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(54) Benævnelse: **VARMEBESTANDIG GUMMISAMMENSÆTNING MED HØJ STYRKE OG FREMGANGSMÅDE TIL FREMSTILLING AF VARMEBESTANDIGT GUMMIPRODUKT MED HØJ STYRKE**

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DESCRIPTION

BACKGROUND OF THE INVENTION

[Field of the Invention]

[0001] The present invention relates to the technical field of rubber compositions, and more particularly to a high strength heat resistant rubber composition and a process for producing a high strength heat resistant rubber product.

[Background Art]

[0002] A rubber product means various rubber products produced from a natural rubber and a synthetic rubber as raw materials. Such rubber product further includes rubber products re-produced by using waste rubber. The rubber products often found on the market are, for example, rubber gloves, rubber sheets or rubber sealing rings, which are mainly used as waterproof, electrically insulating members or sealing members.

[0003] However, it may be necessary to use rubber products in high temperature working environments. The rubber products used in such a relatively high temperature environment are required to have the characteristics of a high temperature resistance and being easy to operate it. In the prior art conventional rubber products, there is a problem that the rubber products easily soften under the high temperature environment and thus that it is possibility to damage the user or other articles in contact with the rubber products. Therefore, it is desired to provide a heat resistant rubber having high stability and high strength as to satisfy the required characteristics when used in a high temperature working environment and having excellent high temperature resistance.

[0004] Conventionally, as such a heat-resistant rubber, for example, a heat-resistant rubber composition using a fluorine-based rubber component (Patent Document 1), a modified ethylene-propylene-diene copolymer (EPDM) (Patent Document 2) and a heat-resistant anti-vibration rubber, which are suitably used in in a high temperature environment such as an automobile engine room, containing a natural rubber (NR) and an ethylene-propylene-diene copolymer (EPDM) as rubber components, an organic peroxide as a vulcanizing agent, and a lower alkylphenol disulfide as a co-crosslinking agent (Patent Document 3) are known.

[0005] However, the heat-resistant rubber composition proposed hitherto is not always sufficiently satisfactory in heat resistance while using relatively expensive material components. Therefore, there is a demand for development of a heat-resistant rubber composition that is excellent in both high stability and high strength and heat resistance and is relatively

advantageous in cost reduction.

[Prior Art Reference]

Patent Documents

[0006]

Patent Document 1: JPH07-286081

Patent Document 2: JP2006-57003

Patent Document 3: JP2011-225717

SUMMARY OF THE INVENTION

[0007] The present invention provides a solution to the above-mentioned problems in the prior art and an object thereof is to provide a high strength heat resistant rubber composition having high stability, high strength and high temperature resistance.

[0008] The above technical problems could be realized by the present invention described below.

[0009] That is, the high strength heat-resistant rubber composition according to the present invention is characterized in that the high strength heat resistant rubber composition having both excellent strength and heat resistance, comprising:

80 to 85 parts by mass of a rubber base material;

5 to 11 parts by mass of attapulgite;

40 to 50 parts by mass of a linear low-density polyethylene;

4 to 6 parts by mass of a ceramic powder;

2 to 6 parts by mass of a cross-linking agent;

5 to 9 parts by mass of a filler;

5 to 9 parts by mass of a cross-linking aid;

8 to 13 parts by mass of rosin;

12 to 16 parts by mass of bismaleimide; and

7 to 12 parts by mass of yttrium oxide.

In a preferred embodiment of the present invention, the filler comprises;

5 to 10 parts by mass of CaSO4;

5 to 11 parts by mass of montmorillonite;

5 to 10 parts by mass of calcium silicate;

3 to 6 parts by mass of sodium stearate;

4 to 7 parts by mass of zinc oxide; and

1 to 2 parts by mass of a carbon black.

[0010] Further the cross-linking agent is preferably a silane coupling agent. Specifically, a silane coupling agent KH 550 and a polyamide 650 are preferably used.

[0011] In the yet another embodiment of the invention, the cross-linking aid is preferably dicumyl peroxide (DCP).

[0012] It should be understood that the content of each component above mentioned means an optimal content which can achieve an excellent strength and heat resistance of the objects of the invention.

[0013] Further, a process for producing a high strength heat resistant rubber composition having both excellent strength and heat resistance according to the invention, comprising the steps of:

a primary kneading step of supplying and mixing 80 to 85 parts by mass of a rubber base material, 5 to 11 parts by mass of attapulgite, 40 to 50 parts by mass of a linear low-density polyethylene and 4 to 6 parts by mass of a ceramic powder in a mixer to obtain a primary kneaded product by primary kneading;

a secondary kneading step of mixing 2 to 6 parts by mass of a cross-linking agent, 5 to 9 parts by mass of a filler, 5 to 9 parts by mass of a cross-linking aid, 8 to 13 parts by mass of rosin, 12 to 16 parts by mass of bismaleimide and 7 to 12 parts by mass of yttrium oxide into the primary kneaded product to obtain a high strength heat resistant rubber kneaded product; and

a forming step of forming the high strength heat resistant rubber kneaded product obtained in the secondary kneading step to obtain a rubber product.

It is note that the components and the content thereof in each step of the process are the

same in the description above of the composition.

BEST MODE FOR CARRYING OUT THE INVENTION

[0014] The high strength heat-resistant rubber composition according to the present invention is characterized in that the high strength heat resistant rubber composition having both excellent strength and heat resistance, comprising: 80 to 85 parts by mass of a rubber base material; 5 to 11 parts by mass of attapulgite; 40 to 50 parts by mass of a linear low-density polyethylene; 4 to 6 parts by mass of a ceramic powder; 2 to 6 parts by mass of a cross-linking agent; 5 to 9 parts by mass of a filler; 5 to 9 parts by mass of a cross-linking aid; 8 to 13 parts by mass of rosin; 12 to 16 parts by mass of bismaleimide; and 7 to 12 parts by mass of yttrium oxide.

[0015] In a preferred embodiment of the invention, the filler comprises; 5 to 10 parts by mass of CaSO4; 5 to 11 parts by mass of montmorillonite; 5 to 10 parts by mass of calcium silicate; 3 to 6 parts by mass of sodium stearate; 4 to 7 parts by mass of zinc oxide; and 1 to 2 parts by mass of a carbon black.

[0016] The carbon black used as a filler is not necessarily essential component depending on application of the rubber product or may be included for coloring the other pigments and dyes.

[0017] Further, montmorillonite is a kind of a swellable clay mineral (silicate mineral) and belongs to a smectite group. Montmorillonite can be replaced with the other smectites.

[0018] Furthermore, the cross-linking agent is preferably a silane coupling agent. Specifically, a silane coupling agent KH 550 and a polyamide 650 are preferably used.

[0019] In the invention, the cross-linking aid is preferably dicumyl peroxide (DCP)

[0020] In a preferred embodiment of the invention, the ceramic powder preferably comprises a waste ceramic powder in view of the reduction of cost and recycle of waste.

[0021] Further, the average particle diameter of the ceramic powder is not especially limited and is suitably selective in accordance with the intended application of the rubber product. The average particle diameter of the ceramic powder (D50) is preferably 10 to 120 μm, more preferably 20 to 100 μm, particularly preferably 30 to 80 mm.

[0022] The average particle diameter (D50) can be measured by using a laser diffraction/scattering type particle size distribution measuring device that is commonly used by those skilled in the art for particle size measurement. For example, it can be determined based on the particle size distribution measured by the laser diffraction/scattering method according

to a conventional method with using "Microtrac MT3000" (manufactured by Nikkiso Co., Ltd, Japan).

[0023] The rubber base material is not limited to a specific natural rubber or a synthetic rubber as long as it is a rubber material capable of forming a rubber component, but from the viewpoint of improving the characteristics, it is particularly desirable to include natural rubber.

[0024] Although the present invention is not bound by any theory, the components of the present invention described above will be described below, including the mechanism of action thereof.

[0025] Attapulgite as a component of the composition is a natural silicate mineral mainly composed of hydrous magnesium and aluminum silicate and is a kind of adsorptive clay that is also collectively called acid clay. Attapulgite however is different from bentonite and kaolin such as adsorbent clays as well as Attapulgite. Attapulgite has a hollow needle-like structure and exhibits excellent colloidal properties and adsorptivity. Therefore, it is presumed that the combination of Attapulgite with other components can improve strength and heat resistance of the resulting rubber product.

[0026] A rosin is an amorphous natural resin obtained by distilling balsams such as pine resin, which is a sap of a Pinaceae plant. The rosin has a relatively reactive chemical structure and thus it is presumed that the composite with the other components can improve strength and heat resistance of the resulting rubber product.

[0027] Bismaleimide as a component of the composition is a component to be impart heat resistance and includes various bismaleimide derivatives. For example, bismaleimide includes 4,4'-diphenylmethane bismaleimide, m-phenylene bismaleimide, bisphenol-A-diphenyl ether bismaleimide, 3,3'-dimethyl-5,5'-diethyl-4,4'-diphenylmethane bismaleimide, 4- Bismaleimides such as methyl-1,3-phenylene bismaleimide, 1,6'-bismaleimide-(2,2,4-trimethyl)hexane.

[0028] Yttrium oxide (Y_2O_3: Yttrium (III) oxide) is an oxide of yttrium to be stable in air, and is expected to act in cooperation with other compounding components to improve the properties as a rubber product. Specifically, it is presumed that Yttrium oxide promotes the formation of a connecting network of yttrium oxide with the above-mentioned bismaleimide and the other than yttrium oxide, and the connecting network sufficiently bonds to the rubber. As a result, a heat resistance performance of the rubber is improved.

[0029] Further, the process for producing a high strength heat resistant rubber composition having both excellent strength and heat resistance according to the invention is characterized in that the process comprises the steps of:

a primary kneading step of supplying and mixing 80 to 85 parts by mass of a rubber base material, 5 to 11 parts by mass of attapulgite, 40 to 50 parts by mass of a linear low-density polyethylene and 4 to 6 parts by mass of a ceramic powder in a mixer to obtain a primary

kneaded product by primary kneading;

a secondary kneading step of mixing 2 to 6 parts by mass of a cross-linking agent, 5 to 9 parts by mass of a filler, 5 to 9 parts by mass of a cross-linking aid, 8 to 13 parts by mass of rosin, 12 to 16 parts by mass of bismaleimide and 7 to 12 parts by mass of yttrium oxide into the primary kneaded product to obtain a high strength heat resistant rubber kneaded product; and

a forming step of forming the high strength heat resistant rubber kneaded product obtained in the secondary kneading step to obtain a rubber product.

[0030] The components used in each step and the content range thereof are the same as those described in the above composition.

[0031] In the above process, first, the ceramic powder in a rubber composition acts as a skeleton linkage to contribute to further development of the strength of the rubber product. At the same time, when mixing and kneading the ceramic powder and a filler (for example, $CaSO_4$, montmorillonite, calcium silicate, sodium stearate, zinc oxide and carbon black), the ceramic powder functions as a connecting medium to reliably connect fillers each other. As a result, a connecting network of the ceramic powder and filler is formed and subsequently the ceramic powder and filler as a stable network are sufficiently mixed with the natural rubber thereby the strength and heat resistance of the rubber are improved.

[0032] Further, the cross-linking aid DCP has a function of curing the rubber and further a rosin has an excellent flowability. These functions are fully put to practical use to allow bismaleimide and yttrium oxide to be sufficiently mixed with other components. It is considered that bismaleimide and yttrium oxide at this time form another connecting network to bond sufficiently well with the rubber thereby the heat resistance of the rubber is improved.

EXAMPLES

[0033] Hereinafter, the present invention will be described by way of examples but the present invention is not limited to the description of the examples below.

< Example 1 >

[0034] The high-strength heat-resistant rubber composition of the example includes, in terms of parts by mass, 80 parts of a natural rubber; 5 parts of attapulgite; 40 parts of a linear low-density polyethylene; 4 parts of a waste ceramic powder; 2 parts of a cross-linking agent; 5 parts of a filler; 5 parts of a cross-linking aid; 8 parts of a rosin; 12 parts of bismaleimide; and 7 parts of yttrium oxide.

[0035] Further, the filler includes, in terms of parts by mass, 5 parts of $CaSO_4$; 5 parts of montmorillonite; 5 parts of calcium silicate; 3 parts of sodium stearate; 4 parts of zinc oxide; and 1 part of a carbon black.

[0036] The cross-linking agent is a silane coupling agent, especially silane coupling agent KH550. Polyamide-650 can also be used as the silane coupling agent.

[0037] The crosslinking aid is DCP.

[0038] In the example, a rubber product was manufactured by the following steps 1 to 3.

Step 1: a primary kneading step of supplying and mixing the defined above parts by mass of a natural rubber, a waste ceramic powder, attapulgite and a linear low-density polyethylene in an internal mixer to obtain a primary kneaded product by primary kneading for 2 hours at 60 °C;

Step 2: a secondary kneading step of mixing the defined above parts of a cross-linking agent, a filler, a cross-linking aid, a rosin, bismaleimide and yttrium oxide into the primary kneaded product to obtain a heat resistant rubber kneaded liquid by secondary kneading for 2 hours at 120 °C; and

Step 3: a forming step of forming a heat resistant rubber product from the heat resistant rubber kneaded liquid obtained in the secondary kneading step to obtain a rubber product by a rubber product molding method.

[0039] An injection molding method was used as the rubber product molding method.

< Example 2 >

[0040] The high-strength heat-resistant rubber composition of the example includes, in terms of parts by mass, 83 parts of a natural rubber; 8 parts of attapulgite; 45 parts of a linear low-density polyethylene; 5 parts of a waste ceramic powder; 4 parts of a cross-linking agent; 7 parts of a filler; 7 parts of a cross-linking aid; 8 parts of a rosin; 14 parts of bismaleimide; and 10 parts of yttrium oxide.

[0041] Further, the filler includes, in terms of parts by mass, 8 parts of $CaSO_4$; 8 parts of montmorillonite; 8 parts of calcium silicate; 4 parts of sodium stearate; 5 parts of zinc oxide; and 2 parts of a carbon black.

[0042] The cross-linking agent is a silane coupling agent, especially silane coupling agent KH550. Polyamide-650 can also be used as the silane coupling agent.

[0043] The crosslinking aid is DCP.

[0044] In the example, a rubber product was manufactured by the following steps 1 to 3.

Step 1: a primary kneading step of supplying and mixing the defined above parts by mass of a natural rubber, a waste ceramic powder, attapulgite and a linear low-density polyethylene in an internal mixer to obtain a primary kneaded product by primary kneading for 3 hours at 70 °C;

Step 2: a secondary kneading step of mixing the defined above parts of a cross-linking agent, a filler, a cross-linking aid, a rosin, bismaleimide and yttrium oxide into the primary kneaded product to obtain a heat resistant rubber kneaded liquid by secondary kneading for 3 hours at 130 °C; and

Step 3: a forming step of forming a heat resistant rubber product from the heat resistant rubber kneaded liquid obtained in the secondary kneading step to obtain a rubber product by a rubber product molding method.

[0045] A press molding method was used as the rubber product molding method.

< Example 3 >

[0046] The high-strength heat-resistant rubber composition of the example includes, in terms of parts by mass, 85 parts of a natural rubber; 11 parts of attapulgite; 50 parts of a linear low-density polyethylene; 6 parts of a waste ceramic powder; 6 parts of a cross-linking agent; 9 parts of a filler; 9 parts of a cross-linking aid; 13 parts of a rosin; 16 parts of bismaleimide; and 12 parts of yttrium oxide.

[0047] Further, the filler includes, in terms of parts by mass, 10 parts of $CaSO_4$; 11 parts of montmorillonite; 10 parts of calcium silicate; 6 parts of sodium stearate; 7 parts of zinc oxide; and 2 parts of a carbon black.

[0048] The cross-linking agent is a silane coupling agent, especially silane coupling agent KH550. Polyamide-650 can also be used as the silane coupling agent.

[0049] The crosslinking aid is DCP.

[0050] In the example, a rubber product was manufactured by the following steps 1 to 3.

Step 1: a primary kneading step of supplying and mixing the defined above parts by mass of a natural rubber, a waste ceramic powder, attapulgite and a linear low-density polyethylene in an internal mixer to obtain a primary kneaded product by primary kneading for 2.5 hours at 75 °C;

Step 2: a secondary kneading step of mixing the defined above parts of a cross-linking agent,

a filler, a cross-linking aid, a rosin, bismaleimide and yttrium oxide into the primary kneaded product to obtain a heat resistant rubber kneaded liquid by secondary kneading for 2.5 hours at 120 °C; and

Step 3: a forming step of forming a heat resistant rubber product from the heat resistant rubber kneaded liquid obtained in the secondary kneading step to obtain a rubber product by a rubber product molding method.

[0051] A wrap forming method was used as the rubber product molding method.

[0052] The rubber product molding method according to the present invention is not limited to the methods used in Examples 1 to 3 described above, and any conventionally known rubber molding method such as a transfer molding method can be used.

[0053] The high-strength heat-resistant rubber products obtained thus above were evaluated. The results of evaluation are shown in Table 1 below.

[0054] It should be noted that the density was measured by using the measuring method B of the sulfurized rubber or the thermoplastic rubber density of GB/T533-2008.

[0055] The hardness test was carried out by using the Shore hardness method which is Part I of the GB/T5331.1-2008 vulcanized rubber or thermosetting rubber indentation hardness test method.

Table 1: Results of evaluation of characteristic each of high strength and heat resistant rubber according to the invention

Measurement Item	Measurement Standard	Example 1	Example 2	Example 3
Density	GB/T 533-2008	1.210	1.212	1.212
Shore hardness	GB/T 5331.1-2008	51	52	52
Elongation at break point (%)	GB/T 528-2009	620	619	620
Permanent strain (%)	GB/T 528-2009	20	21	21
Heat resistant temperature	HG/T 3847-2008	300	300	300

[0056] As can be understood from Table 1, the high strength heat resistant rubber product according to the invention has a high density, a sufficiently high strength, excellent elasticity, elongation at break and permanent strain and also has excellent heat resistance as achieving heat resistant temperature up to 300°C.

REFERENCES CITED IN THE DESCRIPTION

Cited references

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Patent documents cited in the description

- JPH07286081B [0006]
- JP2006057003A [0006]
- JP2011225717A [0006]

Patentkrav

1. Varmebestandig gummisammensætning med høj styrke med fremragende styrke og varmebestandighed, hvilken sammensætning omfatter:
80 til 85 vægtdele af et gummibaseret grundmateriale
5 til 11 vægtdele attapulgit
40 til 50 vægtdele af en lineær polyethylen med lav densitet
4 til 6 vægtdele af et keramisk pulver
2 til 6 vægtdele af et tværbindingsmiddel
5 til 9 vægtdele af et fyldstof
5 til 9 vægtdele af et tværbindingshjælpemiddel
8 til 13 vægtdele kolofonium
12 til 16 vægtdele bismaleimid, og
7 til 12 vægtdele yttriumoxid.

2. Varmebestandig gummisammensætning med høj styrke ifølge krav 1, hvor fyldstoffet omfatter:
5 til 10 vægtdele $CaSO_4$
5 til 11 vægtdele montmorillonit
5 til 10 vægtdele calciumsilicat
3 til 6 vægtdele natriumstearat
4 til 7 vægtdele zinkoxid, og
1 til 2 vægtdele kønrøg.

3. Varmebestandig gummisammensætning med høj styrke ifølge krav 1, hvor tværbindingsmidlet er et silankoblingsmiddel.

4. Varmebestandig gummisammensætning med høj styrke ifølge krav 1, hvor tværbindingsmidlet er dicumylperoxid (DCP).

5. Varmebestandig gummisammensætning med høj styrke ifølge krav 1, hvor det keramiske pulver omfatter et keramisk affaldspulver, og det gummibaserede grundmateriale omfatter et naturgummi.

6. Varmebestandig gummisammensætning med høj styrke ifølge krav 1, hvor det keramiske pulver har en gennemsnitlig

partikeldiameter (D50) på 10 til 120 µm.

7. Fremgangsmåde til fremstilling af en varmebestandig gummisammensætning med høj styrke med fremragende styrke og varmebestandighed, hvilken fremgangsmåde omfatter de følgende trin:
et primært ældningstrin med tilførsel og blanding af 80 til 85 vægtdele af et gummibaseret grundmateriale, 5 til 11 vægtdele attapulgit, 40 til 50 vægtdele af en lineær polyethylen med lav densitet og 4 til 6 vægtdele af et keramisk pulver i en blander for at opnå et primært ældet produkt ved primær ældning
et sekundært ældningstrin med blanding af 2 til 6 vægtdele af et tværbindingsmiddel, 5 til 9 vægtdele af et fyldstof, 5 til 9 vægtdele af et tværbindingshjælpemiddel, 8 til 13 vægtdele kolofonium, 12 til 16 vægtdele bismaleimid og 7 til 12 vægtdele yttriumoxid ind i det primære ældede produkt for at opnå et ældet varmebestandigt gummiprodukt med høj styrke, og
et formningstrin med formning af det ældede varmebestandige produkt med høj styrke, der er opnået i det sekundære ældningstrin, for at opnå et gummiprodukt.

8. Fremgangsmåde ifølge krav 7, hvorved fyldstoffet omfatter:
5 til 10 vægtdele $CaSO_4$
5 til 11 vægtdele montmorillonit
5 til 10 vægtdele calciumsilicat
3 til 6 vægtdele natriumstearat
4 til 7 vægtdele zinkoxid, og
1 til 2 vægtdele kønrøg.

9. Fremgangsmåde ifølge krav 7, hvorved tværbindingsmidlet er et silankoblingsmiddel.

10. Fremgangsmåde ifølge krav 7, hvorved tværbindingshjælpemidlet er dicumylperoxid (DCP).

11. Fremgangsmåde ifølge krav 7, hvorved det keramiske pulver omfatter et keramisk affaldspulver, og det gummibaserede grundmateriale omfatter et naturgummi.

12. Fremgangsmåde ifølge krav 7, hvorved det keramiske pulver har en gennemsnitlig partikeldiameter (D50) på 10 til 120 µm.