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CA 2350719 A1 2000/05/18

(21) **2 350 719**

(12) **DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION**

(13) **A1**

(86) Date de dépôt PCT/PCT Filing Date: 1999/11/08
(87) Date publication PCT/PCT Publication Date: 2000/05/18
(85) Entrée phase nationale/National Entry: 2001/05/07
(86) N° demande PCT/PCT Application No.: NL 99/00683
(87) N° publication PCT/PCT Publication No.: WO 00/27915
(30) Priorité/Priority: 1998/11/06 (98203763.2) EP

(51) Cl.Int.⁷/Int.Cl.⁷ C08L 17/00, C08L 23/16, C08L 23/08,
C08L 23/04, C08L 21/00

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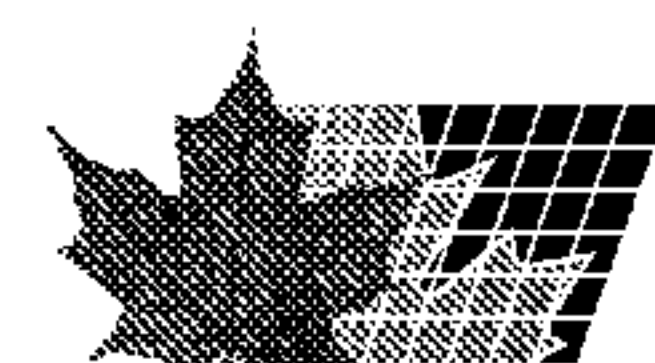
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(54) Title: RUBBER COMPOSITION

(57) **Abrégé/Abstract:**

The invention is directed to a rubber composition comprising: an amount of 5 to 70 parts by weight of vulcanised, ground rubber scrap; an amount of 1 to 30 parts by weight of a combination of at least one EPDM rubber and at least one EVA copolymer, the EPDM rubber and the EVA copolymer having undergone a partial condensation reaction with an ethylene copolymer having short chain branching; an amount of 20 to 95 parts by weight of virgin rubber.



**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C08L 17/00, 21/00 // (C08L 17/00, 21:00, 23:16, 23:08, 23:04) (C08L 21/00, 17:00, 23:16, 23:08, 23:04)	A1	(11) International Publication Number: WO 00/27915 (43) International Publication Date: 18 May 2000 (18.05.00)
(21) International Application Number: PCT/NL99/00683 (22) International Filing Date: 8 November 1999 (08.11.99) (30) Priority Data: 98203763.2 6 November 1998 (06.11.98) EP (71) Applicant (for all designated States except US): BENNET INTELLECTUAL B.V. [NL/NL]; Televisieweg 83, NL-1322 AK Almere (NL). (72) Inventors; and (75) Inventors/Applicants (for US only): VAN DER GROEP, Lambertus, Adrianus [NL/NL]; Gersthove 33, NL-1112 HN Diemen (NL). BILLIET, Johan, Stefaan, Piet [BE/BE]; Rue de Longeau 18, B-6791 Athus (BE). (74) Agent: OTTEVANGERS, S., U.; Vereenigde, Nieuwe Parklaan 97, NL-2587 BN The Hague (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RUBBER COMPOSITION (57) Abstract The invention is directed to a rubber composition comprising: an amount of 5 to 70 parts by weight of vulcanised, ground rubber scrap; an amount of 1 to 30 parts by weight of a combination of at least one EPDM rubber and at least one EVA copolymer, the EPDM rubber and the EVA copolymer having undergone a partial condensation reaction with an ethylene copolymer having short chain branching; an amount of 20 to 95 parts by weight of virgin rubber.		

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Title: Rubber composition

The invention is in the field of recycling used vulcanised, natural and synthetic rubber, more in particular in the field of recycling vulcanised, ground tire rubber, profiles, production waste and post consumer waste, to
5 produce polymer blends having useful properties.

In the recycling of used car tires, the re-use of the rubber part of the tires has always posed substantial problems. As the tire rubber scrap is vulcanised, regular processing methods, like those used for recycling
10 thermoplastic polymers, cannot be used. The rubber scrap is substantially inert. Incineration and landfill are still the major methods for disposal of old tires and recycling is limited.

In a review article on the re-use of ground rubber tire scrap (GRT) in Scheirs, J.; Polymer Recycling-Science, Technology and Applications; John Wiley & Sons; Chichester, 1998; pag. 411-457, it has been indicated that filler
15 applications are still the main use of GRT. Re-use in virgin material is still possible only to extends below about 10 wt.%, as the GRT acts as filler only.
20

In the past some experiments have been done with re-use of vulcanised, ground rubber scrap from tires, by blending them with polyolefins, using compatibility enhancers, such as functionalized olefin polymers. In US
25 patent specification 5,157,082 various compatibility enhancers have been disclosed. However, this method has only limited use because of the expense of the specific additives. Further, the properties of the final material are still not sufficient to gain wide market acceptance.

30 Accordingly, there is a need in the art for systems, wherein vulcanised, ground rubber scrap can be used in such a way that useful rubber compositions are obtained; more in particular in useful blends with the same material as the

origin of the rubber. Further, there is a need for the use of this rubber scrap in said compositions, which compositions may have a wide variety of physical and mechanical properties such as useful hardness, values, ozone resistance, and the ability to process the material on conventional rubber processing equipment. More in particular there is a need for re-use of ground rubber scrap in applications, wherein the scrap replaces virgin rubber, while maintaining the properties of the original virgin rubber. In this respect the term 'virgin rubber' is intended to indicate rubber that has not yet undergone a vulcanisation or other crosslinking treatment. The term 'rubber' is used in the conventional sense of a polymeric substance having a glass transition temperature well below -35°C , as defined in ASTM D3418.

The present invention is accordingly directed to a rubber composition comprising

- an amount of 5 to 70 parts by weight of vulcanised, ground rubber scrap,
- an amount of 1 to 30 parts by weight of a combination of at least one EPDM rubber and at least one EVA copolymer, the EPDM rubber and the EVA copolymer having undergone a partial condensation reaction with an ethylene copolymer having short chain branching
- an amount of 20 to 95 parts by weight of virgin rubber.

Surprisingly, it has been found that such a rubber composition, comprising on the one hand ground rubber scrap and on the other hand the reaction product of EPDM and EVA provides a superior quality rubber composition having properties that may range from thermoplastic rubbers to vulcanisable rubbers.

According to a first embodiment such a rubber composition comprises 10 - 40 parts by weight of vulcanised, ground rubber scrap, 15 - 45 wt.% of the condensation product of EPDM rubber and EVA copolymer and 20 to 75 parts by weight of virgin rubber. According to another embodiment the rubber

composition comprises additionally an amount of from 1 to 20 parts by weight of oil, preferably a paraffinic oil.

When preparing the rubber composition according to the invention it is preferred to react EPDM, EVA, ethylene
5 copolymer and (optional) other components together to give the reaction product, which is then blended with the rubber scrap, the virgin rubber and optional further components.

It is to be noted that the method of making a reaction product from EPDM, EVA and other polymers have been
10 described in various patent publications, such as US patent numbers 4,877,827, 5,001,195, 4,997,880 and 5,017,659. In the invention the product prepared according to these patents may be used, or products having minor modifications thereof. The contents of the said US patent specifications are
15 incorporated herein by way of reference.

In the composition of the present invention at least one EPDM rubber should be present. This rubber is based on ethylene, propylene and at least one diene monomer, such as those conventionally used. Examples are dicyclopentadiene,
20 hexadiene, ethylidene-norbornene and the like. It is preferred to use an EPDM that has a Mooney viscosity ML(1+4) at 125°C between 8 and 60.

With respect to the EVA component, the copolymer of ethylene and vinylacetate, it is to be noted that the same
25 comments apply. According to a preferred embodiment at least one ethylene vinylacetate copolymer having a vinylacetate content of between 25 and 40 wt.% is used. In accordance with another preferred embodiment a combination of at least 2 EVA copolymers is being used, one having a vinylacetate content
30 between 25 and 40 wt.%, whereas the other one has a vinylacetate content between 10 and 20 wt.%. The relative amounts of the two products are preferably between 1 : 2 to 2 :1.

As has been indicated previously the invention
35 requires that part of the EPDM and part of the EVA have undergone a chemical reaction. In the preparation, the

reaction conditions disclosed in the cited US patents can be used.

According to the invention the condensation product has undergone a reaction with an ethylene polymer having
5 short chain branching. This polymer is suitably a linear low density polyethylene, based on ethylene and at least one C₄ to C₈ copolymer. The amount of the copolymer ranges between 5 and 40 wt.% calculated on the weight of EPDM, EVA and the copolymer together.

10 In the present invention it is possible to use vulcanised, ground rubber scrap, such as ground tire rubber (GTR), which forms the largest amount of the rubber to be recycled. However, it is also possible to use other vulcanised natural or synthetic rubbers in the present
15 invention such as vulcanised SBR, vulcanised blends of natural rubber and SBR, and vulcanised EPDM, BAN, butyl, chlorobutyl or chloroprene rubber. Before use in the present invention the vulcanised rubber is comminuted, preferably grinded, preferably under cryogenic conditions until a
20 particle size preferably between 0.05 and 1.0 mm, preferably between 0.05 and 0.5 mm has been obtained. It is to be noted that GTR usually does not contain substantial amounts of fibres or steel from the tires.

It is to be noted that the amounts of the
25 condensation product and the grinded rubber scrap are related. Preferably the amount of scrap is at most 5 time the amount of the condensation product, taking into account the particle size of the scrap, finer particles requiring higher amounts of condensation product.

30 Further a preferred component of the polymer composition according to the invention is an oil component, such as a paraffinic oil. This oil is preferably a regular paraffinic oil that is used for extending rubbers.

The product of the invention further contains an
35 amount of virgin rubber, preferably of the same or comparable type as the scrap. Virgin rubbers suitable are both natural

and synthetic rubbers, or blends of two or more types of rubber. As synthetic rubbers one may use nitril rubber, SBR, EPDM rubber, butadiene rubber, butyl rubber, chlorinated polyethylene (CPE), neoprene rubber, polyisoprene, and the
5 like.

The composition can be processed into conventional rubber compositions, having the same properties as those based on virgin rubbers, using the same or comparable recipes as those valid for virgin materials. In this respect it is to
10 be noted that the recipes can be used as such, just replacing the virgin material by the combination of the scrap and the condensation product. The amounts of rubber that may be replaced vary in dependence of the type of final product. For thermoplastic rubber compositions this may be up to 70 wt.%
15 of the total composition, whereas for vulcanisable materials this may be up to 40 wt.%.

Depending on the required properties the recipe may be changed, such as the type of vulcanisation (or not), amount of oil, fillers and the like.

20 The rubber composition according to the invention can be used as such, as a thermoplastic elastomer. By careful selection of the rubber, which is usually applied in an amount of 20 to 40 wt.% based on the final blend, it is possible to prepare a whole range of products from
25 (re)vulcanisable rubbers to thermoplastic elastomers having a very high hardness value of up to 50 Shore D. Those products may be used in the conventional manner just as the regular virgin products would be used. This means that the rubbers may for example be filled with carbon and other conventional
30 components. It is also possible to vulcanise the rubber composition of the invention.

The invention is now elucidated on the basis of the following examples.

Example

A blend was prepared from 50 wt.% grinded tire scrap, based on a vulcanised blend of NBR and SBR, 10 wt.% oil (OBI 10) and 40 wt.% of the reaction product of 47.5 wt.% of an EVA copolymer having 28 wt.% vinylacetate, 47.5 wt.% EPDM and 5 wt.% of LLDPE, as described in Example 5 of US patent specification No. 4,877,827.

This blend was mixed in a Banbury mixer at a temperature of 180°C and granulated. The resulting material was tested and the results were as follows:

	Hardness (ISO 7619)	57
	Hardness (168h at 70°C)	51
15	Tensile strength (ISO 37)	2.9 MPa
	Tensile strength (168h at 70°C)	3.0 MPa
	Elongation at break (ISO 37)	400%
	Elongation at break(168h at 70°C)	360%
	Ozone resistance (ISO 1431-1)	
20	480 h, 200 pphm, 40°C, 50% elong.	no effect
	Liquid resistance (ISO 1817)	0% [v/v]

Example 2

25

Various compounds were prepared, based on EPDM rubber scrap and virgin EPDM, with various additives as enumerated in Table 1. The amounts given in table 1 are based in wt.%. The results of various tests, showing the importance of adding the reaction product to obtain good properties, have been included in the tables 2-4.

30

TABLE 1

	Compound		
	I a	I b	I c
Virgin EPDM	10	20	35
Grinded EPDM scrap from profiles; 200-300 micron	50	55	55
Reaction product	30	15	
Paraffinic oil	10	10	10
	100	100	100

	Compound	
	II a	II b
Virgin EPDM	42	32
Grinded EPDM scrap from automotive profiles; < 400 micron		8.3
Reaction product		1.7
Paraffinic oil	21	21
Carbon black	33	33
Mixture vulcanization compounds	4	4
	100	100

	Compound		
	III a*	III b*	III c*
Virgin EPDM	100	80	76
Grinded EPDM scrap from profiles; 300-350 micron		20	20
Reaction product			4

*Ratio's of the components are based on the total rubber content of the mixture; the mixture is oil-filled and vulcanized

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TABLE 2

	Compound		
	I a	I b	I c
Hardness	Shore A	69	67
Hardness after thermal aging, 168 hr at 70 °C	69	74	68
Hardness after thermal aging, 168 hr at 70 °C;	Change	+ 5	+ 1
Tensile strength	MPa	3.8	2.7
Tensile strength after thermal aging, 168 hr at 70 °C	MPa	3.9	2.8
Tensile strength after thermal aging, 168 hr at 70 °C;	Change	+ 2,6	+ 2,0
Modulus 100%	MPa	1.9	1.4
Modulus 200%	MPa	2.5	2.0
Modulus 300%	MPa	3.2	2.5
Elongation at break	%	411	318
Elongation at break after thermal aging, 168 hr at 70 °C	%	408	
Elongation at break after thermal aging, 168 hr at 70 °C;	Change	- 7	- 0,7
Tear strength	N/mm	32	8.7
Rebound	%	46	41
Abrasion	mm ³	264	259
Compression set, 22 hr at 21 °C	%	35	36
Compression set, 22 hr at 23 °C	%	32	
Compression set, 22 hr at 50 °C	%	76	
Compression set, 22 hr at 70 °C	%	97	97
Compression set, 22 hr at 100 °C	%	106	
Ozone resistance after 480 hr at 40 °C, 200 pphm, 50% elongation	No cracks		

TABLE 3

	Compound		
	II a	II b	
Hardness	Shore A	67	59
Hardness after thermal aging, 168 hr at 70 °C	Shore A	68	62
Hardness after thermal aging, 168 hr at 70 °C;	Change	+ 1	+ 3
Tensile strength	MPa	14.7	11.4
Modulus 100%	MPa	3.7	1.8
Modulus 200%	MPa	8.2	4.1
Modulus 300%	MPa	13.1	6.4
Elongation at break	%	331	529
Tear strength	N/mm	16	12.3
Rebound	%	48	47
Compression set, 22 hr at 100 °C	%	4.3	12

TABLE 4

	Compound		
	III a	III b	III c
Hardness	72	68	61
Hardness after thermal aging, 168 hr at 70 °C	75	72	61
Hardness after thermal aging, 168 hr at 70 °C;	+ 3	+ 4	0
Mooney ML(1 + 4) 100 °C	50.2	46.2	52.5
Tensile strength	10.0	9.3	10.6
Tensile strength after thermal aging, 168 hr at 70 °C	10.8	5.1	11.1
Hardness after thermal aging, 168 hr at 70 °C;	+ 8	- 45	+ 4.7
Modulus 100%	3.5	3.1	1.9
Modulus 200%	6.8	7.2	3.4
Modulus 300%	9.4	9.1	4.8
Elongation at break	337	308	631
Elongation at break after thermal aging, 168 hr at 70 °C	336	289	656
Elongation at break after thermal aging, 168 hr at 70 °C;	- 0,3	- 6,2	+ 4,0
Tear strength	7.1	5.8	15.7
Rebounce	35	39	40
Abrasion	217	208	198
Compression set, 22 hr at 21 °C	21.7	13.5	16.7
Compression set, 70 hr at 21 °C			
Compression set, 22 hr at 70 °C	18.5	15.8	
Compression set, 24 hr at 70 °C			16.2

Claims

1. Rubber composition comprising
 - an amount of 5 to 70 parts by weight of vulcanised, ground rubber scrap,
 - an amount of 1 to 30 parts by weight of a combination
 - 5 of at least one EPDM rubber and at least one EVA copolymer, the EPDM rubber and the EVA copolymer having undergone a partial condensation reaction with an ethylene copolymer having short chain branching
 - an amount of 20 to 95 parts by weight of virgin
 - 10 rubber.
2. Rubber composition according to claim 1 or 2, further comprising, 1 - 20 wt.% of paraffinic or aromatic oil, preferably paraffinic oil.
3. Rubber composition according to claim 1 or 2,
- 15 comprising
 - 10 - 40 parts by weight of vulcanised, ground rubber scrap,
 - 15 - 45 wt.% of the condensation product of EPDM rubber and EVA copolymer, and
 - 20 to 75 parts by weight of virgin rubber.
- 20 4. Rubber composition according to claim 1-3, wherein the vulcanised, ground rubber scrap is tire rubber scrap, profile scrap, grinded post consumer waste or post production waste.
5. Rubber composition according to claim 1-4, wherein
- 25 the ethylene copolymer having short chain branching is linear low density polyethylene, preferably based on C₄, C₆ and/or C₈ copolymers of ethylene.
6. Rubber composition according to claim 1-5, wherein the amount of ethylene copolymer having short chain branching
- 30 is between 5 and 20 wt.% of the weight of the condensation product.

7. Rubber composition according to claim 1-6, wherein the ground rubber scrap has a particle size of between 0.05 and 1.0 mm, preferably between 0.05 and 0.5 mm.
8. Rubber composition according to claim 1-7, wherein
5 additionally conventional rubber additives are present, including fillers and vulcanisation additives.
9. Use of the rubber composition according to claim 1-8 as virgin rubber composition.