

PATENT SPECIFICATION

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(54) ELASTOMER COMPOSITIONS AND TYRE TREADS COMPRISING THEM

(71) We, DUNLOP LIMITED, a British Company of Dunlop House, Ryder Street, St James's, London SW1, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to elastomer compositions and to their use in tyres, in particular to the ground contacting tread portion of tyres.

Two general principles are currently accepted in the tyre industry when considering tyre treads and their grip performance in wet conditions. These are:

i) the wet grip performance of a tyre tread composition (compound) is a function of the rebound resilience of the composition, the lower the resilience value the better the wet grip performance; and

ii) the wet grip performance of a polymer suitable for a tyre tread is a function of T_g , the glass transition temperature of the polymer, and the higher the T_g the better the wet grip performance. From these two currently accepted principles it is clear that for good wet properties the tread compound should be selected to have a relatively low rebound resilience and the polymer used should have a relatively high T_g .

Currently tyre manufacturers generally use tread compounds made from polymer blends, for example a styrene-butadiene copolymer/polybutadiene blend applying the above requirements. Two general classes of tread compounds have emerged:

a) those giving high wet grip performance combined with high heat build-up characteristics and relatively high rolling resistance, and having a T_g above minus 55°C; and

b) those giving relatively low wet grip performance combined with low heat build-up characteristics and relatively low rolling resistance, and having a T_g below minus 65°C. These two classes are referred to below as Class (a) and Class (b) compounds respectively.

The inventor has now found that improved tread compounds are ones containing an elastomer of relatively high T_g yet the compound having a relatively high rebound resilience value. These new tread compounds have the advantage of good wet grip performance and improved heat build-up/rolling resistance characteristics.

Accordingly, in a first aspect the present invention provides a tyre whose tread comprises a vulcanised elastomer composition containing as elastomer a styrene-butadiene copolymer having a glass transition temperature (as hereinafter defined) above minus 50°C, said composition having a rebound resilience (as hereinafter defined) of 55% or more.

In a second aspect the invention provides an elastomer composition containing as elastomer a styrene-butadiene copolymer having a glass transition temperature (as hereinafter defined) of above minus 50°C., said composition being vulcanisable to provide a vulcanised composition having a rebound resilience (as hereinafter defined) of 55% or more.

There are, therefore, two features of the elastomer compositions and tyres of this invention:

a) the use of a styrene-butadiene copolymer having a glass transition temperature above minus 50°C and

b) the formulation of that copolymer in a composition which can be vulcanised

to provide a vulcanised composition having a rebound resilience of 55% or more. Vulcanisation compounding ingredients and vulcanisation conditions suitable to provide a rebound resilience of 55% or more will be apparent to those skilled in the art.

The rebound resilience referred to herein is that measured using the Dunlop Pendulum at 50°C according to B.S. 903/1950. The elastomer compositions of this invention preferably are ones vulcanisable to provide a vulcanised composition having a rebound resilience of 60% or more, especially in the range from 60% to 95%, and more especially 60% to 75%.

Glass transition temperature (T_g) can be measured by various known methods and in this specification it is defined as the temperature at which there is a change in the shape of a curve of volume plotted against temperature as measured by dilatometry. In the glassy state there is a lower volume coefficient of expansion than in the rubbery state, thus producing the change in shape of the curve.

The polymers used in the elastomer compositions and in the treads of the tyres of this invention are preferably ones having a T_g in the range from minus 45°C to minus 20°C, especially in the range from minus 40°C to minus 25°C, for instance minus 40°C to minus 30°C.

It has been found according to the invention that polymers having a T_g (as hereinbefore defined) above minus 50°C and which provide vulcanised elastomer compositions having a rebound resilience of 55% or more are styrene-butadiene copolymers having a styrene content of not more than 40%, especially in the range 20% to 40% by weight, for instance 20 to 25% by weight. These copolymers are normally formed by the inter-polymerisation of styrene and butadiene without the interaction of any other polymerisable monomer. Preferred copolymers are ones in which a major portion (for example from 50% to 80% and especially from 60 to 75%) of the butadiene has polymerised at the butadiene 1,2 positions.

The copolymers can have small styrene blocks and/or butadiene blocks (for example 5% by weight of the copolymer) at the ends of the copolymer molecules.

The invention is illustrated by the following Examples in which, unless stated otherwise, the proportions of ingredients in the compositions is given in parts by weight.

The compositions of Examples 1 to 3 include as their polymer ingredient solution SBR copolymers referred to as Copolymer P, A and C respectively which are styrene-butadiene copolymers and have average molecular weights in the range 440,000 to 490,000. Copolymer C has part of its butadiene in the form of end blocks which amount to 8% by weight of the copolymer.

The molecular weights of the copolymers are as follows:

	Molecular weight
Copolymer P	475,000
Copolymer A	440,000
Copolymer C	490,000

The salient chemical features of the three copolymers and their T_g values are as follows:

	Copolymer P	Copolymer A	Copolymer C
Styrene content (%)	22.7	22.8	20.2
Vinyl group content (%)	70	66	56
Glass transition temperature (T_g) (°C)	minus 34	minus 34	minus 36

That portion of the copolymers in what the butadiene has reacted by "head-to-tail" 1,4 polymerisation has been found largely to have a *trans* configuration.

Three tyre tread compositions of the invention have been obtained by blending together the following ingredients. The amounts of the ingredients used and physical properties of the cured compositions (40 minutes at 140°C in a steam autoclave) are given below.

Ingredients	Example No.		
	1	2	3
Copolymer P	100		
Copolymer A		100	
Copolymer C			100
Sulphur	1.75	1.75	1.83
N.O.B.S. Santocure MOR (Monsanto Ltd.) Accelerator	1.00	1.00	1.05
N 375 carbon black	50.00	50.00	50.00
Arrconox GP antioxidant	2.00	2.00	2.00
Zinc oxide	3.00	3.00	3.00
Stearic acid	1.00	1.00	1.00
Mechanical Properties			
Tensile strength (M Pa)	8.0	22.2	12.1
Stress @ 300% (M Pa)	—	11.4	—
Elongation @ break (%)	235	475	280
Hardness (I.R.H.D.)	69.8	70.3	74.1
Resilience at 50°C (%)	66.3	60.5	65.5

(Santocure and Arrconox are Trade Marks)

By comparison a Class a) tread compound typically has a hardness of 67 IRHD and a resilience of 51% at 50°C, and a Class b) compound has a hardness of 67 IRHD and a resilience of 71% at 50°C.

Under rolling conditions at constant load a major component to the power consumption of the tread compound of the tyre is proportional to the compound's loss modulus divided by its complex modulus squared ($E''/(E^*)^2$).

Therefore this can be used as a measure of the tread compound's heat build-up/rolling resistance performance—the lower the value the better the heat build-up/rolling resistance performance.

Typical figures for known existing types of compounds are:—

Compound Class (a)	Temperature	E''/E^*^2 MP a ⁻¹
Compound Class (a)	50°C	0.0260
	80°C	0.0241
	100°C	0.0210
Compound Class (b)	50°C	0.0170
	80°C	0.0160
	100°C	0.0170

The power loss values for the tyre tread compositions of the Examples are given in the Table below. The various values have been given reference numbers 1 to 4 whose means and units are as follows:—

	Unit
1. Elastic modulus (E')	M Pa
2. Loss modulus (E'')	M Pa
3. Loss factor (E''/E')	
4. (E''/E^*^2)	M Pa ⁻¹

The results for the four values, each measured at 50, 80 and 100°C, are given below.

	50°C	80°C	100°C
Example 1			
1	7.44	6.68	6.46
2	0.69	0.57	0.51
3	0.093	0.085	0.079
4	0.0123	0.0127	0.0121

Example 2

1	7.14	6.16	5.85
2	0.86	0.62	0.52
3	0.120	0.100	0.089
4	0.0166	0.0161	0.0152

Example 3

1	8.43	7.82	7.65
2	0.81	0.62	0.52
3	0.096	0.079	0.068
4	0.0113	0.0101	0.0089

It can be seen that the E''/E^{*2} values for the compositions of the Examples are all significantly lower than those for both of the known classes of compounds. The compositions of Examples 2 and 3, have been tested to assess their wet grip and rolling resistance properties on a road surface. Each of these compositions was used as the tread compound of model tyres of size 2.25—8 (dimensions in inches). These model tyres were subjected to two tests as follows.

Grip on a wet Delugrip road surface (Delugrip is a Trade Mark) was measured using the variable speed internal drum machine (VSIDM) described in a paper by G Lees and A. R. Williams in Journal of the Institute of the Rubber Industry, Vol. 8, No. 3 June 1974. Measurements of the wet grip were made for both peak and locked wheel friction at speeds of 16, 32, 48, 64, 80 and 96 km/hour (miles/respectively). Rolling resistance was measured using the dynamics machine described in UK Patent 1,392,033. These measurements were made at speeds of 20, 40, 60 and 80 km/hour/respectively.

The results obtained from these tests are shown graphically in Figures 1 and 2 of the accompanying drawings.

In each of Figures 1 and 2 the results obtained using the tread compositions of Examples 2 and 3 are referred to respectively by the letter of their constituent copolymer, that is by A or C.

WHAT WE CLAIM IS:—

1. A tyre whose tread comprises a vulcanised elastomer composition containing as elastomer a styrene-butadiene copolymer having a glass transition temperature (as hereinbefore defined) above minus 50°C, said composition having a rebound resilience (as hereinbefore defined) of 55% or more.

2. A tyre according to Claim 1, in which said glass transition temperature is in the range from minus 45°C to minus 20°C.

3. A tyre according to Claim 2, in which said glass transition temperature is in the range from minus 40°C to minus 25°C.

4. A tyre according to Claim 1, 2 or 3, in which said rebound resilience (as hereinbefore defined) is 60% or more.

5. A tyre according to Claim 4, in which said rebound resilience is in the range from 60% to 75%.

6. A tyre according to any of the preceding claims, in which the said styrene-butadiene copolymer has a styrene content of not more than 40% by weight of the copolymer.

7. A tyre according to Claim 6, in which said copolymer has a styrene content in the range from 20% to 40% by weight of the copolymer.

8. A tyre according to any of the preceding claims, in which from 50% to 80% of the butadiene of said copolymer has polymerised at the butadiene 1,2 positions.

9. A tyre according to Claim 8, in which from 60% to 75% of the butadiene of said copolymer has polymerised at the butadiene 1,2 positions.

10. A tyre according to Claim 6, 7 or 8 in which said copolymer has styrene blocks at the ends of its molecules.

11. A tyre according to Claim 6, 7 or 8, in which said copolymer has butadiene blocks at the ends of its molecules.

12. A tyre according to Claim 1, in which said copolymer is one having a styrene content in the range from 20% to 25% and a butadiene content correspondingly in the range from 80% to 75% by weight, a molecular weight in the range 440,000 to 490,000 a glass transition temperature in the range from minus 30°C to minus 40°C, and in which from 60% to 75% by weight of the butadiene has polymerised at the butadiene 1,2 positions.

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Example 2

1	7.14	6.16	5.85
2	0.86	0.62	0.52
3	0.120	0.100	0.089
4	0.0166	0.0161	0.0152

Example 3

1	8.43	7.82	7.65
2	0.81	0.62	0.52
3	0.096	0.079	0.068
4	0.0113	0.0101	0.0089

It can be seen that the E^*/E^{*2} values for the compositions of the Examples are all significantly lower than those for both of the known classes of compounds. The compositions of Examples 2 and 3, have been tested to assess their wet grip and rolling resistance properties on a road surface. Each of these compositions was used as the tread compound of model tyres of size 2.25—8 (dimensions in inches). These model tyres were subjected to two tests as follows.

Grip on a wet Delugrip road surface (Delugrip is a Trade Mark) was measured using the variable speed internal drum machine (VSIDM) described in a paper by G Lees and A. R. Williams in Journal of the Institute of the Rubber Industry, Vol. 8, No. 3 June 1974. Measurements of the wet grip were made for both peak and locked wheel friction at speeds of 16, 32, 48, 64, 80 and 96 km/hour (miles/respectively). Rolling resistance was measured using the dynamics machine described in UK Patent 1,392,033. These measurements were made at speeds of 20, 40, 60 and 80 km/hour/respectively.

The results obtained from these tests are shown graphically in Figures 1 and 2 of the accompanying drawings.

In each of Figures 1 and 2 the results obtained using the tread compositions of Examples 2 and 3 are referred to respectively by the letter of their constituent copolymer, that is by A or C.

WHAT WE CLAIM IS:—

1. A tyre whose tread comprises a vulcanised elastomer composition containing as elastomer a styrene-butadiene copolymer having a glass transition temperature (as hereinbefore defined) above minus 50°C, said composition having a rebound resilience (as hereinbefore defined) of 55% or more.

2. A tyre according to Claim 1, in which said glass transition temperature is in the range from minus 45°C to minus 20°C.

3. A tyre according to Claim 2, in which said glass transition temperature is in the range from minus 40°C to minus 25°C.

4. A tyre according to Claim 1, 2 or 3, in which said rebound resilience (as hereinbefore defined) is 60% or more.

5. A tyre according to Claim 4, in which said rebound resilience is in the range from 60% to 75%.

6. A tyre according to any of the preceding claims, in which the said styrene-butadiene copolymer has a styrene content of not more than 40% by weight of the copolymer.

7. A tyre according to Claim 6, in which said copolymer has a styrene content in the range from 20% to 40% by weight of the copolymer.

8. A tyre according to any of the preceding claims, in which from 50% to 80% of the butadiene of said copolymer has polymerised at the butadiene 1,2 positions.

9. A tyre according to Claim 8, in which from 60% to 75% of the butadiene of said copolymer has polymerised at the butadiene 1,2 positions.

10. A tyre according to Claim 6, 7 or 8 in which said copolymer has styrene blocks at the ends of its molecules.

11. A tyre according to Claim 6, 7 or 8, in which said copolymer has butadiene blocks at the ends of its molecules.

12. A tyre according to Claim 1, in which said copolymer is one having a styrene content in the range from 20% to 25% and a butadiene content correspondingly in the range from 80% to 75% by weight, a molecular weight in the range 440,000 to 490,000 a glass transition temperature in the range from minus 30°C to minus 40°C, and in which from 60% to 75% by weight of the butadiene has polymerised at the butadiene 1,2 positions.



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13. A tyre according to Claim 1 having a tread formed of an elastomer composition substantially as described herein with reference to the accompanying drawings.

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14. A tyre having a tread formed of an elastomer composition substantially as disclosed in Example 1.

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15. A tyre having a tread formed of an elastomer composition substantially as disclosed in Examples 2 or 3.

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16. An elastomer composition containing as elastomer a styrene-butadiene copolymer having a glass transition temperature (as hereinbefore defined) above minus 50°C, said composition being vulcanisable to provide a vulcanised composition having a rebound resilience (as hereinbefore defined) of 55% or more.

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17. An elastomer composition according to Claim 16, in which said glass transition temperature is in the range from minus 45°C. to minus 20°C.

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18. An elastomer composition according to Claim 17, in which said glass transition temperature is in the range from minus 40°C. to minus 25°C.

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19. An elastomer composition according to Claim 16, 17 or 18, in which said rebound resilience (as hereinbefore defined) is 60% or more.

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20. An elastomer composition according to Claim 19, in which said rebound resilience is in the range from 60% to 75%.

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21. An elastomer composition according to any of Claims 16 to 20, in which said copolymer has a styrene content of not more than 40% by weight of the copolymer.

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22. An elastomer composition according to Claim 21, in which said copolymer has a styrene content in the range from 20% to 40% by weight of the copolymer.

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23. An elastomer composition according to any of Claims 16 to 22, in which from 50% to 80% of the butadiene of the copolymer has polymerised at the butadiene 1, 2 positions.

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24. An elastomer composition according to Claim 23, in which from 60% to 75% of the butadiene has polymerised at the butadiene 1,2 positions.

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25. An elastomer composition according to Claim 21, 22 or 23, in which the copolymer has styrene blocks at the ends of its molecules.

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26. An elastomer composition according to Claim 21, 22 or 23 in which the copolymer has butadiene blocks at the ends of its molecules.

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27. An elastomer composition according to Claim 16, in which the copolymer has a styrene content in the range from 20% to 25% and a butadiene content correspondingly in the range from 80% to 75% by weight, a molecular weight in the range 440,000 to 490,000, a glass transition temperature in the range from minus 30°C. to minus 40°C, and in which from 60% to 75% by weight of the butadiene has polymerised at the butadiene 1,2 positions.

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28. An elastomer composition according to Claim 16 substantially as described herein.

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29. An elastomer composition substantially as disclosed in Example 1.

30. An elastomer composition substantially as disclosed in Example 2 or 3.

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