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(54) **A process for preparing a rubber composition containing a zinc salt of a di-α, β-ethylenically unsaturated carboxylic acid**

(57) A process for preparing a rubber composition containing a zinc salt of an α,β-ethylenically unsaturated carboxylic acid, which comprises reacting an α, β-ethylenically unsaturated carboxylic acid with a zinc compound in a rubber composition in the presence of from 1 to 25 parts by weight of calcium hydroxide or a calcium salt of the carboxylic acid to 100 parts by weight of the carboxylic acid.

Solid moulded golf balls having a high coefficient of restitution are produced by using the rubber composition prepared by the process.

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SPECIFICATION

A process for preparing a rubber composition containing a zinc salt of a di-α,β-ethylenically unsaturated carboxylic acid

This invention relates to a process for preparing a rubber composition containing a zinc salt of a di - α,β - ethylenically unsaturated carboxylic acid which comprises forming a zinc salt of a di - α,β - ethylenically unsaturated carboxylic acid, especially zinc dimethacrylate, in a rubber.

Zinc salts of α,β-unsaturated carboxylic acids, especially zinc methacrylate, are used as cocross-linking agents for cores of solid moulded golf balls and two component golf balls. There are two types of zinc salts, i.e. normal salts formed by reacting one mole of a zinc compound with two moles of an α,β - ethylenically unsaturated carboxylic acid (hereinafter referred simply as "acid(s)") and basic salts formed by reacting one mole of a zinc compound with one mole of acid, the former give golf balls a high coefficient of restitution. The normal salts which are solid are kneaded in a fine powdery state with a rubber. When an internal mixer such as a kneader is used, the normal salts adhere remarkably to the inner wall surface of the mixer. When an open roll is used, adhesion of the normal salts to the roll surface and generation of powdery dust, for instance, tend to cause problems. In both cases, a coagulated mass formed during kneading and that formed by stripping of adhered materials on the mixer wall are kneaded into a rubber, whereby the value of products made therefrom is reduced.

As another method to introduce the zinc salts into a rubber, there is what is called the direct mixing method wherein the zinc compounds are reacted with the acids in the rubber. In the direct mixing method, the zinc compounds for neutralization are kneaded with a rubber and the resultant mixture is put into an internal mixer such as kneader and Banbury together with the acids, and then a neutralization reaction is carried out under kneading conditions. The neutralization reaction may be carried out by kneading the zinc compounds for neutralization with the kneaded mixture of rubber and the acids or by kneading the kneaded mixture of rubber and the acids with the kneaded mixture of rubber and the zinc compounds for neutralization. According to the direct mixing method, a good appearance of rubber texture is obtained and the formation of a coagulated mass and adhesion thereof to the mixer hardly occurs. However, a large excess of the acids to the zinc compounds is generally necessary for the method to obtain the normal salt, especially zinc dimethacrylate, which gives a preferable property to golf balls. Therefore, unreacted acids are left and considerable amounts of the basic salt are formed and moreover the normal salt formed is apt to change into the basic salt with the passage of time.

The present invention sets out to provide a process for preparing a stable zinc salt of a di - α,β - ethylenically unsaturated carboxylic acid by the direct mixing method without aforementioned faults.

The present invention relates to a process for preparing a rubber composition containing a zinc salt of a di-α,β - ethylenically unsaturated carboxylic acid which comprises reacting an α,β - ethylenically unsaturated carboxylic acid with a zinc compound in a rubber mixture in the presence of from 1 to 25 parts by weight of calcium hydroxide and/or calcium salt of the carboxylic acid to 100 parts by weight of the carboxylic acid.

The invention also provides solid moulded golf balls comprising a rubber composition made by the process of the invention.

As the α,β - ethylenically unsaturated carboxylic acids used in the present invention, methacrylic acid, acrylic acid, itaconic acid and crotonic acid are preferred, methacrylic acid being most preferred.

As the zinc compounds which form salts with the carboxylic acids, zinc oxide, zinc hydroxide and zinc carbonate are preferred, zinc oxide being particularly preferable.

The blending ratio of the zinc compounds to the α,β - ethylenically unsaturated carboxylic acids is preferably 50-300 : 100 parts by weight, most preferably 50-200 : 100 parts by weight, the zinc compounds being calculated in terms of zinc oxide.

The amounts of calcium hydroxide or calcium salt of the α,β - ethylenically unsaturated carboxylic acid to be used are preferably 5-15 parts by weight against 100 parts by weight of the α,β - ethylenically unsaturated carboxylic acids. Other metallic compounds such as magnesium hydroxide and metal salts, such as magnesium salts, do not give such a satisfactory effect as the aforesaid one.

The reactions of the α,β - ethylenically unsaturated carboxylic acids with the zinc compounds according to the present invention are carried out in a rubber mixture preferably suitable for solid mouled golf balls. Particularly preferably rubber is polybutadiene, and especially the rubber containing about 90% by weight of cis-1,4-polybutadiene is preferable. If necessary, SBR or natural rubber, for instance, may be blended. The rubber mixture may contain conventional fillers and pigments.

The mode of the reaction of the zinc compounds with α,β - ethylenically unsaturated carboxylic acids is not restricted. For example, the reaction may be carried out by kneading the zinc compound and calcium hydroxide, or the zinc compound and the calcium salt of the α,β - ethylenically unsaturated carboxylic acid, with a prescribed rubber by means of an open roll or an internal mixer and then kneading the resultant mixture with the carboxylic acid charged in an internal mixer such as kneader. The temperature of the kneaded mixture is set to a temperature which is lower than the decomposition temperature of a radical initiator to be blended. The temperature of the kneaded mixture is then reduced, and the mixture is blended with the radical initiator for a suitable period.

Solid moulded golf balls having a high coefficient of restitution may be produced by cutting the resultant rubber composition in lumps which are slightly larger and heavier than the balls and putting the lumps in the mould of standard ball cup and then curing the lumps in the mould at about 130-160°C for

usually 10-40 minutes.

The present invention is illustrated by the following examples and comparative examples.

Examples 1 - 10

The prescribed amounts of zinc oxide and calcium hydroxide were kneaded homogeneously with 100 parts by weight of polybutadiene sold by Nippon Gosei Gomu Co. as BR-01, and then the mixture was kneaded with methacrylic acid for about 10 minutes. The temperature of the mixtures increased gradually to about 80-90°C. The reaction mixture was taken out from the reaction vessel and then the amounts of zinc dimethacrylate in the rubber were determined by X-ray diffraction method. In the X-ray diffraction pattern of zinc dimethacrylate, the characteristic peaks appear in the neighborhood of diffraction angle (2θ) of 10° and 11°. In the X-ray diffraction pattern of zinc methacrylate (basic salt), the characteristic peak appears at 2θ of 7.4°.

The determination of the amounts of zinc dimethacrylate in the rubber was carried out by making use of a calibration curve. The calibration curve was drawn by taking a X-ray diffraction pattern for the kneaded mixture of the polybutadiene with the standard substances, i.e. zinc dimethacrylate sold by Ware Chemical Co. as R-2R/A and zinc methacrylate sold by Steetleg Co. as BZM.

The blending ratios and the amounts of zinc dimethacrylate formed in 100g of the rubber are shown in Table 1.

Table 1

Ingredient [2]	Example										[1]
	1	2	3	4	5	6	7	8	9	10	1
	parts by weight										
BR-1	100	100	100	100	100	100	100	100	100	100	100
Methacrylic acid	30	30	30	30	32.5	35	27.5	27.5	27.5	27.5	30
Zinc oxide	20	30	40	43	43	43	43	43	43	43	40
Calcium hydroxide	3	3	3	3	3	3	1	2	3	4	–
Zinc dimethacrylate (g) [3]	35.8	32.8	26.7	26.0	25.0	25.4	13.7	23.3	25.8	35.5	0

[1] Comparative example
[2] Blending amount
[3] The amount of zinc dimethacrylate formed in 100g of the rubber

Comparative example 1

One hundred parts by weight of polybutadiene sold by Nippon Gosei Gomu Co. as BR-01 were kneaded with 40 parts by weight of zinc oxide homogeneously and then the mixture was kneaded with 30 parts by weight of methacrylic acid for about 10 minutes. The reaction mixture was taken from the reaction vessel and the amounts of zinc dimethacrylate was determined. The result is shown in Table 1.

Examples 11 - 13

One hundred parts by weight of polybutadiene sold by Nippon Gosei Gomu Co. as BR-01 were kneaded with 15 parts by weight of calcium hydroxide homogeneously and then the mixture was kneaded with the prescribed amounts of methacrylic acid for about 10 minutes. The reaction mixture was taken from the reaction vessel and then the amounts of calcium methacrylate in the rubber were determined by X-ray diffraction method (In the X-ray diffraction pattern of calcium methacrylate, the characteristic peak appears in the meighborhood of diffraction angle (2θ) of 8.2°.). The X-ray diffraction pattern showed that no-calcium hydroxide was remained in the rubber.

The determination of the amounts of calcium methacrylate in the rubber was carried out by making use of a calibration curve. The calibration curve was drawn by taking a X-ray diffraction pattern for the kneaded mixture of the polybutadiene with the standard calcium methacrylate sold by Yushi Seiyaku Co.

The blending ratios and the amounts of calcium methacrylate in 100g of the rubber are shown in Table 2.

Table 2

Ingredient [1]	Example 11	12	13
	parts by weight		
BR-01	100	100	100
Methacrylic acid	30	35	40
Calcium hydroxide	15	15	15
Calcium Methacrylate (g)[2]	35.8	41.9	42.2

[1] Blending amount
[2] The amounts of calcium methacrylate formed in 100g of the rubber

Examples 14 - 21

The prescribed amounts of zinc oxide were kneaded homogenously with the mixture of the rubber composition of Example 12 and polybutadiene sold by Nippon Gosei Gomu Co. as BR-01, the total amounts of BR-01 being 100 parts by weight. The kneaded mixture was then kneaded with methacrylic acid for about 10 minutes by means of a kneader. The reaction mixture was taken from the kneader and the amounts of zinc dimethacrylate formed in the rubber were determined in accordance with the procedure of Examples 1 - 10.

The blending ratios and the amounts of zinc dimethacrylate formed in 100g of the rubber are shown in Table 3.

Table 3

Ingredient [1]	Example 14	15	16	17	18	19	20	21
	Parts by weight							
BR-01	86.7	86.7	86.7	86.7	86.7	93.3	86.7	80.0
Methacrylic acid	25.3	25.3	25.3	27.8	30.3	25	25	25
Zinc oxide	20	30	40	40	40	40	40	40
Rubber Composition of Example 12	20	20	20	20	20	10	20	30
Zinc dimethacrylate (g)[2]	34.0	30.3	25.1	24.5	24.8	12.3	25.0	27.2

[1] Blending amount
[2] The amounts of zinc dimethacrylate formed in 100g of the rubber

Examples 22 - 40

The rubber compositions of Examples 1 - 21 were kneaded with the prescribed amounts of dicumyl peroxide respectively by means of roll and then the kneaded compositions were put into the mould of standard ball cup. The rubber compositions in the mould were cured at 150°C for 15 minutes to make balls.

The physical properties of the balls are shown in Table 4 together with the blending ratios of ingredients.

Comparative example 2

In accordance with the procedure of Example 22-40, the ball was made from the rubber composition of Comparative example 1 and dicumyl peroxide. The physical properties of the ball are shown in Table 4 together with blending ratio of ingredients.

Table 4

		Example									
	[2]	22	23	24	25	26	27	28	29	30	31
		Parts by weight									
Ingredient	BR-01	100	100	100	100	100	100	100	100	100	100
	Methacrylic acid	30	30	30	30	32.5	35	27.5	27.5	27.5	27.5
	Zinc Oxide	20	30	40	43	43	43	43	43	43	43
	Calcium hydroxide	3	3	3	3	3	3	1	2	3	4
	Rubber Composition of Example 12	–	–	–	–	–	–	–	–	–	–
	Dicumyl peroxide	2.3	2.0	1.7	2.3	2	1.7	1.8	2.3	2.8	3.2
Physical properties of the balls	Compression value	67.9	61.1	65.7	49.2	46.4	45.1	41.3	49	47.3	52
	Coefficient of restitution [3]	0.6882	0.6876	0.6815	0.6953	0.6876	0.6820	0.6979	0.6946	0.7001	0.7052

[1] Comparative example, [2] Blending amount, [3] Impact speed: 40m/sec

Table 4 (Continue)

		Example									1)
2)		32	33	34	35	36	37	38	39	40	2
		Parts by weight									
Ingredient	BR-01	86.7	86.7	86.7	86.7	86.7	86.7	93.3	86.7	80.0	100
	Methacrylate acid	25.3	25.3	25.3	25.3	26.8	30.3	25	25	25	30
	Zinc Oxide	20	30	40	40	40	40	40	40	40	40
	Calcium hydroxide	–	–	–	–	–	–	–	–	–	–
	Rubber Composition of Example 12	20	20	20	20	20	20	10	20	30	–
	Dicumyl peroxide	2.3	2	1.7	2.3	2	1.7	1.8	2.3	2.8	0.7
Physical properties of the balls	Compression value	67	61	66	49	46	47	43	49	50	50
	Coefficient of restitution 3)	0.690	0.687	0.683	0.697	0.690	0.684	0.683	0.678	0.705	0.671

1) Comparative example, 2) Blending amount, 3) Impact speed: 40m/sec

CLAIMS

1. A process for preparing a rubber composition containing a zinc salt of a di-α,β-ethylenically unsaturated carboxylic acid, which comprises reacting an α,β-ethylenically unsaturated carboxylic acid with a zinc compound in a rubber mixture in the presence of from 1 to 25 parts by weight of calcium hydroxide and/or a calcium salt of the carboxylic acid to 100 parts by weight of the carboxylic acid.

2. A process as claimed in Claim 1 in which the α,β-ethylenically unsaturated carboxylic acid is methacrylic acid.

3. A process as claimed in Claim 1 or Claim 2 in which the zinc compound is zinc oxide.

4. A process as claimed in any one of the preceding claims wherein the amount of calcium hydroxide and the calcium salt is of from 5 to 15 parts by weight to 100 parts by weight of the carboxylic acid.

5. A process as claimed in any one of the preceding claims wherein the ratio of the zinc compound to the carboxylic acid is of from 50-200 : 100 parts by weight, the zinc compound being calculated as zinc oxide.

6. A process as claimed in any one of the preceding claims wherein the rubber mixture comprises substantially 90% by weight of cis-1,4-polybutadiene.

7. A process as claimed in Claim 1 substantially as hereinbefore described in any one of the Examples.

8. A rubber composition whenever produced by a process as claimed in any one of the preceding claims.

9. A solid moulded golf ball comprising a rubber composition as claimed in Claim 8.

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