

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
8 April 2010 (08.04.2010)

PCT

(10) International Publication Number
WO 2010/039327 A1

- (51) **International Patent Classification:**
B60C 1/00 (2006.01) *C08J 11/04* (2006.01)
- (21) **International Application Number:**
PCT/US2009/052329
- (22) **International Filing Date:**
31 July 2009 (31.07.2009)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/101,262 30 September 2008 (30.09.2008) US
- (71) **Applicant (for all designated States except CA, MX, US):** **Societe de Technologie Michelin** [FR/FR]; 23, rue Breschet, F-63000 Clermont-Ferrand (FR).
- (71) **Applicant (for all designated States except US):** **Michelin Recherche et Technique S.A.** [CH/CH]; Route Louis-Braille 10, CH-1763 Granges-Paccot (CH).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only):** **MEREDITH, Michael, Brett** [US/US]; 304 Stewart Street, Greenville, SC 29605 (US). **PENDER, Mark, J.** [US/US]; 6 Leslie Court, Maulding, SC 29662 (US).
- (74) **Agent:** **ULDRICK, Carolyn, G.**; Michelin North America, Inc., Intellectual Property Department, 515 Michelin Road, Greenville, SC 29605 (US).
- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Declarations under Rule 4.17:**
— of inventorship (Rule 4.17(iv))
- Published:**
— with international search report (Art. 21(3))



WO 2010/039327 A1

(54) **Title:** RUBBER WITH RECYCLED CONTENT

(57) **Abstract:** Rubber compositions, methods of making rubber compositions and articles comprising the rubber compositions that have crumb rubber particles in the rubber compositions. A cross-linked rubber composition, comprising a diene rubber and a masterbatch material comprising between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles, wherein the crumb rubber particles are 40 mesh or smaller. A method for preparing a rubber composition having crumb rubber, the method comprising mixing a masterbatch, the masterbatch comprising between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles and mixing the masterbatch with a diene rubber.

RUBBER WITH RECYCLED CONTENT

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] This invention relates generally to crumb rubber and more specifically, to crumb rubber content in rubber compositions.

Description of the Related Art

[0002] In 2005, nearly 300 million tires were generated in the United States and 259 million scrap tires were consumed in end-use markets. Scrap tires are consumed in a variety of scrap tire markets, including tire-derived fuel, civil engineering and ground rubber applications. Ground rubber is also known as crumb rubber or recycled rubber.

[0003] Ground rubber applications used about 12 percent of the scrap tires generated. These applications include, for example, rubber-modified asphalts, molded products, sports surfacing, animal bedding, new tire manufacturing and horticultural applications. New tire manufacturing is thought to include about seven percent of the ground rubber market in the United States. Sources for ground rubber include tire buffings from retread operations and processed whole scrap tires. Whole scrap tires are processed by removing the wire and textile to create ground rubber as specified by the market application.

[0004] Ground rubber is typically classified by particle size or mesh. Mesh is defined as the number of holes per square inch of a screen used for sorting particles into different sizes. The higher the number of holes in the screen, the smaller the hole size. For example, particles that are 100 mesh or smaller are those that will pass through a screen having 100 holes per square inch of screen.

[0005] Only low amounts of ground rubber, usually less than 5% by weight of the rubber in the tire, are used in new tires. The addition of higher percentages of ground rubber has been shown to lower important functional properties such as strain modulus and tensile strength. There is a need for a rubber composition and a method for incorporating ground rubber that does not compromise desirable properties of the rubber composition.

SUMMARY OF THE INVENTION

[0006] Particular embodiments of the present invention include a cross-linked rubber composition comprising a diene rubber and a masterbatch material. The masterbatch comprises between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles, the crumb rubber particles being 40 mesh or smaller.

[0007] Another embodiment of the present invention includes an article comprising the cross-linked rubber composition, wherein the cross-linked rubber composition comprises a diene rubber and a masterbatch material. The masterbatch comprising between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles, the crumb rubber particles being 40 mesh or smaller.

[0008] Particular embodiments of the present invention include a method for preparing a rubber composition utilizing crumb rubber. The method may comprise mixing a masterbatch, the masterbatch comprising between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles and mixing the masterbatch with a diene rubber.

[0009] Particular embodiments of such methods may further include cooling the masterbatch prior to mixing the masterbatch with the diene rubber. Another embodiment may include adding an additives package during the step of mixing the masterbatch with a diene rubber. Still another embodiment of the method includes milling the semi-finished batch and incorporating a curatives package.

[0010] The foregoing and other objects, features and advantages of the invention will be apparent from the following more detailed descriptions of particular embodiments of the invention.

DETAILED DESCRIPTION OF PARTICULAR EMBODIMENTS

[0011] Particular embodiments of the present invention include rubber compositions, methods of making rubber compositions and articles comprising the rubber compositions having crumb rubber particles in the rubber compositions. Typically, when ground rubber is added to a rubber composition certain performance properties deteriorate. The inventors of the present invention have discovered that if the crumb rubber is incorporated into the rubber composition through a masterbatch that contains the crumb

rubber then the resulting rubber composition may be characterized as having comparable and even enhanced performance properties.

[0012] A masterbatch may be a plastic, rubber, or elastomer mixture in which there is a high additives concentration. The additives are then added to the final product composition by adding the masterbatch to the final product composition rather than adding the additive neat. Examples of masterbatches include rubber with carbon black or plastic with color pigment. The masterbatch allows for a homogeneous distribution of the additive throughout the final product composition, in this case, crumb rubber throughout the rubber mixture.

[0013] Particular embodiments of a cross-linked rubber composition in accordance with the present invention include a diene rubber and a masterbatch material. The masterbatch comprises a diene rubber and crumb rubber. Suitable diene rubbers for the masterbatch may include, for example, natural rubber (NR), polybutadienes (BR), polyisoprenes (IR), butadiene copolymers, isoprene copolymers and mixtures of these rubbers. The consistency of the masterbatch is dependant upon the rubber chosen for use. Some materials may require additional mixing to improve the consistency of the masterbatch to improve handling properties. In particular embodiments a natural rubber is the diene rubber used in the masterbatch. The masterbatch material may comprise, for example, between 50 and 75 wt.% diene rubber or in other embodiments between 60 and 70 wt.% diene rubber. Particular embodiments of the present invention include use of only a highly unsaturated dienic rubber, such as, natural rubber.

[0014] The masterbatch also comprises crumb rubber. Crumb rubber particles are characterized by mesh size. As discussed earlier, the mesh size is defined by the number of holes per square inch of screen so the larger the number of holes, the smaller are the holes in the screen. Crumb rubber particles are readily available on the market in 40 to 220 mesh sizes. Typically the smaller particles are easier to process and yield better performance. Particles that are 40 mesh or smaller are particles that pass through a 40 mesh screen. In particular embodiments, the crumb rubber particles are 40 mesh particles or smaller, 60 mesh particles or smaller, 80 mesh particles or smaller, 120 mesh particles or smaller or combinations thereof. Smaller particles sizes may also be used in particular embodiments.

[0015] Crumb rubber particles may be recovered from many types of rubber products, including from whole tires or from the tread only parts of the tires. Particular

embodiments of the present invention use crumb rubber particles from tread only materials. Other embodiments use crumb rubber from whole tires. The tread-only particles may include, for example, natural rubber and styrene-butadiene rubber. The whole tire particles may include, for example, natural rubber, styrene-butadiene rubber and butyl rubber in varying concentrations. Particular embodiments include crumb rubber that has not been biodegraded with a biologic agent.

[0016] Crumb rubber particles may be ground using a cryogenic process or a mechanical grinding process. In both processes the steel components are removed using a magnetic separator and the fiber components are separated by air classifiers or other separation equipment. In the cryogenic process, shredded rubber is frozen at an extremely low temperature then shattered into small particles. The mechanical grinding process uses a variety of grinding techniques, such as cracker mills, granulators, etc. to mechanically break down the rubber into small particles. Particular embodiments of the present invention use crumb rubber particles produced using a cryogenic process. Other embodiments use crumb rubber particles produced through a mechanical grinding process. A suitable crumb rubber for use in the present invention is, for example, commercially available under the trade names PolyDyne (80 mesh and smaller particles) from Lehigh Technologies or Micron (40 mesh and smaller particles & 80 mesh and smaller particles) from Edge Rubber. PolyDyne from Lehigh is produced using a cryogenic process and Micron from Edge is produced using a mechanical wet grinding process.

[0017] While not limiting the invention to any particular range of crumb rubber content, particular embodiments of the present invention include a masterbatch comprising between 25 and 50 wt.% crumb rubber particles, between 30 and 40 wt.% crumb rubber particles, between 1 and 60 wt.% crumb rubber particles or between 15 and 50 wt.% crumb rubber particles.

[0018] Particular embodiments of the present invention include a masterbatch mixed with a diene rubber to form a semi-finished batch or cross-linked rubber composition. The diene rubber included in particular embodiments is an essentially unsaturated diene rubber. Diene elastomers or rubber is understood to mean those elastomers resulting at least in part (*i.e.*, a homopolymer or a copolymer) from diene monomers (monomers bearing two double carbon-carbon bonds, whether conjugated or not). Essentially unsaturated diene elastomers are understood to mean those diene

elastomers that result at least in part from conjugated diene monomers, having a content of members or units of diene origin (conjugated dienes) that are greater than 15 mol.%.

[0019] Thus, for example, diene rubbers such as butyl rubbers, nitrile rubbers or copolymers of dienes and of alpha-olefins of the ethylene-propylene diene terpolymer (EPDM) type or the ethylene-vinyl acetate copolymer type do not fall within the preceding definition, and may in particular be described as "essentially saturated" diene elastomers (low or very low content of units of diene origin, *i.e.*, less than 15 mol.%. Particular embodiments of the present invention may include no essentially saturated diene elastomers.

[0020] Within the category of essentially unsaturated diene elastomers are the highly unsaturated diene elastomers, which are understood to mean in particular diene elastomers having a content of units of diene origin (conjugated dienes) that is greater than 50 mol.%.

[0021] The diene rubber suitable for use with particular embodiments of the present invention include highly unsaturated diene rubbers, for example, polybutadienes (BR), polyisoprenes (IR), natural rubber (NR), butadiene copolymers, isoprene copolymers and mixtures of these rubbers.

[0022] Also suitable for use in particular embodiments of the present invention are diene rubbers that are copolymers and include, for example, butadiene-styrene copolymers (SBR), butadiene-isoprene copolymers (BIR), isoprene-styrene copolymers (SIR) and isoprene-butadiene-styrene copolymers (SBIR), mixtures thereof and/or with other essentially unsaturated and /or highly unsaturated rubber elastomers.

[0023] Also suitable for use in particular embodiments of the present invention are rubber elastomers that include, for example, natural rubber, synthetic cis-1,4 polyisoprenes and mixtures thereof and/or with other essentially unsaturated and/or highly unsaturated rubber elastomers. These synthetic cis-1,4 polyisoprenes may be characterized as possessing cis-1,4 bonds at more than 90 mol.% or alternatively, at more than 98 mol.%.

[0024] Particular embodiments of the present invention include cross-linked rubber compositions that provide at least 10 phr parts of crumb rubber. Another embodiment of the cross-linked rubber composition provides at least 15 phr parts of crumb rubber in the semi-finished batch. 10-15 phr of the rubber is a measure of crumb rubber particles present in the total rubber composition that includes both the rubber from the

masterbatch and the diene rubber in the rubber composition or semi-finished batch. This amounts to at least 10-15 phr parts of crumb rubber in rubber articles comprising the cross-linked rubber composition of the invention.

[0025] Particular embodiments of a rubber composition in accordance with the present invention may further include other components such as, for example, reinforcing fillers, coupling agents, plasticizers, various processing aids, oil extenders, antidegradants, or combinations thereof as known to those having ordinary skill in the art. Suitable fillers include carbon black as well as inorganic fillers ("white fillers") such as silica, alumina, aluminum hydroxide, clays, calcium carbonate, glass fibers, microspheres, polymeric fibers such as polyester, nylon, or aramid fibers. Selection of these materials and the quantities of these materials to use are dependent on the elastomers used and the final application of the rubber composition and are easily selected by one having ordinary skill in the art.

[0026] Particular embodiments of the present invention include a masterbatch mixed with a diene rubber to form a semi-finished batch or cross-linked rubber composition. The cross-linked rubber composition has a fatigue life, defined as the number of cycles to failure, that is at least 90% of the fatigue life of an identical composition without the crumb rubber particles. In another embodiment of the cross-linked rubber composition the fatigue life is at least 95% of the fatigue life of an identical composition without the crumb rubber particles. In yet another embodiment of the cross-linked rubber composition the fatigue life is at least 99% of the fatigue life of an identical composition without the crumb rubber particles. In still another embodiment of the cross-linked rubber composition the fatigue life is greater than the fatigue life of an identical composition without the crumb rubber particles.

[0027] As used herein, fatigue life is measured using ASTM method D 4482-99 where rubber samples undergo a cyclical straining action until failure. Failure is a complete rupture of the test specimen. Fatigue testing results have shown a large standard deviation that is compound dependent. Therefore, fatigue is determined as the average of a set of 12 samples. According to the ASTM method, natural rubber has shown a narrower distribution than many synthetic rubbers.

[0028] In particular embodiments of the present invention, the masterbatch is made by combining a diene rubber with crumb rubber particles. For example, the masterbatch material may be mixed in a Werner and Pfleiderer GK 5 U/K mixer until the

batch temperature is 170°C. The consistency of the batch is dependent upon the diene rubber chosen for use. The batch may be further mixed in the mixer to achieve a more consistent material. The masterbatch material may then be transferred to an external mixer mill (such as a Lescuyer Villeneuve 300 x 700) for 4 to 7 minutes. Other types of mixers and mills may be used. The masterbatch forms a thick film on the mill rollers. The film is cut and removed from the rollers and laid flat to cool for about one hour. This time may be shortened or extended. The masterbatch material, the additional diene rubber and the additives package may be mixed in the mixer until the mix reaches 155°C. The mix may then be placed on the mill and the curatives package incorporated with the mix while on the mill. The material may then be milled for approximately seven minutes.

[0029] Embodiments of the present invention further include articles comprising the cross-linked rubber composition. The cross-linked rubber compositions disclosed herein may be used for various rubber products such as a tread compound, undertread compound, sidewall compound, wire skim compound, inner liner compound, bead, apex, any compound used in a tire carcass, including carcass reinforcement and in other components for tires, industrial rubber products, seals timing belts, power transmission belting, and other rubber goods. As such, the present invention includes products made from the cross-linked rubber compositions disclosed herein. One embodiment of this article is a tire.

[0030] A tire includes many different structures including, for example, the tread, the sidewall, the undertread, inner liner, bead, apex and tire carcass. The cross-linked rubber composition of the present invention is particularly suited for use in tire sidewalls. Such structures and tire architecture are well known to one having ordinary skill in the art and therefore, a detailed disclosure of such information is neither required nor proper.

[0031] A particular embodiment of the present invention includes methods for preparing a rubber composition utilizing crumb rubber. The method includes mixing a masterbatch, the masterbatch comprising between 50 and 75 wt% natural rubber and between 25 and 50 wt% crumb rubber. The method further comprises cooling the masterbatch and mixing the masterbatch with a diene rubber. Another embodiment of the method includes milling the masterbatch for 4 to 7 minutes at a mill temperature of 30°C prior to mixing the masterbatch with a diene rubber. Still another embodiment of the method includes sub-steps to the mixing the masterbatch with a diene rubber step that includes adding all ingredients except for the curatives package to the mixer and removing

from the mixer at 155°C and milling the semi-finished batch for seven minutes. Another embodiment of the method includes incorporating a curatives package during the milling the semi-finished batch step.

[0032] The invention is further illustrated by the following example, which is to be regarded only as an illustration and not delimitative of the invention in any way.

Example 1

[0033] Rubber formulations were prepared using the components shown in Table 1. The amount of each component making up the rubber formulations shown in Table 1 are provided in parts per hundred weight (phr) of the rubber. The antidegradant and curing package included typical amounts of antidegradants and curing compounds including TMQ, stearic acid, 6PPD, zinc oxide, sulfur and an accelerator as known to one having ordinary skill in the art.

[0034] The masterbatch formulations noted as MB1, MB2, MB3 and MB4 were prepared by mixing natural rubber and crumb rubber in an 8.225 L Werner and Pfleiderer GK 5 U/K mixer at 81% fill ratio with a water temperature of 27°C and a rotor speed of 70 rpm. Peptisant DBD was added to formulation MB2. The material of masterbatches was allowed to mix until it reached 170°C then it was transferred to a Lescuyer Villeneuve 300x 700 External mixer mill for 4 to 7 minutes. The mill transformed the batch into a thick film. The masterbatch material in this film form was allowed to cool for about an hour.

[0035] The rubber formulations R1-R7 were prepared by mixing the components given in Table 1, except for the curing package, with the masterbatch in an 8.225 L Werner mixer at 72% fill ratio with a water temperature of 45°C and a rotor speed of 55 rpm. The piston was raised, cleaned and lowered when the material reached 75°C and again at 135°C. The material was transferred to a Lescuyer Villeneuve mill when the temperature reached 155°C. The material processed on the mill for about 7 minutes. The curatives package was incorporated in the material during this milling time.

[0036] The material was milled to a thickness of 1.85 mm and cured at 170°C for 30 minutes. Sample pieces were cut from the cured sheets and tested according to the relevant ASTM testing methods on a Monsanto MFTR apparatus.

[0037] Twelve samples per formulation were evaluated for fatigue life. Samples were cut with a standard die. The samples were gripped in place on a rack with one

stationary end and one movable end. Each cycle of the fatigue tester consists of increasing strain for one quarter of the cycle time, decreasing strain for one quarter of the cycle time and zero imposed strain for one half of the cycle time. An extension ratio of 75% was used. Samples ran for 5000 cycles then were adjusted on the rack to accommodate for creep. An LED measured the cycle where failure occurred.

Table 1 – Rubber Formulation and Fatigue Results

Rubber Composition	MB1	MB2	MB3	MB4	R1 (Witness)	R2	R3	R4	R5	R6	R7
Natural Rubber	100	100	100	100	50	33.50					
Masterbatch MB1							50				50
Masterbatch MB2								50			
Masterbatch MB3									50		
Masterbatch MB4										50	
BR					50	50	50	50	50	50	50
Lehigh CR (80 mesh, cryo)	50	50				16.5					
Edge CR (40 mesh, wet)			50								
Edge CR (80 mesh, wet)				50							
Peptisant DBD		0.15									
Naphthenic oil					25	20.9	25	25	25	25	25
Carbon Black					60	50.1	60	60	60	60	60
Antidegradant & Curing Package					12	12	12	12	12	12	12
Test Results											
Fatigue Life (cycles)					89925	4664 2	842 42	8947 5	9635 0	1522 17	1084 25

[0038] Compositions R1 and R2 are the witness formulas to be used for performance comparisons. R1 contains a 50/50 blend of natural rubber and butadiene rubber. R2 contains a blend of natural rubber, butadiene rubber and crumb rubber where the crumb rubber is added to the semi-finished batch. The test compositions contain a 50/50 blend of butadiene rubber and a masterbatch where the masterbatch contains natural rubber and crumb rubber. The witness R1 is the identical rubber composition without the crumb rubber particles used in the comparison of fatigue life. The witness R2

demonstrates performance of formulations with the same amount of crumb rubber added without the aid of the masterbatch.

[0039] The results of fatigue testing show the poor performance of the R2 formula which is known in the art. Compositions R3 – R7 show comparable to improved fatigue life results when compared to the identical rubber composition without the crumb rubber particles. The lowest fatigue life value of the test compositions is within 7% of the witness fatigue life value.

[0040] The terms “comprising,” “including,” and “having,” as used in the claims and specification herein, shall be considered as indicating an open group that may include other elements not specified. The term “consisting essentially of,” as used in the claims and specification herein, shall be considered as indicating a partially open group that may include other elements not specified, so long as those other elements do not materially alter the basic and novel characteristics of the claimed invention. The terms “a,” “an,” and the singular forms of words shall be taken to include the plural form of the same words, such that the terms mean that one or more of something is provided. The terms “at least one” and “one or more” are used interchangeably. The term “one” or “single” shall be used to indicate that one and only one of something is intended. Similarly, other specific integer values, such as “two,” are used when a specific number of things is intended. The terms “preferably,” “preferred,” “prefer,” “optionally,” “may,” and similar terms are used to indicate that an item, condition or step being referred to is an optional (not required) feature of the invention. . Ranges that are described as being “between a and b” are inclusive of the values for “a” and “b.”

[0041] It should be understood from the foregoing description that various modifications and changes may be made to the embodiments of the present invention without departing from its true spirit. The foregoing description is provided for the purpose of illustration only and should not be construed in a limiting sense. Only the language of the following claims should limit the scope of this invention.

CLAIMS

What is claimed is:

1. A cross-linked rubber composition, comprising:
 - a diene rubber; and
 - a masterbatch material comprising between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles, wherein the crumb rubber particles are 40 mesh or smaller.
2. The cross-linked rubber composition of claim 1, wherein a fatigue life (cycles to failure) of the rubber composition is at least 90% of a fatigue life of an identical rubber composition without the crumb rubber particles.
3. The cross-linked rubber composition of claim 1, wherein the masterbatch comprises between 60 and 70 wt.% natural rubber and between 30 and 40 wt.% crumb rubber particles.
4. The cross-linked rubber composition of claim 1, wherein the crumb rubber particles are cryogenically processed.
5. The cross-linked rubber composition of claim 1, wherein the crumb rubber particles are mechanically processed.
6. The cross-linked rubber composition of claim 1, wherein the diene rubber is a highly unsaturated diene rubber.
7. The cross-linked rubber composition of claim 6, wherein the diene rubber is selected from a natural rubber, a synthetic polyisoprene rubber or combinations thereof.
8. The cross-linked rubber composition of claim 6, wherein the diene rubber is a natural rubber.

9. The cross-linked rubber composition of claim 2, wherein the fatigue life of the rubber composition is at least 95% of the fatigue life of the identical rubber composition without the crumb rubber particles.

10. The cross-linked rubber composition of claim 2, wherein the fatigue life of the rubber composition is at least 99% of the fatigue life of the identical rubber composition without the crumb rubber particles.

11. The cross-linked rubber composition of claim 2, wherein the fatigue life of the rubber composition is greater than 100% of the fatigue life of the identical rubber composition without the crumb rubber particles.

12. The cross-linked rubber composition of claim 1, wherein the crumb rubber particles are 60 mesh or smaller.

13. The cross-linked rubber composition of claim 12, wherein the crumb rubber particles are 80 mesh or smaller.

14. The cross-linked rubber composition of claim 1, wherein the rubber composition comprises 10 phr of crumb rubber provided by the masterbatch.

15. The cross-linked rubber composition of claim 1, wherein the rubber composition comprises 15 phr of crumb rubber provided by the masterbatch.

16. An article comprising a cross-linked rubber composition, the cross-linked rubber composition comprising:

a diene rubber;

a masterbatch material comprising between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles, wherein the crumb rubber particles are 40 mesh or smaller.

17. The cross-linked rubber composition of claim 16, wherein a fatigue life (cycles to failure) of the rubber composition is at least 90% of a fatigue life of an identical rubber composition without the crumb rubber particles.
18. The article of claim 16, wherein the masterbatch comprises between 60 and 70 wt% natural rubber and between 30 and 40 wt.% crumb rubber particles.
19. The article of claim 16, wherein the crumb rubber particles are cryogenically processed.
20. The article of claim 16, wherein the crumb rubber particles are mechanically processed.
21. The article of claim 16, wherein the diene rubber is a highly unsaturated diene rubber.
22. The article of claim 21, wherein the diene rubber is selected from a natural rubber, a synthetic polyisoprene rubber or combinations thereof.
23. The article of claim 21, wherein the diene rubber is a natural rubber.
24. The article of claim 17, wherein the fatigue life of the rubber composition is at least 95% of the fatigue life of the identical rubber composition without the crumb rubber particles.
25. The article of claim 17, wherein the fatigue life of the rubber composition is at least 99% of the fatigue life of the identical rubber composition without the crumb rubber particles.
26. The article of claim 17, wherein the fatigue life of the rubber composition is greater than 100% of the fatigue life of the identical rubber composition without the crumb rubber particles.
27. The article of claim 16, wherein the crumb rubber particles are 60 mesh or smaller.
28. The article of claim 27, wherein the crumb rubber particles are 80 mesh or smaller.

29. The article of claim 16, wherein the rubber composition comprises 10 phr of crumb rubber provided by the masterbatch.
30. The article of claim 16, wherein the rubber composition comprises 15 phr of crumb rubber provided by the masterbatch.
31. The article of claim 16, wherein the article is a tire.
32. A method for preparing a rubber composition having crumb rubber, the method comprising:
 mixing a masterbatch, the masterbatch comprising between 50 and 75 wt.% natural rubber and between 25 and 50 wt.% crumb rubber particles; and
 mixing the masterbatch with a diene rubber.
33. The method of claim 30, wherein the masterbatch comprises between 60 and 70 wt.% natural rubber and between 30 and 40 wt.% crumb rubber particles.
34. The method of claim 30, further comprising:
 cooling the masterbatch before the step of mixing the masterbatch and the diene rubber.
35. The method of claim 30, further comprising:
 milling the masterbatch for 4 to 7 minutes at a mill temperature of 30°C before the step of mixing the masterbatch and the diene rubber.
36. The method of claim 30, wherein the step of mixing the masterbatch with a diene rubber further comprises the sub-steps of:
 adding all ingredients (the additives package) to the mixer;
 dropping the semi-finished batch at 155°C; and
 milling the semi-finished batch for 7 minutes.

37. The method of claim 36, wherein the step of milling the semi-finished batch further comprises incorporating a curatives package.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/52329

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - B60C 1/00; C08J 11/04 (2009.01)
 USPC - 152/209.5; 524/492; 521/41
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC(8) - B60C 1/00; C08J 11/04 (2009.01); USPC - 152/209.5; 524/492; 521/41

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 USPC ? 152/209.5,905; 524/492,445,500; 428/97; 264/211.24; 521/41; 252/182.13

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 PubWEST (PGPB,USPT,EPAB,JPAB), GooglePatents Database, GoogleScholar Database (rubber, crumb, composition, diene, mesh, fatigue, cryogenic, synthetic, natural, mix, mill, polyisoprene, tire)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007/0167555 A1 (Amino, et al.) 19 Jul 2007 (19.07.2007) paragraphs 0020, 0028-0029, 0038-0041, 0049, 0065, 0076, 0091	1-37
Y	US 2005/0203197 A1 (Tang) 15 Sep 2005 (15.09.2005) paragraphs 0011, 0020, 0032-0033, 0038-0039, 0049	1-37

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 29 Aug 2009 (29.08.2009)	Date of mailing of the international search report 16 SEP 2009
---	--

Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774
---	--