is an integer selected from 0, 1 and 2; wherein $s + t + u = 4$;

R^1 is independently selected from a hydrogen atom and (C_1-C_6) alkyl;
R^2 is independently selected from (C_1-C_{16}) alkyl, (C_7-C_{16}) alkylaryl and (C_7-C_{16}) arylalkyl;
R^3 is at least divalent and is independently selected from (C_1-C_{16}) alkyl, (C_8-C_{16}) alkylarylalkyl, (C_7-C_{16}) arylalkyl and (C_7-C_{16}) alkylaryl, and each group may be substituted with one or more of the following groups: tertiary amine group, silyl group, (C_7-C_{18}) aralkyl group and (C_6-C_{18}) aryl group;
R^4 is independently selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) alkylaryl; and
X is independently selected from chloride, bromide and $-OR^5$; wherein R^5 is selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) arylalkyl.

18. The silane sulfide modified elastomeric macromolecular compound according to Claim 17, wherein R^3 is divalent (C_1-C_{16}) alkyl.

19. The silane sulfide modified elastomeric macromolecular compound according to Claim 17 or 18, wherein X is selected from chloride, bromide and $-OR^5$; wherein R^5 is selected from (C_1-C_{16}) alkyl.

20. The silane sulfide modified elastomeric macromolecular compound according to any one of Claims 17 to 19, wherein R^2 and R^4 are independently selected from (C_1-C_{16}) alkyl.

21. The silane sulfide modified elastomeric macromolecular compound according to any one of Claims 17 to 20, wherein R^1, R^2, R^4 and R^5 are independently selected from (C_1-C_4) alkyl.

22. The silane sulfide modified elastomeric macromolecular compound according to any one of Claims 17 to 21, wherein s and t are each 2 and u is 0; or s is 3, t is 1 and u is 0.

23. The silane sulfide modified elastomeric macromolecular compound according to any one of Claims 17 to 22, wherein r is 1, x is 1 and y is 1; or r is 1, x is 0 and y is 2.

24. A method of making the silane sulfide modified elastomeric macromolecular compound as defined in any one of Claims 16 to 23, said method comprising the following steps A to D:

(A) reacting a polymerization initiator with one or more monomer species, including monomers selected from butadiene, styrene, isoprene, alpha methyl-styrene and combinations thereof, in a polymerization solvent to form a reaction mixture A,

(B) optionally reacting reaction mixture A with at least one coupling agent to form a reaction mixture B,

(C) reacting the reaction mixture A or B with at least one silane sulfide modifier of Formula 1, Formula 5 or Formula 6 as defined in any one of Claims 1 to 12 to produce a silane sulfide modified macromolecular compound,

(D) optionally further reacting the reaction mixture obtained in step (C) with a further modifying agent.

25. The method according to Claim 24, wherein the at least one coupling agent used in step (B) is selected from the group consisting of $SnCl_4$, $(R_1)_3SnCl$, $(R_1)_2SnCl_2$, R_1SnCl_3, $SiCl_4$, $(R_1)_3SiCl$, $(R_1)_2SiCl_2$, R_1SiCl_3, $Cl_3Si\text{-}SiCl_3$, $Cl_3Si\text{-}O\text{-}SiCl_3$, $Cl_3Sn\text{-}SnCl_3$, $Cl_3Sn\text{-}O\text{-}SnCl_3$, wherein R_1 is as defined above, $Sn(OMe)_4$, $Si(OMe)_4$, $Sn(OEt)_4$ and $Si(OEt)_4$.

26. The method according to Claim 24 or 25, wherein the further modifying agent used in step (D) is represented by the following Formula 7:

$$(RO)_x(R)_ySi\text{-}R'\text{-}S\text{-}M^1R_3,$$

Formula 7,

wherein

M^1 is silicon or tin; x is an integer selected from 1, 2 and 3; y is an integer selected from 0, 1, and 2; x + y = 3; R is independently selected from (C_1-C_{16}) alkyl; and R' is (C_1-C_{16}) alkyl, (C_8-C_{16}) alkylarylalkyl, (C_7-C_{16}) arylalkyl and (C_7-C_{16}) alkylaryl.

27. A polymer composition comprising at least one silane sulfide modified macromolecular compound as defined in any one of Claims 1 to 12 and one or more further components selected from components which are added to or formed as a result of the polymerization process used for making the modified macromolecular compound and components which remain after solvent removal from the polymerization process.

28. The polymer composition according to Claim 27, which comprises at least one filler.

29. The polymer composition according to Claim 28, wherein the filler is one or more selected from carbon black, silica, carbon-silica dual-phase-filler, clay, calcium carbonate, magnesium carbonate, lignin, and glass particles.

30. The polymer composition according to Claim 29, wherein the filler comprises silica.

31. The polymer composition according to Claim 29 or 30, wherein the filler comprises carbon black.

32. The polymer composition according to any one of Claims 27 to 31, which comprises a vulcanization agent.

33. The polymer composition according to any one of Claims 27 to 32, which comprises at least one polymer selected from the group consisting of polybutadiene, butadiene-styrene copolymers, butadiene-isoprene copolymers, polyisoprene and butadiene-styrene-isoprene terpolymers.

34. A vulcanized polymer composition comprising the reaction product of at least the following:

1) at least one vulcanization agent; and

2) the polymer composition as defined in any one of Claims 27 to 33.

35. A method for making a vulcanized polymer composition comprising reacting at least the following components:

1) at least one vulcanization agent; and

2) the polymer composition as defined in any one of Claims 27 to 33.

36. An article comprising at least one component formed from the vulcanized polymer composition as defined in Claim 35.

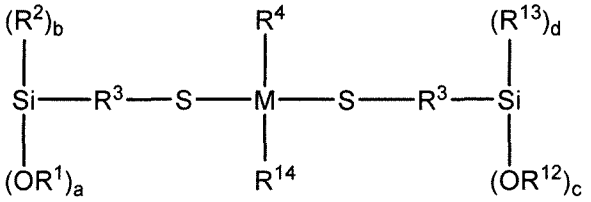
37. The article according to Claim 36, which is selected from the group consisting of a tire, a tire tread, a tire side wall, a tire carcass, a belt, a hose, a vibration damper, and a footwear component.

CLAIMS

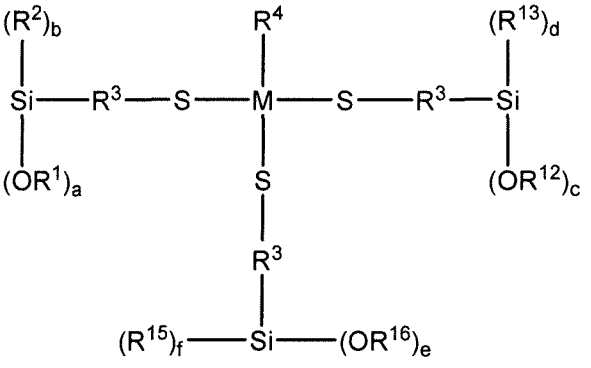
1. A silane sulfide modified elastomeric macromolecular compound obtainable by reacting

i) a living anionic elastomeric polymer and

ii) a silane sulfide modifier represented by the following Formula (5) or Formula (6):



Formula (5)



Formula (6)

wherein

M is a silicon atom or a tin atom;

R^3 is at least divalent and is (C_8-C_{16}) alkylarylalkyl, (C_7-C_{16}) arylalkyl, (C_7-C_{16}) alkylaryl, or (C_1-C_{16}) alkyl, and each group may be substituted with one or more of the following groups: tertiary amine group, silyl group, (C_7-C_{18}) aralkyl group and (C_6-C_{18}) aryl group;

R^1, R^{12} and R^{16} are each independently selected from a hydrogen atom and (C_1-C_4) alkyl;

R^2, R^{13} and R^{15} are each independently selected from (C_1-C_{16}) alkyl, (C_7-C_{16}) alkylaryl and (C_7-C_{16}) arylalkyl;

R^4 and R^{14} are each independently selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) alkylaryl;

b, d and f are each independently selected from an integer of 0, 1 and 2; a, c and e are each independently selected from an integer of 1, 2 and 3; a + b = 3; c + d = 3; and e + f = 3.

2. The silane sulfide modified elastomeric macromolecular compound according to Claim 1, which is represented by the following Formula (P1)

$$((P)_r(R^1O)_{x-r}(R^2)_ySi\text{-}R^3\text{-}S)_sM(R^4)_t(X)_u$$

(Formula P1),

wherein

P is a polymer chain comprising monomer units derived from at least one of the following monomer groups: butadiene, isoprene, styrene and alpha-methylstyrene, the number of monomer units per macromolecule ranging from 10 to 50.000;

M is a silicon atom or a tin atom;

x is an integer selected from 1, 2 and 3; y is an integer selected from 0, 1, and 2; r is an integer selected from 1, 2 and 3; wherein x + y + r = 3;

s is an integer selected from 2, 3 and 4; t is an integer selected from 0, 1 and 2; u is an integer selected from 0, 1 and 2; wherein s + t + u = 4;

R^1 is independently selected from a hydrogen atom and (C_1-C_6) alkyl;

R^2 is independently selected from (C_1-C_{16}) alkyl, (C_7-C_{16}) alkylaryl and (C_7-C_{16}) arylalkyl;

R^3 is at least divalent and is independently selected from (C_1-C_{16}) alkyl, (C_8-C_{16}) alkylarylalkyl, (C_7-C_{16}) arylalkyl and (C_7-C_{16}) alkylaryl, and each group may be substituted with one or more of the following groups: tertiary amine group, silyl group, (C_7-C_{18}) aralkyl group and (C_6-C_{18}) aryl group;

R^4 is independently selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) alkylaryl; and

X is independently selected from chloride, bromide and –OR^5; wherein R^5 is selected from (C_1-C_{16}) alkyl and (C_7-C_{16}) arylalkyl.

3. The silane sulfide modified elastomeric macromolecular compound according to Claim 2, wherein R^3 is divalent (C_1-C_{16}) alkyl.

4. The silane sulfide modified elastomeric macromolecular compound according to Claim 2, wherein X is selected from chloride, bromide and -OR^5; wherein R^5 is selected from (C_1-C_{16}) alkyl.

5. The silane sulfide modified elastomeric macromolecular compound according to Claim 2, wherein R^2 and R^4 are independently selected from (C_1-C_{16}) alkyl.

6. The silane sulfide modified elastomeric macromolecular compound according to Claim 2, wherein R^1, R^2, R^4 and R^5 are independently selected from (C_1-C_4) alkyl.

7. The silane sulfide modified elastomeric macromolecular compound according to Claim 2, wherein s and t are each 2 and u is 0; or s is 3, t is 1 and u is 0.

8. The silane sulfide modified elastomeric macromolecular compound according to Claim 2, wherein r is 1, x is 1 and y is 1; or r is 1, x is 0 and y is 2.

9. A polymer composition comprising at least one silane sulfide modified macromolecular compound as defined in Claim 1 and one or more further components selected from components which are added to or formed as a result of the polymerization process used for making the modified macromolecular compound and components which remain after solvent removal from the polymerization process.

10. The polymer composition according to Claim 9, which comprises at least one filler.

11. The polymer composition according to Claim 10, wherein the filler is one or more selected from carbon black, silica, carbon-silica dual-phase-filler, clay, calcium carbonate, magnesium carbonate, lignin, and glass particles.

12. The polymer composition according to Claim 11, wherein the filler comprises silica.

13. The polymer composition according to Claim 11, wherein the filler comprises carbon black.

14. The polymer composition according to Claim 9, which comprises a vulcanization agent.

15. The polymer composition according to Claim 9, which comprises at least one polymer selected from the group consisting of polybutadiene, butadiene-styrene copolymers, butadiene-isoprene copolymers, polyisoprene and butadiene-styrene-isoprene terpolymers.

16. A vulcanized polymer composition comprising the reaction product of at least the following: at least one vulcanization agent; and the polymer composition as defined in Claim 9.

17. A method for making a vulcanized polymer composition comprising reacting at least the following components: at least one vulcanization agent; and the polymer composition as defined in Claim 9.

18. An article comprising at least one component formed from the vulcanized polymer composition as defined in Claim 16.

19. The article according to Claim 18, which is selected from the group consisting of a tire, a tire tread, a tire side wall, a tire carcass, a belt, a hose, a vibration damper, and a footwear component.

20. The silane sulfide modified elastomeric macromolecular compound according to Claim 1, wherein R^3 is a (C_1-C_{16}) divalent alkyl group or (C_8-C_{16}) divalent alkylarylalkyl group.

21. The silane sulfide modified elastomeric macromolecular compound according to Claim 1, wherein R^3 is selected from $-CH_2-$, $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-CH_2-C_6H_4-CH_2-$ and $-C_6H_4-C(CH_3)_2-C_6H_4-$.

22. The silane sulfide modified elastomeric macromolecular compound according to Claim 1, wherein R^2, R^4, R^{13} and R^{15} are each independently selected from (C_1-C_{16}) alkyl.

23. The silane sulfide modified elastomeric macromolecular compound according to Claim 1, wherein M is a silicon atom; a, c and e are each an integer selected from 2 and 3; and b, d and f are each an integer selected from 0 and 1.