

Description

This invention relates to an impact-resistant polystyrene resin composition offering a well-balanced combination of impact strength and gloss.

Rubber-modified polystyrene has widely been used in components of domestic electric appliances and other; however, this material is inferior to the conventional ABS resin in relation to gloss and impact strength of finished products. Another drawback has been its poor colorability. Recently, there has been a growing demand for rubber-modified polystyrene that would compare favorably with ABS resin from the standpoint of cost and applicability to the thin-walled products.

The resin composition under this invention excels in gloss, impact strength, and rigidity. Thus, the resin composition of the present invention enables the production of injection-molded products, extruded sheets, and extruded vacuum-molded products with high impact strength and good gloss which is comparable to those obtained by using expensive ABS resin. Thus, it can be of considerable value as an economical resin.

Rubber-modified polystyrene has long been widely used in the industry. Normally elastomeric polymer particles (hereinafter denoted as : particles) dispersed in polystyrene matrix are of 1.0-5.0 μm in size. Recently, to achieve high gloss in molded products, rubber-modified polystyrenes with smaller particle size have been developed and introduced to the market. However, products with 1.0 μm or less in particle size have a substantially low impact strength, and for this reason, desirable resins have not been obtained yet from these products. Further, to improve the balance of impact strength and gloss, a composition comprised of a blend of rubber-modified polystyrene containing particles less than 1.0 μm in particles, have been disclosed in existing literature, such as Japanese Patent Publication B46-41487, Japanese Patent Publication B59-1519, U.S. Patent 4,146,589, U.S. Patent 4,214,056, and U.S. Patent 4,493,922. However, the large particles used in these prior art were of 2 μm or greater and this large particles gave low surface gloss of the molded article (Particularly, the large particles gave a large "gloss gradient" which means the gloss value of the parts in the molded articles farther from the injection gate have a sharply lower gloss compared with that of the part near the gate.) Also, when these products are molded under low mold temperature, the gloss markedly decreased.

Another, high impact resin compositions made of rubber-modified styrene resin and organic polysiloxane have been disclosed in existing literature such as Modern Plastics, November 1972, pp. 114-115; Plastics Age, 1974, Vol. 20, May, p. 107; Japanese Patent Laid-Open A55-3494; Japanese Patent Laid-Open A53-124561; Japanese Patent Laid-Open A57-172948; Japanese Patent Laid-Open A57-187345; and Japanese Patent Laid-Open A57-187346. However, such mixtures, in case that rubber-modified polystyrene with a small particle size is used, have not yielded a resin composition with both high impact strength high gloss.

Further, another resin composition made of rubber-modified polystyrene resin, polydimethylsiloxane, and metallic salts of higher fatty acids is disclosed in Japanese Patent Laid-Open A61-183339; and those comprised of rubber-modified styrene resin, polydimethylsiloxane, and amides of higher fatty acids are disclosed in Japanese Laid-Open A61-183341; these products, to, have not yielded a resin composition with desirable properties in case that rubber-modified polystyrene with a small particle size is used.

To meet the market demand for rubber-modified polystyrene with a well-balanced combination of properties, as noted above, it is necessary to produce a rubber-modified polystyrene resin with a well-balanced combination of properties such as good surface gloss of the molded products (especially a high gloss value and a small gloss gradient) high impact strength, and high rigidity.

The purpose of the present invention aims at providing a low-cost rubber-modified polystyrene resin with a well-balanced combination of properties such as good surface gloss of in molded products, high impact strength, and high rigidity, as noted above.

The composition of the present invention is attained through use of the resin composition comprised of rubber-modified polystyrene with a special microstructure.

The composition can be attained even more effectively through the addition of a specific amount of polydimethylsiloxane, mineral oil, metallic salts of higher fatty acids, or amides of higher fatty acids to rubber-modified polystyrene having the specific microstructure.

Specifically, this invention relates to a polystyrene resin composition offering excellent gloss and impact strength, wherein elastomeric polymers are dispersed in particle form in the rubber-modified polystyrene of the said composition, such that the dispersed particles have a particle size distribution consisting of two peaks, a small particle component and a large particle component; such that the small-particle component has a mean particle diameter of 0.1-0.6 μm and consists of single-occlusion-structure particles, while the large-particle size component has a mean particle diameter of 0.7-1.9 μm and consists of cellular (or "salami") structure particles, and wherein said small-particle component is present in a proportion of from 20 to 95 % by weight and said large-particle component is present in a proportion of from 80 to 5% by weight.

The rubber-modified polystyrene under this invention can be manufactured by the bulk polymerization or

bulk suspension polymerization process, in which aromatic monovinyl monomers are polymerized in the presence of elastomeric polymers. The rubber-modified polystyrene with a special microstructure, which is a special feature of this invention, can be produced through appropriate control of mixing during the polymerization process or under conditions of stirring during the formation of particles.

The aromatic monovinyl monomers employed in this invention include the following; styrene and o-methylstyrene, p-methylstyrene, m-methylstyrene, 2,4-dimethylstyrene, ethylstyrene, p-tert-butylstyrene, and other nuclear alkyl substituted styrenes; α -methylstyrene; α -methyl-p-methylstyrene, and related α -alkyl substituted styrenes. As elastomeric polymers, polybutadiene and styrene-polybutadiene copolymers can be used. As a polybutadiene, high-cis polybutadiene containing high concentrations of the cis isomer or low-cis polybutadiene containing low concentrations of the cis isomer can be used.

Under this invention, the rubber-modified polystyrene having a particle distribution consisting of two particle size peaks which is essential in the invention, can be manufactured by separately preparing rubber-modified polystyrene containing small particles and rubber-modified polystyrene containing large particles, and by blending the two in an extruder. Alternatively, it can be manufactured by mixing a prepolymer solution of rubber-modified polystyrene containing small-particles and a prepolymer solution of rubber-modified polystyrene containing large particles in a polymerization reactor.

The small-particle component should have a mean particle size of 0.1-0.6 μm , and preferably 0.2-0.5 μm . A mean particle size less than 0.1 μm will result in reduced impact strength; a mean particle size greater than 0.6 μm will result in low surface gloss, large gloss gradient, in molded products. Furthermore, the small particles must have a single-occlusion structure (also referred to as the "shell-core" form); otherwise, the product will have inferior balance of gloss and impact strength. Such small particles having a single-occlusion structure can be manufactured by polymerizing styrene in the presence of polybutadiene or block copolymers of styrene and butadiene. It is necessary that the large-particle component has a mean particle size of 0.7-1.9 μm , preferably 1.0-1.8 μm , more preferably 1.0-1.5 micron. A mean particle diameter of less than 0.7 μm would result in lower impact strength; likewise, a mean particle diameter greater than 1.9 μm would result in lower surface gloss and large gloss gradient of the molded products especially at a low mold temperature.

In this invention, the term "mean particle size" refers to a mean particle size as determined by photographing rubber-modified polystyrene under a transmission electron microscope through use of the ultra-thin slicing method, measuring the diameters of 1,000 elastomeric polymer particles in the photograph, and calculating the mean particle size according to the following formula:

$$\text{Mean particle diameter} = \frac{\sum n_i D_i^4}{\sum n_i D_i^3}$$

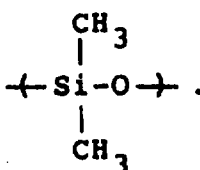
where n_i denotes the number of elastomeric polymer particles having particle diameter D_i .

The term "polybutadiene component" in this invention means the polybutadiene segment(s) which constitute(s) a part(s) of the elastomeric polymers of the present invention.

Under this invention, the small-particle component represents 20-95%, or preferably 50-90%, or even more preferably 60-90%, by weight of the total weight of the polybutadiene component of the elastomeric polymer in the composition; likewise, the large-particle component represents 5-80%, or preferably 10-50%, or even more, preferably 10-40%, by weight. A small-particle component of less than 20% by weight in the composition would result in lower surface gloss, whereas that exceeding 95% by weight in the composition would result in reduced impact strength, neither of which is desirable.

Furthermore, to ensure the adequate surface gloss of molded products, the rubber-modified polystyrene used for the purpose of this invention should not contain any substantial amount of particles larger than 1.9 μm . The condition "not containing any substantial amount" means that particles 2 μm or larger in size constitute less than 20%, by weight, of the polybutadiene component of the elastomeric polymers or preferably, less than 5% by weight. When particles being 2 μm or larger in size constitute more than 20% by weight, the composition will have an increased gloss gradient and lower gloss in molded products made at a low molding temperature.

In addition, to ensure more effective realization of the objective of this invention, the polydimethylsiloxane used must have a structural unit that can be expressed as



For the rubber-modified polystyrene having the particle diameters of this invention, none of the organic polysiloxane described in the existing literature, other than polydimethylsiloxane, will yield desirable resin compositions. Preferably, the polydimethylsiloxane should have a viscosity of 10^{-5} - 10^{-2} m²s⁻¹ (10-10,000 centistokes) at 25°C, which is a relatively low molecular weight range.

Further, the content of polydimethylsiloxane in the impact-resistant polystyrene resin composition should be in the range of 0.005-0.8% by weight. A content less than 0.005% by weight would make it difficult to obtain high impact strength; whereas a content in excess of 0.8% by weight would reduce colorability and harm secondary processing (chemical binding, printing, and painting) of molded resin products. While the cause of reduced colorability and secondary processing properties when the amount of additives is increased is not well understood, it is suspected that this is related to a poor miscibility of polydimethylsiloxane in the rubber-modified polystyrene. For this reason, elaborate control of the polydimethylsiloxane content is essential from the standpoint of obtaining polystyrene resin composition with a desirable impact strength.

Mineral oil is used in conjunction with polydimethyl siloxane for the purpose of realizing the objectives of this invention more effectively. Said mineral oil is commonly used oil, such as a plasticizer of polystyrene, with no particular restrictions as to viscosity or other parameters. Also, the metallic salts of higher fatty acids and amides of higher fatty acids employed in this invention are those fatty acid derivatives, of common use such as those used as slipping agent. Examples include zinc stearate, magnesium stearate, calcium stearate, and ethylene-bis-stearylamide.

In the present invention, the above mineral oils and/or metallic salts of higher fatty acids or amides of higher fatty acids, when used together with the above polydimethylsiloxane, and added to the above rubber-modified polystyrene with a special microstructure, can significantly enhance the impact strength. In case, that the rubber-modified polystyrene contained only small particles, addition of additives such as polydimethylsiloxane and metallic salts of high fatty acids yields little improvement in impact strength.

Desirable physical properties can be obtained through the combination, described in this invention, of special microstructures and additives.

Any mineral oil used in conjunction with polydimethylsiloxane in an impact-resistant polystyrene composition should constitute 0.25-4.0% by weight; a content less than 0.25% by weight would contribute little toward enhancing the impact strength, and a content in excess of 4.0% by weight would result in lower heat distortion temperature as well as poor colorability.

Any metallic salt of a higher fatty acid and/or amide of a higher fatty acid used in conjunction with polydimethylsiloxane in an impact-resistant polystyrene composition should be at least 0.1%, but no more than 0.5%, by weight; a content less than 0.1% by weight would contribute little toward enhancing the impact strength. Beyond 0.5% by weight, impact strength will not improve any more than would be expected from the added amount of said additives.

For the production of the impact-resistant polystyrene resin composition under this invention, there are no particular restrictions on the mixing method of the aforementioned polydimethylsiloxane or mineral oil, metallic salts of higher fatty acids, or amides of higher fatty acids to the above-mentioned rubber-modified polystyrene having a special microstructure. It is possible to add polydimethylsiloxane, for example, by polymerizing styrene monomer mixed with, polydimethylsiloxane; also, it is possible to add polydimethylsiloxane by melting and blending rubber-modified polystyrene and polydimethylsiloxane through the use of an extruder. It is also possible to produce master pellets containing high concentrations of polydimethylsiloxane from polydimethylsiloxane and polystyrene, and to produce molded products by mixing the master pellets and rubber-modified polystyrene together.

Also, it is possible to add dyes and pigments, slipping agents, fillers, mold-release agents plasticizers, or anti-static agents to the impact-resistant polystyrene resin composition of this invention, as additives.

The resin composition of this invention excels in an overall balance of properties, such as impact strength, gloss and rigidity. In particular, the resin composition obtained by combination of rubber-modified polystyrene possessing a special microstructure and polydimethylsiloxane, and mineral oil (or metallic salts of higher fatty acids or amides of higher fatty acids), exhibit a significantly improved impact strength over the conventional rubber-modified polystyrene. Also, they offer superior surface gloss when fabricated into molded products, especially injection-molded products, in terms of excellent gloss of parts that are located far from gates. Because of these characteristics, the constituent are useful for the production of large-scale injection-molded products. Further, its excellent colorability reduces the cost of pigmentation.

The resin of this invention can be used as molded products in electronics and in daily goods. It gives especially favorable results in molded products in which bright color is of prime importance.

Examples

Examples of this invention are given below. The data shown in the Examples were measured by the following methods:

Izod impact strength: ASTM D256.

Flexural strength and flexural modulus: ASTM D790

Gloss: ASTM D638. (The glossiness of the gate part and end-gate part of dumbbell samples were measured.)

[Examples 1-3 and Comparison Examples 1 and 2]

Rubber-modified polystyrene (A) with a mean particle diameter of 0.2 μm having single occlusion structure, in which the content of the polybutadiene component is 9% by weight, is obtained by mixing and polymerizing styrene monomer in the presence of styrenebutadiene block copolymers. On the other hand, rubber-modified polystyrene (B) with a mean particle diameter of 1.5 μm having cellular structure, in which the content of the polybutadiene component is 12% by weight, is obtained by mixing and polymerizing styrene in the presence of polybutadiene. The rubber-modified polystyrene (A) and the rubber-modified polystyrene (B) are mixed in the ratios shown in Table 1. The mixtures were melted and blended in an extruder to obtain the resin composition. The gloss, Izod impact strength, flexural modulus of the resin composition were evaluated. Results are shown in Table 1.

Mixing rubber-modified polystyrene (A) containing small particles and rubber-modified polystyrene (B) containing large particles in appropriate ratios produces a composition offering excellent gloss, especially a high gloss value in the end-gate part, as well as high impact strength. Rubber-modified polystyrene (A) by itself yields a composition with poor impact strength.

[Example 4 and Comparison Examples 3 and 4]

Styrene monomers were mixed in the presence of polybutadiene, by controlling the stirring force. This process yield 3 kinds of rubber-modified polystyrene (B), with mean particle diameters of 0.8 μm , 0.9 μm , and 2.7 μm , having a cellular structure, and in which the polybutadiene content was 12% by weight. The rubber-modified polystyrene (B) obtained in this manner, 25% by weight, was added to the rubber-modified polystyrene (A), 75% by weight, used in Examples 1-3, as shown in Table 2. The physical properties of the resulting compositions were evaluated as those obtained in Example 1, as shown in Table 2. If the rubber-modified polystyrene (B) to be combined with rubber-modified polystyrene (A) has a mean particle diameter of greater than 1.9 μm , it produces an undesirable result, that is, a large gloss gradient (with a low gloss value at the end-gate part). Also, a mean particle diameter of less than 0.7 μm gives the undesirably low impact strength.

[Comparison Example 5]

In Example 3, rubber-modified polystyrene (A) was replaced with a rubber-modified polystyrene having a salami structure with a mean particle diameter of 0.7 μm , and with a polybutadiene component, in the resin, constituting 9% by weight; and similar evaluations were conducted. The results are shown in Table 2. The results indicate undesirably large gloss gradient.

Table 1

		Comparison Example 1	Example 1	Example 2	Example 3	Comparison Example 2
Composi- tion	Rubber-modified poly- styrene (A)(mean particle diameter: 0.2 μm)	100%	90%	85%	75%	-
	Rubber-modified poly- styrene (B) (mean particle diameter: 1.5 μm)	-	10%	15%	25%	100%
Physical proper- ties	Izod impact strength in J/m ² (Kg.cm/cm)	25 (2.5)	62 (6.3)	74 (7.5)	88 (9.0)	167 (17.0)
	Gloss	96	96	95	91	55
	End-gate part					
	Gate part	99	99	99	99	88
Flexural modulus (Kg/cm ²) in MPa		(21,700) 2130	(22,500) 2210	(22,300) 2190	(22,200) 2180	(22,000) 2160

Table 2

		Comparison Example 3	Example 4	Example 3	Comparison Example 4	Comparison Example 5
Composi- tion	Rubber-modified polystyrene (A) 75% Mean particle diameter (μm)	0.2	0.2	0.2	0.2	0.7
	Rubber-modified polystyrene (B) 25% Mean particle diameter (μm)	0.6	0.9	1.5	2.7	1.5
Physical proper- ties	Izod impact strength in J/m (Kg.cm/cm)	34 (3.5)	64 (6.5)	88 (9.0)	83 (8.5)	113 (11.5)
	Gloss (%)	95	93	91	70	70
	End-gate part					
	Gate part	99	99	99	88	88
Flexural modulus		2320 (23,700)	2280 (23,200)	2180 (22,200)	2000 (20,400)	2060 (21,000)

[Examples 5-14]

Polydimethylsiloxane, mineral oils, and zinc stearate were mixed onto the resin composition of Example 1. The additive contents in the final compositions are shown in Table 3. Results of physical property measurements are given in Table 3.

In case that rubber-modified polystyrenes contain both small particle having appropriate mean diameter and large particle having appropriate mean diameter, both of which being mixed in an appropriate ratio, the addition of appropriate amounts of polydimethylsiloxane and mineral oil (Examples 5 and 6); or addition of appropriate amounts of polydimethylsiloxane and zinc stearate (Examples 7 and 8), would make compositions with high impact strength and high gloss at end gate parts.

Further, if the rubber-modified polystyrene comprising as such small particles and large particles contains appropriate amounts of mineral oil and zinc stearate, in addition to polydimethylsiloxane, the composition with substantially high impact strength is obtained (Example 14).

Table 3

Composi- tion	Polydimethylsiloxane (wt. %)	Example 5	Example 6	Example 7	Example 8	Example 9
		0.05	0.05	0.05	0.05	0
Physical proper- ties	Mineral oil (wt. %)	2.5	1.0	0	0	2.5
	Zinc stearate (wt. %)	0	0	0.3	0.1	0.3
	Izod impact strength in J/m (Kg.cm/cm)	109 (11.1)	91 (9.3)	109 (11.1)	89 (9.1)	64 (6.5)
	Flexural modulus in MPa (Kg/cm ²)	2060 (21,000)	2090 (21,300)	2110 (21,500)	2130 (21,700)	2060 (21,000)
	Vicat softening point (°C)	99	103	105	105	99
Gloss (%)	End gate part	97	97	97	97	97
	Gate part	99	99	99	99	99

- cont'd -

Table 3 (cont'd)

Example 10	Example 11	Example 12	Example 13	Example 14
0.05	0.05	0.05	0.05	0.05
0	0.1	0	5.0	2.5
0	0	0.03	0	0.3
72 (7.3)	75 (7.6)	76 (7.7)	111 (11.3)	132 (13.5)
2030 (21,700)	2030 (21,700)	2030 (21,700)	1940 (19,800)	2060 (21,000)
105	105	105	92	99
97	97	97	94	97
99	99	99	97	99

[Comparison Example 8, Example 15, and Comparison Examples 7, 8]

Resin compositions were obtained in the same manner as in Example 14, except that the rubber-modified polystyrene (B) of Example 14 was substituted with the respective rubber-modified polystyrene: (B) having the butadiene content of 12% by weight cellular structure and the mean particle diameter as specified in Table 4 below. Results of physical property measurements are given in Table 4.

[Example 16]

Resin compositions were obtained in the same manner as in Example 7, except that zinc stearate was replaced by ethylene-bis-stearyl amide, such that its content in the compositions was adjusted to 0.5% by weight. The results were: Izod impact strength: 100 J/m (10.2 Kg.cm/cm); flexural modulus: 2080 MPa (21,200 Kg/cm²); and gloss: 97% at the end-gate part and 99% at the gate part.

Table 4

Composi- tion	The mean particle diameter of rubber-modified polystyrene (B) to be combined with rubber-modified polystyrene (A)	Comparison Example 6	Example 5	Example 14	Comparison Example 7	Comparison Example 8
Content in the composi- tion	Polydimethyl- siloxane (wt. %)	0.05	0.05	0.05	0.05	0.05
	Mineral oil (wt. %)	2.5	2.5	2.5	2.5	2.5
	Zinc stearate (wt. %)	0.3	0.3	0.3	0.3	0.3
Physical proper- ties	Izod impact strength in J/m (Kg.-cm/cm)	44 (4.5)	88 (9.0)	132 (13.5)	83 (8.5)	74 (7.5)
	Flexural modulus in MPa (Kg/cm ²)	2110 (21,500)	2060 (21,000)	2060 (21,000)	2060 (21,000)	1960 (20,000)

- cont'd -

Table 4 (cont'd)

Gloss (%)	Vicat softening point (°C)	99	99	99	99	99
	End-gate part	98	97	97	82	72
	Gate part	99	99	99	92	88



Claims

1. A high-gloss, impact-resistant rubber-modified polystyrene composition, characterized in that said rubber-modified polystyrene consists essentially of
 - (i) a polystyrene; and
 - (ii) dispersed particles of elastomeric polymers having two peaks in particle size distribution, one peak being a small-particle component having a mean particle diameter of 0.1 to 0.6 μm with single occlusion structure and the other being a large-particle component having a mean particle diameter of 0.7 to 1.9 μm with cellular particle structure, said small-particle component being present in a proportion of from 20 to 95 % by weight and said large-particle component being present in a proportion of from 80 to 5 % by weight
 and optionally 0.005 to 0.8% by weight of polydimethylsiloxane and at least one member selected from the group consisting of 0.25 to 4.0% by weight of mineral oil, and 0.1 to 0.5% by weight of metallic salts and amides of higher fatty acids based on the total weight of the composition.
2. The composition of Claim 1, wherein 50 to 90% by weight of the total amount of the polybutadiene component of the elastomeric polymers in the composition are the small-particle component, and 50-10% by weight thereof are large-particle component.
3. The composition of Claim 1 or 2, wherein said small-particle component has a mean particle diameter of 0.2-0.5 μm .
4. The composition of Claim 1 through 3, wherein the large-particle component has a mean particle diameter of 1.0-1.8 μm .
5. The composition of Claim 1 through 4, wherein said metallic salt of a higher fatty acid is a zinc salt.

Patentansprüche

1. Hochglänzende, schlagfeste, kautschukmodifizierte Polystyrolzusammensetzung, dadurch gekennzeichnet, daß das kautschukmodifizierte Polystyrol im wesentlichen aus
 - (i) einem Polystyrol und
 - (ii) dispergierten Teilchen von elastomeren Polymeren mit zwei Maxima in der Korngrößenverteilung, wobei ein Maximum das einer feinteiligen Komponente mit einem mittleren Teilchendurchmesser von 0,1 bis 0,6 μm mit einer Einfach-Einschlußstruktur und das andere das einer grobteiligen Komponente mit einem mittleren Teilchendurchmesser von 0,7 bis 1,0 μm und mit zelliger Teilchenstruktur ist, und wobei die feinteilige Komponente in einem Anteil von 20 bis 95 Gewichtsprozent und die grobteilige Komponente in einem Anteil von 80 bis 5 Gewichtsprozent vorliegt,
 und gegebenenfalls 0,005 bis 0,8 Gew.-%, bezogen auf das Gesamtgewicht der Zusammensetzung, an Polydimethylsiloxan und mindestens einem Mitglied aus der aus 0,25 bis 4,0 Gew.-% Mineralöl und 0,1 bis 0,5 Gew.-% Metallsalzen und Amiden von höheren Fettsäuren, bestehenden Gruppe, besteht.
2. Zusammensetzung gemäß Anspruch 1, in der 50 bis 90 Gew.-% der Gesamtmenge der Polybutadienkomponente der elastomeren Polymeren in der Zusammensetzung die feinteilige Komponente sind und 50 bis 10 Gew.-% davon die grobteilige Komponente sind.
3. Zusammensetzung nach Anspruch 1 oder 2, in der die feinteilige Komponente einen durchschnittlichen Teilchendurchmesser von 0,2 bis 0,5 μm hat.
4. Zusammensetzung gemäß Anspruch 1 bis 3, in der die grobteilige Komponente einen mittleren Teilchendurchmesser von 1,0 bis 1,8 μm hat.
5. Zusammensetzung gemäß Anspruch 1 bis 4, in der das Metallsalz einer höheren Fettsäure ein Zinksalz ist.

**Revendications**

1. Composition de polystyrène modifiée au caoutchouc, d'un grand brillant et résistant aux chocs, caracté-
risée en ce que le polystyrène modifié au caoutchouc consiste essentiellement en :
 - (i) un polystyrène ; et
 - (ii) des particules dispersées de polymères élastomères ayant deux pics de répartition granulométrique ; un pic correspondant à un constituant de petites particules d'un diamètre moyen de particule de 0,1 à 0,6 μm avec une structure unique d'occlusion et l'autre étant un constituant à grandes particules d'un diamètre moyen de particule de 0,7 à 1,9 μm , avec une structure cellulaire de particule, le constituant à petites particules représentant de 20 à 95 % en poids et le constituant à grandes particules représentant de 80 à 5 % en poids,
et, éventuellement, de 0,005 à 0,8 % en poids de polydiméthylsiloxane et d'au moins un élément choisi parmi le groupe consistant en de 0,25 à 4,0 % en poids d'une huile minérale, et de 0,1 à 0,5 % en poids de sels métalliques et d'amides d'acides gras supérieurs, par rapport au poids total de la composition.
2. Composition suivant la revendication 1, dans laquelle de 50 à 90 % en poids de la quantité totale du constituant de polybutadiène des polymères élastomères de la composition sont le constituant à petites particules et de 50 à 10 % en poids de cette quantité totale sont le constituant à grandes particules.
3. Composition suivant la revendication 1 ou 2, dans laquelle le constituant à petites particules a un diamètre moyen de particule de 0,2 à 0,5 μm .
4. Composition suivant l'une des revendications 1 à 3, dans laquelle le constituant à grandes particules a un diamètre moyen de particule de 1,0 à 1,8 μm .
5. Composition suivant l'une des revendications 1 à 4, dans laquelle le sel métallique d'un acide gras supérieur est un sel de zinc.