

DESCRIPTION

MOLD CONDITIONING RUBBER COMPOSITION

Technical Field

[0001]

5 This invention relates to a mold conditioning rubber composition and more particularly a mold conditioning rubber composition used to impart release properties to the surface of a mold after removal of stains deposited during molding of a curing resin, the composition being characterized by containing a specific unvulcanized rubber as a base resin and a specific mold release agent.

10 Background Art

[0002]

 In encapsulation molding of integral circuits, etc. with a thermosetting resin molding compound, such as an epoxy resin molding compound, a release agent contained in the thermosetting resin molding compound oozes out in the interface
15 between a molded part and the surface of a mold to display releasability from the cull, cavity, and runner of the mold. After over several hundred consecutive molding cycles, the release agent, low-molecular components of the resin, and the like contained in the molding compound deteriorate by oxidation as a result of repetition of high-temperature molding and gradually build up on the mold surface to cause
20 noticeably poor mold release, poor appearance, such as rough surface of the molded product, and printing defects after the molding.

 To avert such a situation, a mold needs cleaning. However, cleaning operation not only cleans the mold surface but removes a release agent from the mold surface. As a result, if encapsulation molding is resumed immediately after the cleaning
25 operation, the molded parts show extremely poor release. Therefore, mold cleaning should be followed by shots with a mold conditioning resin composition containing a release agent to migrate the release agent to the mold surface thereby restoring mold release properties.

[0003]

A method of cleaning a mold surface by using an unvulcanized rubber compound containing a cleaning component in place of the thermosetting melamine resin molding compound is known. According to this method, while the unvulcanized
5 rubber compound is vulcanized in a mold into a vulcanized rubber, a layer of oxidatively deteriorated substances, such as a deteriorated release agent, existing on the surface of the mold is decomposed by the cleaning component and integrated into the vulcanized rubber, which is taken out of the mold. A rubber composition containing a butadiene rubber and an ethylene-propylene rubber as unvulcanized rubber components
10 at a ratio of 90/10 to 50/50 by weight has also been proposed (see, for example, U.S. Patent 4935175 and JP 4-357007A).

Mold cleaning materials are roughly classified into a transfer type and a compression type. Melamine resin molding compounds are used as a transfer type cleaning material. Melamine resin molding compounds and rubber compositions are
15 used as a compression type cleaning material.

With the recent increasing integration scale and decreasing device thickness and the spreading use of surface mount technology in fabrication of integral circuits, etc. (IC/LSIs), the shapes and structures of molded packages have been increasingly diversified. To cope with this tendency, fluidity and environmental responsiveness of
20 a molding compound for semiconductor encapsulation have been improved.

A high fluidity epoxy molding compound is liable to clog the air vent. If air vent clogging occurs, air is not allowed to escape, and the resin compound does not flow and fails to fill the cavity, making consecutive molding difficult. To avoid the problem, cleaning is required. It has been difficult, however, to remove the cured resin
25 clogging the air vent with a transfer type cleaning material because the cleaning resin does not flow normally for the reason described above.

[0004]

To clean a clogged air vent, a compression type cleaning material has been used. Although a melamine resin molding compound of compression type is able to clean
30 the clogged air vent, a molded product thereof tends to be brittle in its peripheral portion because the resin flows out from the mold and fails to be pressurized sufficiently. This

makes removal of the molded product from the mold laborious. On the other hand, a rubber composition evenly cures to produce a single molded sheet that can easily be removed from the mold, which brings about improved workability. However, a rubber composition has lower fluidity than a melamine resin molding compound so that it has poor filling properties and is incapable of removing stains from a hard-to-reach part of a mold, such as a cavity corner.

[0005]

When a rubber composition is applied to molds having deep cavities for small size packages, such as plastic dual inline packages (hereinafter abbreviated as PDIPs) and small outline integrated circuits (hereinafter abbreviated as SOICs), and particularly molds for small packages with a small number of pins, there is a likelihood that a cured product clings to the mold because of so many cavities per mold. As a result, the molded product of sheet form is liable to chip when removed from the mold and remain in the cavity as debris of the rubber composition. If chipping occurs in such a multi-cavity mold, much time is needed to remove the debris from many cavities. This greatly reduces productivity.

To settle down the problems alluded to above, it has been demanded to develop a mold conditioning rubber composition which has good workability (mold release) and excellent molding properties and provides long-lasting release properties to achieve an increase in the number of consecutive molding cycles for encapsulation molding.

[0006]

Patent Document 1: U.S. Patent 4935175

Patent Document 2: JP 4-357007A

Disclosure of the Invention

[0007]

The present invention is contemplated to eliminate the disadvantages with conventional mold conditioning rubber compositions which, while providing good workability (facile mold release), have the problem of void formation or chipping, and to provide a mold conditioning rubber composition that is free from the problem of void

formation or chipping and provides long-lasting release properties to achieve an increase in the number of consecutive molding cycles for encapsulation molding.

[0008]

5 The invention is also contemplated to eliminate the disadvantages with conventional mold conditioning rubber compositions which, while providing good workability (facile mold release), have the problem of void formation or chipping, and to provide a mold conditioning rubber composition that is free from the problem of void formation or chipping even when applied to molds having deep cavities for small packages such as PDIPs and SOICs or molds for particularly small packages with a small number of pins, and provides long-lasting release properties to achieve an increase in the number of consecutive molding cycles for encapsulation molding.

[0009]

The above objects of the invention have been accomplished by the provision of compression type mold conditioning rubber compositions (1) to (3) below.

15 (1) A compression type, mold conditioning rubber composition for conditioning a mold surface after removing a stain formed during molding of a curing resin, which comprises, as a base resin, an unvulcanized rubber comprising an ethylene-propylene rubber and a butadiene rubber at a mixing ratio of 90/10 to 50/50 by weight, a metal soap release agent, and at least one release agent selected from an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide release agent. The unvulcanized rubber has a 90% cure time (optimum cure point) $t_c(90)$ in the range of from 50 to 100 seconds at a mold temperature of 175°C and, after cure, an elongation of 80% to 800%, a tensile strength of 3 to 10 MPa, and a rubber hardness (durometer A hardness) of 60 to 95. The mold cleaning rubber composition will be referred to as a first mold conditioning rubber composition.

(2) A compression type, mold conditioning rubber composition for conditioning a mold surface after removing a stain formed during molding of a curing resin, which comprises, as a base resin, an unvulcanized rubber comprising an ethylene-propylene rubber and a butadiene rubber at a mixing ratio of 90/10 to 50/50 by weight, a metal soap release agent, and at least one release agent selected from an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide release agent.

The unvulcanized rubber has a 90% cure time (optimum cure point) $t_c(90)$ in the range of from 200 to 400 seconds at a mold temperature of 175°C and, after cure, an elongation of 80% to 800%, a tensile strength of 3 to 10 MPa, and a rubber hardness (durometer A hardness) of 60 to 95. The mold conditioning rubber composition will
5 be referred to as a second mold conditioning rubber composition.

(3) A compression type, mold conditioning rubber composition for conditioning a mold surface after removing a stain formed during molding of a curing resin, which comprises, as a base resin, an unvulcanized rubber comprising an ethylene-propylene rubber and a butadiene rubber at a mixing ratio of 90/10 to 50/50 by weight and at least
10 one release agent selected from a metal soap release agent, an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide release agent. The unvulcanized rubber has a 90% cure time (optimum cure point) $t_c(90)$ in the range of from 200 to 400 seconds at a mold temperature of 175°C and, after cure, an elongation of 80% to 800%, a tensile strength of 3 to 10 MPa, and a rubber hardness (durometer A
15 hardness) of 60 to 95. The mold conditioning rubber composition will be referred to as a third mold conditioning rubber composition.

[0010]

The first, second, and third mold conditioning rubber compositions are excellent in molding properties and strength as well as workability (mold release) and free from
20 the problem of void formation or chipping and provide long-lasting release properties after mold conditioning to achieve an increase in the number of consecutive molding cycles in encapsulation molding.

[0011]

The second and third mold conditioning rubber compositions are particularly
25 suited to condition molds having deep cavities for small size packages such as PDIPs and SOICs or molds for particularly small packages with a small number of pins.

Best Mode for Carrying out the Invention

[0012]

The first mold conditioning rubber composition of the invention will be

described first.

The unvulcanized rubber that can be used in the invention is a mixture of an ethylene-propylene rubber and a butadiene rubber. As used herein, the term "ethylene-propylene rubber" (hereinafter abbreviated as EPM) is intended to include
5 both an ordinary ethylene-propylene rubber (EPM) and an ethylene-propylene-diene rubber (hereinafter abbreviated as EPDM).

[0013]

EPM having an ethylene/ α -olefin (particularly propylene) copolymerization ratio of from 55/45 to 83/17 by mole and a Mooney viscosity ML_{1+4} (100°C) of 5 to 300
10 is preferably used. EPM having the copolymerization ratio of from 55/45 to 61/39 by mole and a Mooney viscosity ML_{1+4} (100°C) of 36 to 44 is more preferred.

[0014]

EPDM is a terpolymer of ethylene, an α -olefin, and a cyclic or acyclic monomer having a non-conjugated double bond, more particularly a terpolymer of ethylene, an
15 α -olefin (particularly propylene), and a polyene. Examples of the polyene monomer include dicyclopentadiene, 5-cyclooctadiene, 1,7-cyclododecadiene, 1,5,9-cyclododecatriene, 1,4-cycloheptadiene, 1,4-cyclohexadiene, norbornadiene, methylene norbornene, 2-methylpentadiene-1,4, 1,5-hexadiene, 1,6-heptadiene, methyl tetrahydroindene, and 1,4-hexadiene. The copolymerization ratio in the terpolymer is
20 preferably from 30 to 80 mol% ethylene, from 0.1 to 2 mol% polyene, and the rest being an α -olefin. The terpolymer containing 30 to 60 mol% ethylene is more preferred. The Mooney viscosity ML_{1+4} (100°C) of the terpolymer as EPDM is preferably 20 to 70.

[0015]

25 The butadiene rubber (hereinafter abbreviated as BR) that can be used in the invention preferably has a high cis structure with a cis-1,4 bond content of 90% by weight or more and a Mooney viscosity ML_{1+4} (100°C) of 20 to 60, more preferably 30 to 45.

[0016]

The ethylene-propylene rubber and the butadiene rubber are used in a mixing ratio of 90/10 to 50/50, preferably 80/20 to 60/40, by part by weight.

An ethylene-propylene rubber content exceeding 90 parts by weight results in poor mold release. If a butadiene rubber content exceeds 50 parts by weight, mold
5 release is improved, but the resulting cured product is hard and brittle and apt to chip.

[0017]

A vulcanization-cured product of the unvulcanized rubber has an elongation of 80% to 800%, preferably 100% to 300%. When the elongation is less than 80%, the rubber composition has poor molding properties.

10 A vulcanization-cured product of the unvulcanized rubber has a tensile strength of 3 to 10 MPa, preferably 5 to 8 MPa. When the tensile strength is 3 MPa or less, chipping occurs.

A vulcanization-cured product of the unvulcanized rubber has a rubber hardness (durometer A hardness) of 60 to 95, preferably 70 to 90. When the rubber hardness is
15 out of the range, the chipping problem or the void formation problem occurs.

The unvulcanized rubber has a 90% cure time (optimum cure point) $t_c(90)$ at a mold temperature of 175°C is 50 to 100 seconds, preferably 70 to 100 seconds. When the $t_c(90)$ of the unvulcanized rubber is in that range, the rate of cure is not too high to allow the rubber composition to fill every part of a mold cavity, so that mold
20 conditioning is successfully accomplished without troubles, like sticking.

[0018]

The first mold conditioning rubber composition of the invention contains, in addition to the unvulcanized rubber, a metal soap release agent and at least one release agent selected from an organic fatty acid ester release agent, a synthetic wax, and a fatty
25 acid amide release agent.

Examples of the metal soap release agent include calcium stearate, zinc stearate, and zinc myristate. The fatty acid ester release agent, synthetic wax, and fatty acid

amide release agent are exemplified by Licowax OP (partially saponified montanic acid ester, from Clariant Japan K.K.), Loxiol G-78 (polymeric complex ester, from Cognis Japan, Ltd.), Licolub H-4 (modified hydrocarbon wax, from Clariant Japan K.K.), Loxiol VPN881 (mineral oil-based synthetic wax, from Cognis Japan, Ltd.), Amide S (fatty acid amide, from Kao Corp.), Kao Wax EB-P (fatty acid amide, from Kao Corp.), and Alflow HT-50 (fatty acid amide, from NOF Corp.).

The metal soap release agent and the other release agent(s) (selected from an organic fatty acid ester release agent, a synthetic wax, and a fatty acid amide release agent) are used in a ratio of 90:10 to 30:70. Use of the other release agent in too high a ratio tends to deteriorate the performance of the rubber composition in securing an increase in the number of consecutive molding cycles.

The total amount of the metal soap release agent and the other release agents (selected from an organic fatty acid ester release agent, a synthetic wax, and a fatty acid amide release agent) is preferably 0.5 to 30 parts by weight per 100 parts by weight of the unvulcanized rubber. When the total amount of the release agents is insufficient, the mold release properties reduce. Addition of too much release agents brings about good mold release, but the mold conditioning rubber composition will have markedly reduced fluidity on melting only to have poor molding properties, and the number of dummy shots needed after the mold conditioning operation will increase.

[0019]

The first mold conditioning rubber composition of the invention may contain, in addition to the unvulcanized rubber and the release agents, a filler, a cleaning agent, a cleaning aid, a vulcanizing agent, a vulcanization aid, a vulcanization accelerator, a vulcanization acceleration aid, and so on.

[0020]

Examples of useful fillers (reinforcing agents) are silica, alumina, calcium carbonate, aluminum hydroxide, and titanium oxide. The amount of the filler to be used is preferably 10 to 70 parts, more preferably 30 to 60 parts, by weight per 100 parts by weight of the unvulcanized rubber.

Examples of useful cleaning agents include amines, such as monoethanolamine, diethanolamine, triethanolamine, N-methyldiethanolamine, and N,N-di-n-butylethanolamine; glycol ethers, such as ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, and triethylene glycol dimethyl ether; imidazoles; and indazolines. The amount of the cleaning agent to be used is preferably 5 to 50 parts, more preferably 5 to 30 parts, by weight per 100 parts by weight of the unvulcanized rubber. In addition to the cleaning agent, a cleaning aid, such as a surface active agent, may be used.

[0021]

Examples of useful vulcanizing agents include organic diallyl peroxides, such as di-t-butyl peroxide, di-t-amyl peroxide, dicumyl peroxide, and 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane; and organic peroxy ketals, such as 1,1-bis(t-butyl peroxy)-3,3,5-trimethylcyclohexane, 1,1-bis(t-butyl peroxy)cyclohexane, 2,2-bis(t-butyl peroxy)octane, n-butyl 4,4-bis(t-butyl peroxy)valerate, and 2,2-bis(t-butyl peroxy)butane. Peroxy ketals generally have a longer half-life period than diallyl peroxides. The vulcanizing agents recited above may be used either individually, or a vulcanizing agent with a long half-life period and a vulcanizing agent with a short half-life period may be used in combination to control the rate of cure, which depends on the composition design. The amount of the vulcanizing agent to be used is preferably 1 to 6 parts, more preferably 2 to 4 parts, by weight per 100 parts by weight of the unvulcanized rubber. In addition to the vulcanizing agent, a vulcanization aid, such as an acrylic acid monomer or sulfur, may be used.

[0022]

Examples of useful vulcanization accelerators include guanidines, such as diphenylguanidine and triphenylguanidine; aldehyde-amine or aldehyde-ammonia reaction products, such as a formaldehyde-paratoluidine condensate and an acetaldehyde-aniline reaction product; and thiazoles, such as 2-mercaptobenzothiazole and dibenzothiazyl disulfide. A vulcanization acceleration aid, such as magnesia, litharge, or lime, may also be used.

[0023]

If desired, the first mold conditioning rubber composition of the invention may further contain a pigment or a coloring agent to be made distinguishable from, for

example, a cleaning material. Examples of pigments or coloring agents that can be used include inorganic pigments, such as titanium oxide, carbon black, zinc flower, cadmium yellow, red oxide, iron blue, iron black, ultramarine blue, lithopone, titanium yellow, and cobalt blue; organic pigments, such as phthalocyanine pigments, azo pigments, diazo pigments, Hanza yellow, and quinacridone red; fluorescent pigments, such as benzoxazole pigments, naphthotriazole pigments, and coumarin; and coloring agents, such as anthraquinone dyes, indigo dyes, and azo dyes. The amount of the pigment or coloring agent to be added is preferably about 0.01 to 1 part by weight per 100 parts by weight of the unvulcanized rubber.

10 [0024]

The second mold conditioning rubber composition of the invention is then described.

The second mold conditioning rubber composition is the same as the first one except that the unvulcanized rubber used as a base resin has a 90% cure time (optimum cure point) $t_c(90)$ in the range of from 200 to 400 seconds, preferably 250 to 350 seconds, at a mold temperature of 175°C.

The $t_c(90)$ value can be adjusted appropriately by the kinds and amounts of the diene monomer, peroxide, vulcanization accelerator, co-crosslinking agent, and so forth.

[0025]

20 When the $t_c(90)$ of the unvulcanized rubber is in the range of from 200 to 400 seconds, the rate of cure is not too high to allow the rubber composition to fill every part of a mold cavity, so that mold conditioning is successfully accomplished without troubles, like sticking.

[0026]

25 The third mold conditioning rubber composition of the invention is then described.

The third mold conditioning rubber composition is the same as the second one, except that the release agent is at least one member selected from a metal soap release

agent, an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide release agent.

[0027]

5 The at least one release agent selected from a metal soap release agent, an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide release agent is preferably used in an amount of 10 to 50 parts by weight per 100 parts by weight of the unvulcanized rubber. With an insufficient amount of the release agent, the composition has reduced conditioning performance when applied to, of molds having deep cavities for small sized packages such as PDIPs and SOICs, those for
10 particularly small packages with a small number of pins. Addition of too much release agent brings about good mold release, but the mold conditioning rubber composition will have markedly reduced fluidity on melting only to have poor molding properties, and the number of dummy shots needed after the mold conditioning operation will increase.

15 [0028]

The first, second, and third mold conditioning rubber compositions can be prepared by any known method. For example, EPM and BR are put into a jacketed pressure kneader and started to be kneaded. Kneading is continued until the EPM/BR mixture becomes a homogeneous rubber mass like glutinous rice cake while monitoring
20 the rubber mass temperature. After the rubber mass reaches to 70° to 110°C, the release agent(s), white carbon, an amino-alcohol compound, a cyclic amide compound, process oil, a nonionic surface active agent, stearic acid, and the like are added thereto, followed by kneading for an additional few minute period. An organic peroxide, sulfur, and so on are then added and rapidly dispersed, and the resulting rubber mass is
25 taken out of the kneader to provide a mold conditioning rubber composition of the invention. Where necessary, the rubber mass is shaped into an appropriate form, such as a sheet.

[0029]

Kneading machines that can be used include a Banbury mixer and a roll mixer in
30 addition to the pressure kneader referred to above.

[0030]

While the form of the first, second, and third mold conditioning resin compositions is not particularly limited, they are preferably shaped into a sheet form that is easy to cool in a short time because the rubber mass may undergo accelerated vulcanization by the residual heat after kneading and fail to exhibit stable performance unless it is rapidly cooled after completion of kneading.

Examples

[0031]

The present invention will now be illustrated in greater detail with reference to Examples, but it should be understood that the invention is not construed as being limited thereto. Unless otherwise noted, all the percents and parts are by weight.

[0032]

Testing methods:

The testing methods used in Examples and Comparative Examples to evaluate various physical properties are as follows.

(1) Elongation and tensile strength

Elongation and tensile strength were measured in accordance with the method of measuring tensile strength and elongation at break specified in JIS K6251.

(Condition for preparing test specimen)

The test specimen was prepared by molding the rubber composition in a 37T automatic press at a mold temperature of 175°C and a molding pressure of 10 MPa (gauge pressure) for a pressing time of 5 minutes into a sample sheet of 80 mm in width, 160 mm in length, and 2 mm in thickness and punching the sheet to make a dumbbell specimen of size No. 3 according to JIS.

[0033]

(2) Rubber hardness

Rubber hardness was measured in accordance with "Rubber, vulcanized or thermoplastic-Determination of hardness" of JIS K6253. A durometer hardness of a stack of three sample sheets (80x160x2 mm) prepared in the same manner as described

in (1) above was measured with a durometer of the type chosen according to the hardness.

[0034]

(3) Rate of cure

- 5 The 90% cure time (optimum cure point) $t_c(90)$, at a mold temperature of 175°C, of the rubber composition was determined using the method specified in JIS K6300-2, "Determination of cure characteristics with oscillating curemeters".

[0035]

(4) Mold conditioning test

10 (4-1) Mold initialization

- Before testing the mold conditioning rubber compositions, the surface of a mold was made into an initial steady condition by making 5 shots for cleaning by transfer molding with a commercially available melamine resin mold cleaning compound (Nikalet ECR-CL, from Nippon Carbide Kogyo K.K.) followed by two shots for
15 cleaning by compression molding with a commercially available melamine resin mold cleaning compound (Nikalet ECR-SW7320, from Nippon Carbide Kogyo K.K.).

(Molding conditions)

Mold: QFP in Examples 1 to 8

PDIP-8L (8 pots, 96 cavities) in Examples 9 to 12

20 Mold temperature: 175°C/175°C

Cure time: 300 seconds for ECR-CL; 180 seconds for SW7320

(4-2) Mold conditioning test

- After the cleaning operation for mold initialization, three shots of a test mold conditioning rubber composition were made by compression molding for a cure time of
25 200 seconds. Then, a commercially available biphenyl epoxy resin molding compound (EME-7351T, available from Sumitomo Bakelite Co., Ltd.) was consecutively molded in the thus conditioned mold under the following molding conditions to evaluate release properties and duration of mold release action in terms of the number of possible consecutive molding cycles.

(Molding conditions)

Mold: QFP or PDIP-8L

Mold temperature: 175°C/175°C

Cure time: 100 seconds

5 [0036]

Example 1 (the first mold conditioning rubber composition of the invention)

In a 3000 ml jacketed pressure kneader were put 1050 g of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and 450 g of BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) and kneaded under pressure for about 3 minutes while
 10 cooling, whereby the mixture became a homogeneous rubber mass like glutinous rice cake having a temperature of about 80°C. To the mass were added 45 g (3 parts, per 100 parts of the EPDM/BR blend (hereinafter the same)) of a polyoxyalkylene decyl ether surface active agent, 15 g (1 part) of stearic acid, 630 g (42 parts) of white carbon, 45 g (3 parts) of process oil (PW-380, from Idemitsu Kosan Co., Ltd.), 75 g (5 parts) of
 15 calcium carbonate, 75 g (5 parts) of titanium oxide, 75 g (5 parts) of zinc oxide, 60 g (4 parts) of zinc stearate, and 85 g (5.7 parts) of Licowax OP (partially saponified montanic acid ester, from Clariant Japan K.K.), followed by kneading for about 3 minutes. Finally, 48 g (3.2 parts) of 1,1-bis(t-butyl peroxy)cyclohexane was added, followed by kneading for about 1 minute. The temperature of the rubber mixture was controlled
 20 not to exceed 100°C throughout the kneading operation. The resulting rubber mass was rapidly passed through pressure rollers to be shaped into a sheet and to be cooled to 25°C or lower to provide a mold conditioning rubber composition of sheet form of 6 mm in thickness (designated composition A).

The characteristics and the mold conditioning test results of the rubber
 25 composition A are shown in Table 1 below. As can be seen from the test results, the composition A exhibited good molding properties and mold conditioning performance.

[0037]

Example 2 (the first mold conditioning rubber composition of the invention)

A mold conditioning rubber composition of sheet form with a thickness of 6 mm
 30 (designated composition B) was prepared in the same manner as in Example 1, except for changing the amounts of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) as base resins to

900 g and 600 g, respectively, changing the amount of the process oil (PW-380, from Idemitsu Kosan) from 45 g (3 parts) to 75 g (5 parts), and replacing 85 g (5.7 parts) of Licowax OP with 85 g (5.7 parts) of Loxiol G-78 (polymeric complex ester, from Cognis Japan, Ltd.).

5 The characteristics and the mold conditioning test results of the rubber composition B are shown in Table 1. The test results prove the composition B to exhibit good molding properties and mold conditioning performance.

[0038]

Example 3 (the first mold conditioning resin composition of the invention)

10 A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition C) was prepared in the same manner as in Example 1, except for replacing 60 g (4 parts) of zinc stearate with 60 g (4 parts) of calcium stearate and replacing 85 g (5.7 parts) of Licowax OP with 85 g (5.7 parts) of Licolub H-4 (modified hydrocarbon, from Clariant Japan K.K.).

15 The characteristics and the mold conditioning test results of the rubber composition C are shown in Table 1. The test results prove the composition C to exhibit good molding properties and mold conditioning performance.

[0039]

Example 4 (the first mold conditioning rubber composition of the invention)

20 A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition D) was obtained in the same manner as in Example 1, except for using, as base resins, 825 g of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and 675 g of BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%), replacing 60 g (4 parts) of zinc stearate with 60 g (4 parts) of calcium stearate, and
25 replacing 85 g (5.7 parts) of Licowax OP with 85 g (5.7 parts) of Amide S (aliphatic acid amide from Kao Corp.).

The characteristics and the mold conditioning test results of the rubber composition D are shown in Table 1. The test results prove the composition D to exhibit good molding properties and mold conditioning performance.

[0040]

Comparative Example 1

A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition E) was obtained in the same manner as in Example 1, except for changing the amounts of the of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) to 600 g and 900 g, respectively.

The characteristics and the mold conditioning test results of the rubber composition E are shown in Table 1. As can be seen from the test results, the rubber composition E forms voids and fails to provide the mold with long-lasting release properties.

[0041]

Table 1

Items	Example 1	Example 2	Example 3	Example 4	Comp. Example 1
	Composition A	Composition B	Composition C	Composition D	Composition E
Ratio of EPDM	70	60	70	55	40
Ratio of BR	30	40	30	45	60
Elongation (%)	247	138	243	82	54
Tensile Strength (MPa)	4.8	3.9	4.6	4.1	3.8
Rubber Hardness	91	92	90	92	92
tc(90) (sec)	63	57	69	56	60
Molding Properties	A	A	A	A	B
Mold Releasability	A	A	A	A	C
Freedom from Void Formation	A	A	A	A	C
Number of Consecutive Molding Cycles	>1000	>1000	>1000	>1000	395

The molding properties, mold releasability, and freedom from void formation were evaluated according to following standards (standards for evaluating are the same in Table 2 and 3).

Standards for evaluating molding properties:

- 5 A: Rate of occurrence of incomplete filling is lower than 3%.
 B: Rate of occurrence of incomplete filling is 3% or higher and lower than 10%.
 C: Rate of occurrence of incomplete filling is 10% or higher.

Standards for evaluating mold releasability:

- 10 A: Rate of occurrence of chipping is lower than 3%.
 B: Rate of occurrence of chipping is 3% or higher and lower than 10%.
 C: Rate of occurrence of chipping is 10% or higher.

Standards for evaluating freedom from void formation:

- A: Rate of occurrence of void formation is lower than 3%.
 15 B: Rate of occurrence of void formation is 3% or higher and lower than 10%.
 C: Rate of occurrence of void formation is 10% or higher.

[0042]

Example 5 (the second mold conditioning rubber composition of the invention)

- 20 In a 3000 ml jacketed pressure kneader were put 1050 g of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and 450 g of BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) and kneaded under pressure for about 3 minutes while cooling, whereby the mixture became a homogeneous rubber mass like glutinous rice cake having a temperature of about 80°C. To the mass were added 45 g (3 parts, per 100 parts of the EPDM/BR blend (hereinafter the same)) of a polyoxyalkylene decyl
 25 ether surface active agent, 15 g (1 part) of stearic acid, 600 g (40 parts) of white carbon, 45 g (3 parts) of process oil (PW-380, from Idemitsu Kosan Co., Ltd.), 75 g (5 parts) of calcium carbonate, 75 g (5 parts) of titanium oxide, 75 g (5 parts) of zinc oxide, 60 g (4 parts) of zinc stearate, and 85 g (5.7 parts) of Licowax OP (partially saponified montanic acid ester, from Clariant Japan K.K.), followed by kneading for about 3 minutes.
 30 Finally, 48 g (3.2 parts) of dicumyl peroxide was added, followed by kneading for about 1 minute. The temperature of the rubber mixture was controlled not to exceed 110°C

throughout the kneading operation. The resulting rubber mass was rapidly passed through pressure rollers to be shaped into a sheet and to be cooled to 25°C or lower to provide a mold conditioning rubber composition of sheet form of 6 mm in thickness (designated composition F).

5 The characteristics and the mold conditioning test results of the rubber composition F are shown in Table 2 below. As can be seen from the test results, the composition F exhibited good molding properties and mold conditioning performance.

[0043]

Example 6 (the second mold conditioning rubber composition of the invention)

10 A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition G) was prepared in the same manner as in Example 5, except for changing the amounts of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) as base resins to 900 g and 600 g, respectively, changing the amount of the process oil (PW-380, from
15 Idemitsu Kosan) from 45 g (3 parts) to 75 g (5 parts), and replacing 85 g (5.7 parts) of Licowax OP with 85 g (5.7 parts) of Loxiol G-78 (polymeric complex ester, from Cognis Japan, Ltd.).

 The characteristics and the mold conditioning test results of the rubber composition G are shown in Table 2. The test results prove the composition G to
20 exhibit good molding properties and mold conditioning performance.

[0044]

Example 7 (the second mold conditioning resin composition of the invention)

 A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition H) was prepared in the same manner as in Example 5, except
25 for replacing 48 g (3.2 parts) of dicumyl peroxide with 28 g (1.9 parts) of dicumyl peroxide and 20 g (1.3 parts) of n-butyl 4,4-bis(t-butyl peroxy)valerate, replacing 60 g (4 parts) of zinc stearate with 60 g (4 parts) of calcium stearate, and replacing 85 g (5.7 parts) of Licowax OP with 85 g (5.7 parts) of Licolub H-4 (modified hydrocarbon, from Clariant Japan K.K.).

The characteristics and the mold conditioning test results of the composition H are shown in Table 2. The test results prove the composition H to exhibit good molding properties and mold conditioning performance.

[0045]

5 Example 8 (the second mold conditioning resin composition of the invention)

A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition I) was prepared in the same manner as in Example 5, except for replacing 450 g of the BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) with 450 g of BR (Mooney viscosity ML_{1+4} (100°C): 35; 1,4-cis bond
10 content: 95%), replacing 48 g (3.2 parts) of dicumyl peroxide with 13 g (0.9 parts) of 1,1-bis(t-butyl peroxy)cyclohexane and 35 g (2.3 parts) of dicumyl peroxide, replacing 60 g (4 parts) of zinc stearate with 60 g (4 parts) of calcium stearate, and replacing 85 g (5.7 parts) of Licowax OP with 85 g (5.7 parts) of Amide S (aliphatic acid amide, from Kao Corp).

15 The characteristics and the mold conditioning test results of the composition I are shown in Table 2. The test results prove the composition I to have good molding properties and cleaning performance.

[0046]

Comparative Example 2

20 A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition J) was prepared in the same manner as in Example 5, except for changing the amounts of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) to 450 g and 1050 g, respectively.

25 The characteristics and the mold conditioning test results of the composition J are shown in Table 2. As can be seen from the test results, the rubber composition J suffered void formation, and the mold conditioning performance was poor in terms of the number of possible consecutive molding cycles.

[0046]

Table 2

Items	Example 5	Example 6	Example 7	Example 8	Comp. Example 2
	Composition F	Composition G	Composition H	Composition I	Composition J
Ratio of EPDM	70	60	70	70	40
Ratio of BR	30	40	30	30	60
Elongation (%)	150	120	184	188	54
Tensile Strength (MPa)	5.8	5.2	4.3	4.1	4.4
Rubber Hardness	83	87	75	80	92
tc(90) (sec)	329	287	278	267	58
Molding Properties	A	A	A	A	B
Mold Releasability	A	A	A	A	C
Freedom from Void Formation	A	A	A	A	C
Number of Consecutive Molding Cycles	>1000	>1000	>1000	>1000	486

[0048]

5 Example 9 (the third mold conditioning rubber composition of the invention)

In a 3000 ml jacketed pressure kneader were put 900 g of EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and 600 g of BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) and kneaded under pressure for about 3 minutes while cooling, whereby the mixture became a homogeneous rubber mass like glutinous rice cake having a temperature of about 80°C. To the mass were added 45 g (3 parts, per 100 parts of the EPDM/BR blend (hereinafter the same)) of a polyoxyalkylene decyl ether surface active agent, 15 g (1 part) of stearic acid, 900 g (60 parts) of white carbon, 75 g (5 parts) of titanium oxide, 1.5 g (0.1 parts) of carbon black, 225 g (15 parts) of zinc stearate, 150 g (10 parts) of Loxiol G-78 (polymeric complex ester, from Cognis Japan, Ltd.), and 150 g (10 parts) of Licolub H-4 (modified hydrocarbon, from Clariant Japan K.K.), followed by kneading for about 3 minutes. Finally, 18 g (1.2 parts) of

dicumyl peroxide was added, followed by kneading for about 1 minute. The temperature of the rubber mixture was controlled not to exceed 110°C throughout the kneading operation. The resulting rubber mass was rapidly passed through pressure rollers to be shaped into a sheet and to be cooled to 25°C or lower to provide a mold conditioning rubber composition of sheet form of 6 mm in thickness (designated composition K).

The characteristics and the mold conditioning test results of the composition K are shown in Table 3. As can be seen from the test results, the composition K exhibited good molding properties and mold conditioning performance.

10 [0049]

Example 10 (the third mold conditioning resin composition of the invention)

A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition L) was prepared in the same manner as in Example 9, except for changing the amount of white carbon from 900 g (60 parts) to 1050 g (70 parts), replacing 225 g (15 parts) of zinc stearate with 225 g (15 parts) of calcium stearate, and changing the amount of Loxiol G-78 from 150 g (10 parts) to 225 g (15 parts).

The characteristics and the mold conditioning test results of the composition L are shown in Table 3. The test results prove the composition L to exhibit good molding properties and mold conditioning performance.

20 [0050]

Example 11 (the third mold conditioning resin composition of the invention)

A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition M) was prepared in the same manner as in Example 9, except for changing the amounts the EPDM (Mooney viscosity ML_{1+4} (100°C): 23) and the BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) to 1050 g and 450 g, respectively, replacing 225 g (15 parts) of zinc stearate with 150 g (10 parts) of calcium stearate, changing the amount of Loxiol G-78 from 150 g (10 parts) to 105 g (7 parts), replacing 150 g (10 parts) of Licolub H-4 with 45 g (3 parts) of Amide S (fatty acid amide, from Kao Corp.), and changing the amount of dicumyl peroxide from 18 g (1.2 parts) to 30 g (2 parts).

The characteristics and the mold conditioning test results of the composition M are shown in Table 3. The test results prove that the composition M exhibits good molding properties and mold conditioning performance.

[0051]

5 Example 12 (the third mold conditioning resin composition of the invention)

A mold conditioning rubber composition of sheet form with a thickness of 6 mm (designated composition N) was prepared in the same manner as in Example 9, except for replacing 600 g of the BR (Mooney viscosity ML_{1+4} (100°C): 42; 1,4-cis bond content: 95%) with 450 g of BR (Mooney viscosity ML_{1+4} (100°C): 35; 1,4-cis bond
10 content: 95%), changing the amount of white carbon from 900 g (60 parts) to 1050 g (70 parts), replacing 225 g (15 parts) of zinc stearate with 105 g (7 parts) of zinc stearate of 195 g (13 parts) of calcium stearate, changing the amount of Loxiol G-78 from 150 g (10 parts) to 300 g (20 parts), and replacing 18 g (1.2 parts) of dicumyl peroxide with 35 g (2.3 parts) of dicumyl peroxide and 13 g (0.9 parts) of 1,1-bis(t-butyl
15 peroxy)cyclohexane.

The characteristics and the mold conditioning test results of the rubber composition N are shown in Table 3. The test results prove the composition N to exhibit good molding properties and mold conditioning performance.

[0052]

Table 3

Items	Example 9	Example 10	Example 11	Example 12
	Composition K	Composition L	Composition M	Composition N
Ratio of EPDM	60	60	70	60
Ratio of BR	40	40	30	40
Elongation (%)	138	116	163	112
Tensile Strength (MPa)	5.8	5.1	4.6	5.3
Rubber Hardness	85	89	88	89
tc(90) (sec)	329	312	287	283
Moldability	A	A	A	A
Releasability	A	A	A	A
Freedom from Void Formation	A	A	A	A
Number of Consecutive Molding cycle	>1000	>1000	>1000	>1000

Industrial Applicability

5 [0053]

The mold conditioning rubber composition of the invention provides a mold with excellent release properties and prevents sticking of a molded part to the cavity, air vent, etc. that would otherwise occur with the recent improvement of epoxy encapsulating resins and advancement of semiconductor devices. The thus imparted mold release properties last long, achieving an increase in the number of possible consecutive molding cycles and leading to improved productivity.

10

CLAIMS

1. A compression type, mold conditioning rubber composition for imparting release properties to a mold surface after removing a stain formed during molding of a curing resin, which comprises
 - 5 an unvulcanized rubber comprising an ethylene-propylene rubber and a butadiene rubber at a mixing ratio of 90/10 to 50/50 by weight as a base resin,
 - a metal soap release agent, and
 - at least one release agent selected from an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide release agent,
 - 10 the unvulcanized rubber having a 90% cure time (optimum cure point) $t_c(90)$ in the range of from 50 to 100 seconds at a mold temperature of 175°C and, after cure, an elongation of 80% to 800%, a tensile strength of 3 to 10 MPa, and a rubber hardness (durometer A hardness) of 60 to 95.
2. A compression type, mold conditioning rubber composition for imparting release properties to a mold surface after removing a stain formed during molding of a curing resin, which comprises
 - 15 an unvulcanized rubber comprising an ethylene-propylene rubber and a butadiene rubber at a mixing ratio of 90/10 to 50/50 by weight as a base resin,
 - a metal soap release agent, and
 - 20 at least one release agent selected from an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide release agent,
 - the unvulcanized rubber having a 90% cure time (optimum cure point) $t_c(90)$ in the range of from 200 to 400 seconds at a mold temperature of 175°C and, after cure, an elongation of 80% to 800%, a tensile strength of 3 to 10 MPa, and a rubber hardness
 - 25 (durometer A hardness) of 60 to 95.
3. A compression type, mold conditioning rubber composition for imparting release properties to a mold surface after removing a stain formed during molding of a curing resin, which comprises

an unvulcanized rubber comprising an ethylene-propylene rubber and a butadiene rubber at a mixing ratio of 90/10 to 50/50 by weight as a base resin and

at least one release agent selected from a metal soap release agent, an organic fatty acid ester release agent, a synthetic wax release agent, and a fatty acid amide
5 release agent,

the unvulcanized rubber having a 90% cure time (optimum cure point) $t_c(90)$ in the range of from 200 to 400 seconds at a mold temperature of 175°C and, after cure, an elongation of 80% to 800%, a tensile strength of 3 to 10 MPa, and a rubber hardness (durometer A hardness) of 60 to 95.

10 4. The mold conditioning rubber composition according to any one of claims 1 to 3, wherein the organic fatty acid ester release agent is partially saponified montanic acid ester or a polymeric complex ester.

5. The mold conditioning rubber composition according to any one of claims 1 to 3, wherein the synthetic wax is a modified hydrocarbon wax or a mineral oil-based
15 synthetic wax.

6. The mold conditioning rubber composition according to any one of claims 1 to 3, further comprising at least one of a filler, a cleaning agent, a cleaning aid, a vulcanizing agent, a vulcanization aid, a vulcanization accelerator, a vulcanization acceleration aid, and a pigment.

20 7. A method of conditioning a mold comprising using the mold conditioning rubber composition according to any one of claims 1 to 6.