

DESCRIPTION

RESIN COMPOSITION FOR CLEANING DIE

Technical Field

[0001] The present invention relates to a resin composition for cleaning a die.

Background Art

[0002] Continuing a long-term sealing molding operation of an integrated circuit element or the like using a sealing molding material containing a curable resin composition of which an epoxy resin is representative causes a defect of staining the inner surface of a molding die due to a stain originating from the sealing molding material. Making such a stain remain unprocessed allows the stain to adhere to the surface of a sealing-molded product such as an integrated circuit element. Therefore, it is necessary to remove the stain on the inner surface of the molding die in a sealing molding step. Specifically, a resin composition for cleaning a die is molded instead of the sealing molding material at a rate of several shots based on several hundred shots of sealing molding, to thereby remove the stain on the inner surface of the molding die.

[0003] Such a resin composition for cleaning a die has been conventionally proposed. For example, International Publication No. WO 2009/57479 discloses a rubber-based composition for cleaning a die, which is an unvulcanized rubber including an ethylene-propylene rubber and a butadiene rubber at a blending rate of 90/10 to 50/50 parts by weight in a base material resin, wherein after vulcanization curing of the unvulcanized rubber, elongation, tensile strength, rubber hardness (durometer hardness), and 90% vulcanizing time at a die temperature of 175°C are specified in certain ranges. According to the patent literature, releasability from a die and reduction in voids and chipping can be solved. In the rubber-based composition for cleaning a die, for example, monoethanolamine is used as a cleaning agent.

[0004] Japanese Patent Application Laid-Open (JP-A) No. H02-20538 discloses a rubber composition for cleaning a die, including 1 to 70 parts by weight of a urea derivative based on 100 parts by weight of an ethylene-propylene rubber. According to the patent literature, it is described that a cleaning effect is obtained by adding a urea derivative such as diphenylurea or dimethylurea to reduce an odor in cleaning.

[0005] In recent years, in order to conform to the higher performance of integrated circuit elements and the like, sealing molding shapes and structures have been diversified and made

to be precise. Therefore, it has been also demanded that the shape and structure of a molding die are diversified and made to be precise, and the examination of conditions in a molding operation, e.g., molding conditions such as temperature, and the material of the molding die has been pursued. For example, there have been widely used molding dies of which the hardness is increased using a cemented carbide alloy to improve wear resistance.

[0006] A molding die having a material containing a cemented carbide alloy has had a defect that the molding die is deteriorated due to a small amount of cobalt contained in the cemented carbide alloy. The defect has been considered to be because application of heat allows cobalt contained in the cemented carbide alloy to be oxidized, whereby bonding strength is decreased to lead to the elimination of tungsten carbide in the cemented carbide alloy. Furthermore, in the molding die having the material containing the cemented carbide alloy, the discoloration of the molding die occurs with oxidation of cobalt. A sealing molding operation with the deteriorated molding die may cause the poor appearance of a sealing-molded product such as an integrated circuit element, to thereby further prevent a die shape from being accurately transferred.

[0007] In recent years, it has been demanded that in order to improve the workability of the step of molding a thermosetting resin, the cleaning performance of a resin composition for cleaning a die is improved to decrease the number of shots of the resin composition for cleaning a die. Not only in the step of molding a thermosetting resin composition using a molding die containing a cemented carbide alloy but also in a cleaning step, deterioration resistance of the molding die has been demanded.

SUMMARY OF INVENTION

Technical Problem

[0008] However, the resin composition for cleaning a die according to International Publication No. WO 2009/57479 is susceptible to improvement in cleaning performance. Further, the present inventors found that the resin composition for cleaning a die according to the literature may accelerate deterioration of a molding die containing a cemented carbide alloy.

[0009] Further, the rubber composition for cleaning a die according to JP-A No. H02-20538 has insufficient cleaning performance. Further, the effect of suppressing deterioration of a molding die containing a cemented carbide alloy in a cleaning step is insufficient.

[0010] An object of the present invention is to provide a resin composition for cleaning a die, improved in performance for cleaning the inner surface of a molding die in removal of a stain, generated in the step of molding a curable resin composition, on the inner surface of the

molding die.

Solution to Problem

[0011] The present invention encompasses the following embodiments.

(1) A resin composition for cleaning a die, comprising an ethylene-propylene rubber (A), a butadiene rubber (B), an inorganic filler (C), and a urea derivative (D),

a mass ratio of a content of a constitutional unit originating from ethylene to a content of a constitutional unit originating from propylene in the ethylene-propylene rubber (A) being in a range of from 55/45 to 60/40, and

a mass ratio (A/B) of a content of the ethylene-propylene rubber (A) to a content of the butadiene rubber (B) being in a range of from 30/70 to 70/30.

[0012] (2) The resin composition for cleaning a die according to (1), wherein the urea derivative (D) is at least one selected from the group consisting of 1,3-dimethylurea and monomethylurea.

[0013] (3) The resin composition for cleaning a die according to (1) or (2), wherein a content of the urea derivative (D) is from 0.3 parts by mass to 15 parts by mass based on a total content of the ethylene-propylene rubber (A) and the butadiene rubber (B) of 100 parts by mass.

[0014] (4) The resin composition for cleaning a die according to any one of (1) to (3), having a Mooney viscosity at 100°C of from 60ML (1+4) 100°C to 90ML (1+4) 100°C.

[0015] (5) The resin composition for cleaning a die according to any one of (1) to (4), having durometer hardness after molding at 175°C for 5 minutes of from A70 to A100.

[0016] (6) The resin composition for cleaning a die according to any one of (1) to (5), wherein the inorganic filler (C) comprises silica.

Advantageous Effect of Invention

[0017] According to the present invention, there can be provided a resin composition for cleaning a die, improved in performance for cleaning the inner surface of a molding die in removal of a stain, generated in the step of molding a curable resin composition, on the inner surface of the molding die.

DESCRIPTION OF EMBODIMENTS

[0018] A numerical value range indicated by using "from ... to ..." as used herein refers to a range including numerical values described before and after "to" as the minimum and maximum values, respectively. Further, when plural substances corresponding to each

component are present in a composition, an amount of each component in the composition means a total amount of the plural substances present in the composition unless otherwise specified.

[0019] [Resin composition for cleaning die]

The resin composition for cleaning a die of the present invention is used as, for example, a compression-type resin composition for cleaning a die, wherein a stain on a die surface, generated in the step of molding a curable resin composition selected from the group consisting of epoxy resins, silicone resins, phenolic resins, and polyimide resins, is removed. The resin composition for cleaning a die according to the embodiments of the present invention is explained in detail below.

[0020] The resin composition for cleaning a die of the present invention includes an ethylene-propylene rubber (A), a butadiene rubber (B), an inorganic filler (C), and a urea derivative (D), in which a mass ratio of a content of a constitutional unit originating from ethylene to a content of a constitutional unit originating from propylene in the ethylene-propylene rubber (A) being in a range of from 55/45 to 60/40, and a mass ratio (A/B) of a content of the ethylene-propylene rubber (A) to a content of the butadiene rubber (B) being in a range of from 30/70 to 70/30. The resin composition for cleaning a die includes the ethylene-propylene rubber and the butadiene rubber having a specific configurations at a specific ratio, and further includes the urea derivative. The resin composition thereby has excellent performance of cleaning an inner surface of a molding die. Further, deterioration of a cemented carbide alloy on an inner surface of a molding die can be effectively suppressed, and occurrence of poor appearance of a sealing-molded product such as an integrated circuit element in sealing molding can be suppressed.

[0021] (A) Ethylene-propylene rubber

The resin composition for cleaning a die includes at least one ethylene-propylene rubber (A). As used herein, the ethylene-propylene rubber means at least one of an ethylene-propylene rubber and an ethylene-propylene-diene rubber. The ethylene-propylene rubber (A) contained in the resin composition for cleaning a die has a mass ratio of a content of a constitutional unit originating from ethylene to a content of a constitutional unit originating from propylene (hereinafter also simply referred to as an "ethylene/propylene ratio") in a range of from 55/45 (1.22) to 60/40 (1.50). The ethylene/propylene ratio is preferably from 55/45 (1.22) to 59/41 (1.44). The ethylene/propylene ratio of less than 55/45 may result in insufficient tensile strength after vulcanization. The ethylene/propylene ratio of more than 60/40 may result in increased temperature dependency of the strength of a raw rubber which may cause deterioration in processability.

[0022] The ethylene/propylene ratio in the ethylene-propylene rubber can be calculated by measuring an ¹H-NMR (proton nuclear magnetic resonance) spectrum of the resin composition for cleaning a die at an ¹H resonance frequency of 500 MHz. The ethylene/propylene ratio may be more definitely calculated by isolating the ethylene-propylene rubber from the resin composition for cleaning a die by a usual method using HPLC (high performance liquid chromatograph) and then measuring its ¹H-NMR spectrum in the same manner.

[0023] The ethylene-propylene rubber preferably further includes a constitutional unit originating from a diene component in addition to the constitutional unit originating from ethylene and the constitutional unit originating from propylene. Examples of the diene component include ethylidene norbornene (ENB), methylidene norbornene, dicyclopentadiene, and vinylidene norbornene. Among these, the diene component preferably includes at least one selected from the group consisting of ethylidene norbornene and dicyclopentadiene, and more preferably includes ethylidene norbornene, from the viewpoint of cleaning performance.

[0024] When the ethylene-propylene rubber further includes the constitutional unit originating from the diene component, a content of the constitutional unit originating from the diene component is preferably from 6.5 mass% to 9.5 mass%, more preferably from 7.0 mass% to 9.0 mass%, and further preferably from 7.5 mass% to 8.5 mass%, based on a total mass of the ethylene-propylene rubber. When the ethylene-propylene rubber further includes the constitutional unit originating from the diene component, an iodine value of the ethylene-propylene rubber is preferably from 12 to 22, and more preferably from 14 to 18.

[0025] The ethylene-propylene rubber preferably includes from 6.5 mass% to 9.5 mass% of a constitutional unit originating from ethylidene norbornene in its total mass as well as the constitutional unit originating from ethylene and the constitutional unit originating from propylene, and more preferably includes from 7.0 mass% to 9.0 mass% of a constitutional unit originating from ethylidene norbornene in its total mass.

[0026] A Mooney viscosity ML (1+4) 100°C of the ethylene-propylene rubber is not particularly limited. Especially, the Mooney viscosity is preferably from 5 to 40, and more preferably from 5 to 30, from the viewpoint of cleaning performance. The Mooney viscosity is measured according to JIS K 6300-1 "Rubber, unvulcanized -Physical property- Part 1: Determination of Mooney viscosity and pre-vulcanization characteristics with Mooney viscometer".

[0027] A content of the ethylene-propylene rubber is preferably from 20 mass% to 80 mass%, more preferably from 30 mass% to 70 mass%, in a total mass of the resin composition for cleaning a die, from the viewpoint of cleaning performance. The resin

composition for cleaning a die may contain one ethylene-propylene rubber alone or two or more kinds thereof in combination.

[0028] (B) Butadiene rubber

The resin composition for cleaning a die includes at least one butadiene rubber. The butadiene rubber is not particularly limited, and may be appropriately selected from commonly used butadiene rubbers. Especially, from the viewpoint of cleaning performance, a butadiene rubber having a high-cis structure with a cis-1,4-bond content of 90 mass% or more and a Mooney viscosity ML (1+4) 100°C of from 20 to 60 is preferable, and a butadiene rubber having the high-cis structure and a Mooney viscosity ML (1+4) 100°C of from 30 to 45 is more preferable. The butadiene rubbers may be used singly or in combination of two or more kinds.

[0029] Since the resin composition for cleaning a die includes the ethylene-propylene rubber (A) and the butadiene rubber (B), a hardness of the resin composition for cleaning a die can be suitably kept maintained in removal of a stain on an inner surface of a molding die, and the resin for cleaning a die can be suitably filled into fine portions on the inside of the molding die. Further, since the strength of the resin composition for cleaning a die can be kept, the resin composition for cleaning a die does not become brittle, and an operation of releasing the resin composition for cleaning a die from a molding die can be easily performed after removal of a stain. Further, since the resin composition for cleaning a die of the present invention includes the ethylene-propylene rubber (A) and the butadiene rubber (B), dispersing of the urea derivative (D) such as 1,3-dimethylurea described below into the resin composition can be regulated, and thus cleaning performance is improved to obtain the effect of preventing deterioration of a cemented carbide alloy on an inner surface of the molding die. Details on the regulation of the dispersing of the urea derivative (D) such as 1,3-dimethylurea into the resin composition are described below.

[0030] The mass ratio (A)/(B) of the content of the ethylene-propylene rubber (A) contained in the resin composition for cleaning a die to the content of the butadiene rubber (B) is in a range of from 30/70 to 70/30. When the mass ratio (A)/(B) of the ethylene-propylene rubber (A) to the butadiene rubber (B) is less than 30/70, the resin composition for cleaning a die tends to become brittle, whereby, for example, an operation of releasing the cured resin composition for cleaning a die from a molding die after the operation of stain removal may become difficult. Further, when the mass ratio (A)/(B) of the ethylene-propylene rubber (A) to the butadiene rubber (B) exceeds 70/30, the cured resin composition for cleaning a die may adhere to an inner surface of a molding die in an operation of removing a stain on a heated molding die, whereby cleaning time tends to increase. Further, the mass ratio (A)/(B) out of

the range tends to preclude the regulation of the dispersibility of the urea derivative (D) such as 1,3-dimethylurea described below into the ethylene-propylene rubber (A) and the butadiene rubber (B) and to result in insufficient cleaning performance and insufficient effect in preventing deterioration of a cemented carbide alloy on an inner surface of the molding die.

[0031] The mass ratio of the content of the ethylene-propylene rubber (A) to the content of the butadiene rubber (B) in the resin composition for cleaning a die can be calculated by measuring the ^1H -NMR (proton nuclear magnetic resonance) spectrum of the resin composition for cleaning a die at a ^1H resonance frequency of 500 MHz.

[0032] (C) Inorganic filler

The resin composition for cleaning a die includes at least one inorganic filler (C). The inorganic filler is not particularly limited, and can be appropriately selected from commonly used inorganic fillers. Specific examples of the inorganic filler include silica, alumina, calcium carbonate, aluminum hydroxide, and titanium oxide. Especially, use of, as the inorganic filler (C), at least one selected from the group consisting of silica and titanium oxide is preferable since flaws in a die are slight and an elongation in cleaning molding of the resin composition for cleaning a die can be appropriately regulated.

[0033] A particle diameter range of the inorganic filler (C) is not particularly limited. Especially, the particle diameter range is preferably from 0.1 μm to 20 μm , and more preferably from 5 μm to 18 μm , from the viewpoint of cleaning performance. The particle diameter range is a volume average particle diameter measured with a Coulter counter (manufactured by Beckman Coulter, Inc.) using an aperture diameter of 70 μm .

[0034] The resin composition for cleaning a die preferably includes the inorganic filler (C) in an amount of from 20 parts by mass to 50 parts by mass, more preferably from 20 parts by mass to 40 parts by mass, and further preferably from 25 parts by mass to 40 parts by mass, based on a total amount of the ethylene-propylene rubber (A) and the butadiene rubber (B) as 100 parts by mass. The inclusion of 20 parts by mass or more of the inorganic filler (C) suppresses excessive elongation of the resin composition for cleaning a die in cleaning molding, to thereby allow the resin composition for cleaning a die to remain in an inner surface of a die in cleaning. The inclusion of 50 parts by mass or less thereof may result in an appropriate elongation in cleaning molding of the resin composition for cleaning, to thereby obtain superior cleaning performance.

[0035] (D) Urea derivative

The resin composition for cleaning a die includes at least one urea derivative. The urea derivative is not particularly limited as long as it is a compound having at least one ureido group. Especially, a urea derivative that is solid at ordinary temperature (25°C) is

preferable, and a compound that is solid at ordinary temperature and has at least one hydrogen atom on a nitrogen atom of a ureido group is more preferable, from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die. The urea derivative may be used singly or in combination of two or more kinds.

[0036] The resin composition for cleaning a die includes the urea derivative (D). The present inventors consider that the urea derivative (D) is a cleaning component and acts on a stain on an inner surface of a heated molding die to thereby contribute to properties of die surface cleaning. Further, it is considered that the properties of die cleaning can be further improved by regulating dispersing of the urea derivative (D) in the resin composition for cleaning a die. Further, fluidity of the resin composition for cleaning a die in itself, specifically, viscosity and elongation are important for the cleaning property as described below. The present inventors consider that the dispersing state of the urea derivative (D) in the resin composition for cleaning a die affects the fluidity of the resin composition for cleaning a die in itself.

[0037] The melting point of the urea derivative is preferably 70°C or more, more preferably from 70°C to 200°C, and further preferably from 90°C to 150°C, from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die. The urea derivative having a melting point of 70°C or more, i.e., being solid at ordinary temperature (25°C), is preferable since the dispersing of a cleaning component in the resin composition for cleaning a die can be more easily regulated.

[0038] Further, the boiling point of the urea derivative is preferably 90°C or more, more preferably from 150°C to 350°C, and further preferably from 180°C to 300°C, from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die. When the boiling point is 90°C or more, thermal stability is sufficiently obtained and is the effect of suppressing deterioration of a molding die containing a cemented carbide alloy is more effectively obtained.

[0039] The urea derivative is preferably a compound having a melting point of 70°C or more and a boiling point of 90°C or more, more preferably a compound having a melting point of from 70°C to 200°C and a boiling point of from 150°C to 350°C, and further preferably a compound having a melting point of from 90°C to 150°C, a boiling point of from 180°C to 300°C, and at least one hydrogen atom on a nitrogen atom of a ureido group, from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die.

[0040] The urea derivative is preferably a compound having an alkyl group having 1 to 15

carbon atoms on a nitrogen atom of a ureido group, more preferably a compound having one to three alkyl groups having 1 to 15 carbon atoms on a nitrogen atom of a ureido group, and further preferably a compound having one or two alkyl groups having 1 to 3 carbon atoms on a nitrogen atom of a ureido group, from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die. An alkyl group of the urea derivative may be a straight-chain or branched-chain.

[0041] Specific examples of the urea derivative include monomethylurea (melting point: 93°C, boiling point: 240°C), monoethylurea (melting point: 90°C, boiling point: 136°C), 1,1-dimethylurea (melting point: 183°C, boiling point: >185°C), 1,3-dimethylurea (melting point: 102°C, boiling point: 268°C), 1,1-diethylurea (melting point: 71°C), and 1,3-diethylurea (melting point: 113°C, boiling point: 268°C). Especially, at least one urea derivative selected from the group consisting of monomethylurea and 1,3-dimethylurea is preferable from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die.

[0042] Monomethylurea and 1,3-dimethylurea, which are preferably used as the urea derivatives, have melting points of from 93°C and 102°C, respectively, and are solid at ordinary temperature. A cleaning component that is a solid compound at ordinary temperature is preferable, since the dispersing of the cleaning component in the resin composition for cleaning a die can be easily regulated when the resin composition for cleaning a die is produced. On the other hand, a cleaning component used in a conventional resin composition for cleaning a die, e.g., monoethanolamine has a melting point of 10°C and is liquid at ordinary temperature. A cleaning component that is liquid at ordinary temperature may result in insufficient dispersibility in a resin composition for cleaning a die.

[0043] The inorganic filler (C) and the urea derivative (D) are preferably contained in a dispersed state in a rubber component containing the ethylene-propylene rubber (A) and the butadiene rubber (B) in the resin composition for cleaning a die. The present inventors consider that the sufficient dispersing of the urea derivative (D) in the resin composition in the production of the resin composition for cleaning a die result in more effective exertion of the action of the urea derivative (D) on a stain on a die surface during cleaning, to thereby further improve a cleaning property. Further, it is considered that poor dispersing in the resin composition may result in bleed-out of the urea derivative (D) after the production of the resin composition for cleaning a die, leading to fail contributing to the properties of cleaning a die surface in a cleaning operation and to deteriorate a cleaning property.

[0044] The resin composition for cleaning a die preferably has a Mooney viscosity at 100°C

of from 60ML (1+4) 100°C to 90ML (1+4) 100°C, more preferably from 60ML (1+4) 100°C to 80ML (1+4) 100°C, and further preferably from 62ML (1+4) 100°C to 80ML (1+4) 100°C. The Mooney viscosity of the resin composition for cleaning a die of 60ML (1+4) 100°C or more tends to result in further improvement in the moldability of the resin composition for cleaning a die in the production of the resin composition for cleaning a die. Further, the Mooney viscosity of 90ML (1+4) 100°C or less allows the dispersibility of the inorganic filler (C) and the urea derivative (D) in the ethylene-propylene rubber (A) and the butadiene rubber (B) in the production of the resin composition for cleaning a die to be further suitably controlled.

[0045] The present inventors found that a Mooney viscosity of the resin composition for cleaning a die is increased by the inclusion of the urea derivative (D) in the resin composition for cleaning a die. Further, it is considered that when the resin composition for cleaning a die has a Mooney viscosity at 100°C in a range of from 60ML (1+4) 100°C to 90ML (1+4) 100°C, the state of dispersing of the urea derivative (D) in the resin composition for cleaning a die exhibits a more suitable state for the cleaning characteristics of a die.

[0046] Herein, the Mooney viscosity is measured according to JIS K 6300-1 "Rubber, unvulcanized -Physical property- Part 1: Determination of Mooney viscosity and pre-vulcanization characteristics with Mooney viscometer".

[0047] The durometer hardness of a cured product obtained after molding the resin composition for cleaning a die at 175°C for 5 minutes is preferably from A70 to A100, more preferably from A72 to A95, and further preferably from A80 to A95. When the durometer hardness of the cured product obtained after the molding at 175°C for 5 minutes is A70 or more, needed molding pressure tends to be able to be more easily obtained to further improve cleaning performance. When the durometer hardness is A100 or less, the excessive embrittlement of the molded product tends to be suppressed to further improve cleaning performance.

[0048] A method for measuring the durometer hardness at 175°C is as described below. A test piece for rubber hardnesses is produced by molding using a 37T molding machine at a die temperature of 175°C and a molding pressure of 10 MPa (gauge pressure) for a molding time of 5 minutes. The durometer hardness of the resultant test piece for rubber hardnesses is measured by a method according to JIS K 6253 "Hardness testing methods for rubber, vulcanized or thermoplastic". Specifically, three test pieces obtained on the above test piece production conditions are stacked to perform the measurement using a durometer A type.

[0049] The present inventors further consider that a cleaning component, of which

monoethanolamine is representative, contained in a conventional resin composition for cleaning a die further promotes deterioration of a molding die containing a cemented carbide alloy. The step of sealing-molding an integrated circuit element or the like is usually performed at a high temperature of 170°C or more and the subsequent step of cleaning a molding die is also similarly performed at 170°C or more. The present inventors found that the resin composition for cleaning a die containing the urea derivative (D) does not cause deterioration of a molding die containing a cemented carbide alloy and does not cause performance deterioration due to decomposition or volatilization in the step of cleaning a molding die performed at a high temperature of 170°C or more. The findings are considered to be because for example, a urea derivative generally has comparatively high melting and boiling points as compared with a conventional cleaning component and is a thermally stable substance. Specifically, the findings are considered to be because 1,3-dimethylurea, which has a melting point of 102°C and a boiling point of 268°C, and monomethylurea, which has a melting point of 93°C and a boiling point of 240°C, are thermally stable substances.

Accordingly, it is considered that use of a cleaning component having a boiling point of, e.g., 180°C or more results in further effective improvement of the characteristics of cleaning a molding die and further effectively provides the effect of suppressing deterioration of a molding die containing a cemented carbide alloy.

[0050] The resin composition for cleaning a die is considered to allow the state of dispersing of the urea derivative (D) in the resin composition for cleaning a die to be appropriate because of containing the ethylene-propylene rubber (A) and the butadiene rubber (B). For example, in a resin composition for cleaning a die that contains the ethylene-propylene rubber (A) and the urea derivative (D) but does not contain the butadiene rubber (B), the effect of suppressing deterioration of a molding die containing a cemented carbide alloy is deteriorated at a high temperature of 175°C or more. The effect of suppressing deterioration is considered to be reduced due to, e.g., the occurrence of the poor dispersing of the urea derivative (D) in the resin composition for cleaning a die.

[0051] A content of the urea derivative in the resin composition for cleaning a die is not particularly limited. Especially, it is preferable to contain from 0.1 part by mass to 20 parts by mass of the urea derivative (D), it is more preferable to contain from 0.2 part by mass to 17 parts by mass thereof, and it is further preferable to contain from 0.3 parts by mass to 15 parts by mass thereof, based on 100 parts by mass of a total amount of the ethylene-propylene rubber (A) and the butadiene rubber (B). The content of the urea derivative (D) of 0.1 part by mass or more results in further improvement in cleaning performance and in more

effective suppression of deterioration of a cemented carbide alloy on an inner surface of a molding die in the removal of a stain on an inner surface of a molding die, generated in the step of molding a curable resin composition. Further, the content of the urea derivative (D) of 20 parts by mass or less enables the moldability of the resin composition for cleaning a die to be further improved to efficiently remove a stain on an inner surface of a molding die.

[0052] The content of the urea derivative in the resin composition for cleaning a die is preferably from 0.1 parts by mass to 30 parts by mass, more preferably from 0.2 parts by mass to 25 parts by mass, and further preferably from 0.4 parts by mass to 22 parts by mass, based on 100 parts by mass of the ethylene-propylene rubber (A), from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die. Further, the content of the urea derivative in the resin composition for cleaning a die is preferably from 0.2 part by mass to 67 parts by mass, more preferably from 0.7 parts by mass to 57 parts by mass, and further preferably from 1 part by mass to 50 parts by mass, based on 100 parts by mass of the butadiene rubber (B), from the viewpoint of cleaning performance and the effect of suppressing deterioration of a molding die.

[0053] The resin composition for cleaning a die preferably includes from 0.1 parts by mass to 20 parts by mass of the urea derivative having a melting point of 70°C or more, a boiling point of 90°C or more, and an alkyl group having 1 to 15 carbon atoms based on 100 parts by mass of a total amount of the ethylene-propylene rubber (A) and the butadiene rubber (B), more preferably includes from 0.2 parts by mass to 17 parts by mass of the urea derivative having a melting point of from 70°C to 200°C, a boiling point of from 150°C to 350°C, and an alkyl group having 1 to 15 carbon atoms based on 100 parts by mass of a total amount of the ethylene-propylene rubber (A) and the butadiene rubber (B), and further preferably includes from 0.3 parts by mass to 15 parts by mass of the urea derivative having a melting point of from 150°C to 350°C, a boiling point of from 180°C to 300°C, and an alkyl group having 1 to 3 carbon atoms based on 100 parts by mass of a total amount of the ethylene-propylene rubber (A) and the butadiene rubber (B).

[0054] A content of the urea derivative in the resin composition for cleaning a die can be calculated by measuring a ¹H-NMR (proton nuclear magnetic resonance) spectrum of the resin composition for cleaning a die at a ¹H resonance frequency of 500 MHz.

[0055] As the urea derivative (D) such as monomethylurea and 1,3-dimethylurea, which are preferably used in the resin composition for cleaning a die, e.g., N-methylurea and 1,3-dimethylurea, which are commercially available as products manufactured by Wako Pure Chemical Industries, Ltd., can be preferably used respectively.

[0056] In addition to the urea derivative, the resin composition for cleaning a die may

further include another cleaning agent other than urea derivatives as necessary. The additional cleaning agent can be appropriately selected from commonly used cleaning agents. Examples of the additional cleaning agent may include a surfactant and an alkali metal salt. When the resin composition for cleaning a die includes the other cleaning agent, a content thereof is preferably 50 mass% or less, more preferably 30 mass% or less, and further preferably 1 mass% or less, based on the urea derivative.

[0057] (Vulcanizing agent)

The resin composition for cleaning a die preferably includes at least one vulcanizing agent. The vulcanizing agent may be appropriately selected from commonly used vulcanizing agents. Examples thereof include organic peroxides based on dialkyl peroxides, such as di-*t*-butylperoxide, di-*t*-amylperoxide, dicumylperoxide, and 2,5-dimethyl-2,5-di(*t*-butylperoxy)hexane; organic peroxides based on peroxyketals such as 1,1-di(*t*-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-di(*t*-butylperoxy)cyclohexane, 2,2-di(*t*-butylperoxy)octane, *n*-butyl-4,4-di(*t*-butylperoxy)valerate, and 2,2-di(*t*-butylperoxy)butane. Such vulcanizing agents may be used singly or in combination of two or more kinds to adjust a vulcanization rate.

[0058] When the resin composition for cleaning a die includes the vulcanizing agent, a content thereof may be appropriately selected depending on, e.g., the kind of the vulcanizing agent. Especially, it is preferable to include from 0.1 part by mass to 6 parts by mass of the vulcanizing agent, it is more preferable to include from 1 part by mass to 5 parts by mass thereof, and it is further preferable to include from 2 parts by mass to 4 parts by mass thereof, based on 100 parts by mass of a total amount of the ethylene-propylene rubber (A) and the butadiene rubber (B). The content of the vulcanizing agent of 0.1 part by mass or more results in further improvement in cleaning performance and in more effective suppression of deterioration of a cemented carbide alloy on an inner surface of a molding die in a removal of a stain which is on the inner surface of the molding die and is generated in the step of molding a curable resin composition. Further, the content of the vulcanizing agent of 6 parts by mass or less tends to enable further suppression of generation of an odor.

[0059] (Mold release agent)

The resin composition for cleaning a die cleaning preferably includes at least one mold release agent. Examples of the mold release agent include fatty acid ester mold release agents, synthetic waxes, and fatty acid amide mold release agents. Examples of metal soap mold release agents may include calcium stearate, zinc stearate, and zinc myristate. Examples of the fatty acid ester mold release agents, the synthetic waxes, and the fatty acid amide mold release agents include LICOWAX O P (partially saponified ester of montanic

acid, manufactured by Clariant (Japan) K.K.), LOXIOLE G-78 (polymer composite ester, manufactured by Cognis Japan Ltd.), LICOLUB H-4 (modified hydrocarbon, manufactured by Clariant (Japan) K.K.), LOXIOLE VPN881 (mineral oil-based synthetic wax, manufactured by Cognis Japan Ltd.), FATTY AMIDE S (fatty acid amide, manufactured by Kao Corporation), KAO WAX EB-P (fatty acid amide, manufactured by Kao Corporation), and ALFLOW HT-50 (fatty acid amide, manufactured by Nippon Oil & Fats Co., Ltd.).

[0060] When the resin composition for cleaning a die includes the mold release agent, a content thereof may be appropriately selected depending on the kind of the mold release agent. Especially, it is preferable to include from 0.1 part by mass to 5 parts by mass of the mold release agent and it is more preferable to include from 0.5 part by mass to 3 parts by mass thereof, based on 100 parts by mass of a total amount of the ethylene-propylene rubber (A) and the butadiene rubber (B).

[0061] (Other component)

The resin composition for cleaning a die may further include another additive such as a cleaning auxiliary, a vulcanization auxiliary, a vulcanization accelerator, or a vulcanization acceleration auxiliary as necessary unless precluding the effects of the present invention. Examples of the cleaning auxiliary include various surfactants. Examples of the vulcanization auxiliary include acrylic acid monomers, and sulfur. Examples of the vulcanization accelerator include those based on guanidine such as diphenyl guanidine and triphenyl guanidine, those based on aldehyde-amine or aldehyde-ammonia such as formaldehyde-para-toluidine condensates and acetaldehyde-aniline reactants, and those based on thiazole such as 2-mercaptobenzothiazole and dibenzothiazyl disulfide. Further, examples of the vulcanization acceleration auxiliary include magnesia, litharge, and lime.

[0062] The resin composition for cleaning a die may further include an inorganic or organic pigment such as iron oxide red, Prussian blue, iron black, ultramarine blue, carbon black, lithopone, titan yellow, cobalt blue, Hansa yellow, or quinacridone red unless precluding the effects of the present invention.

[0063] A method for preparing the resin composition for cleaning a die is not particularly limited. For example, the resin composition can be prepared by adding the inorganic filler (C) and the urea derivative (D) to a mixture material containing the ethylene-propylene rubber (A) and the butadiene rubber (B) and by kneading the resultant. In this case, an additive of which a mold release agent or the like is representative may also be added. A kneading means is not particularly limited, and can be appropriately selected from commonly used methods of kneading means. Examples of the kneading means include pressurization-type kneaders, Banbury mixers, and roll mixers.

[0064] A shape of the resin composition for cleaning a die is not particularly limited. For example, a sheet shape is preferable. When the resin composition for cleaning a die cleaning has a sheet shape, it can be easily cooled in a short time. Vulcanization due to preheating in kneading can be suppressed by immediately cooling the kneaded resin composition, and stable performance can be obtained. When the resin composition for cleaning a die is molded in a sheet shape, a thickness and a size thereof is not particularly limited, and can be appropriately selected depending on a purpose. For example, the thickness may be from 3 mm to 10 mm, and preferably from 5 mm to 7 mm.

[0065] A mode of use of the resin composition for cleaning a die is not particularly limited. For example, use as a compression type is preferable. Thereby, a release operation of the resin composition for cleaning a die from a molding die can be easily performed after removing a stain. Examples of cemented carbide metals in a die in which the resin composition for cleaning a die is used include WC-Co alloys, WC-TiC-Co alloys, WC-TaC-Co alloys, WC-TiC-TaC-Co alloys, WC-Ni alloys, and WC-Ni-Cr alloys. Especially, at least one selected from the group consisting of WC-Ni alloys and WC-Ni-Cr alloys is preferable.

EXAMPLES

[0066] The effects of the present invention are specifically explained with reference to examples and comparative examples below, but the present invention is not limited to the examples.

[0067] [Example 1]

Into a 3000 mL pressurization-type kneader with a jacket, 1050 g of an ethylene-propylene rubber (trade name EPT4021, manufactured by Mitsui Chemicals, Inc., ethylene/propylene ratio = 55.5/44.5) and 450 g of a butadiene rubber (trade name: JSR BR01, manufactured by JSR Corporation) were added and subjected to pressurization-kneading for about 3 minutes while being cooled. The mixture material became a dough and had a temperature of about 80°C. Then, 7.5 g (0.5 part by mass based on 100 parts by mass of a total amount of the ethylene-propylene rubber and the butadiene rubber) of 1,3-dimethylurea (manufactured by Wako Pure Chemical Industries, Ltd.), 15 g of stearic acid, 525 g of white carbon (trade name: NIPSIL LP, manufactured by TOSOH SILICA CORPORATION), and 75 g of titanium oxide (trade name: CR-80, manufactured by ISHIHARA SANGYO KAISHA, LTD.) were added and kneaded for about 3 minutes. Finally, 48 g of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane was added and subsequently kneaded for about 1 minute. The temperature of the kneaded product during the operation was regulated so as

not to exceed 100°C. The resultant kneaded product was immediately passed through a pressure roll, processed into a sheet shape, and cooled to 25°C or less, to thereby obtain a sheet-shaped resin composition for cleaning a die with a thickness of 6 mm.

[0068] [Evaluation]

The cleaning performance and molding die deterioration suppression property (corrosiveness) of the resultant resin composition for cleaning a die were evaluated as described below. The evaluation results are listed in Table 1 and Table 2. In all cases, a cleaning property was evaluated on a condition of a die temperature of 175°C. The unit of each composition in Table 1 and Table 2 is part(s) by mass and "-" denotes non-blending.

[0069] [Cleaning property test]

With a die of PDIP-14L (8 pots-48 cavities) having a plunger having a nose provided with a tip made of a cemented carbide alloy, 500-shot molding was performed using a commercially available biphenyl epoxy resin molding material (EME-7351T, manufactured by Sumitomo Bakelite Co., Ltd.), to thereby form a stain on an inner surface of the molding die.

The resin composition for cleaning a die obtained as described above was repeatedly molded using the molding die having the stain on the inner surface of the molding die, and the cleaning performance was evaluated by a number of times of the molding (the number of shots) needed for removing the stain from the inner surface of the molding die. A state of removing the stain on the inner surface of the molding die was judged by visual observation. When the number of times of repeated molding of the resin composition for cleaning a die (number of cleaning completion shots) needed for removing the stain on the inner surface of the die was four times or less, it was regarded as acceptable.

[0070] [Deterioration suppression test for molding die]

The resin composition for cleaning a die was maintained at 20°C in a condition of being contacting the tip made of the cemented carbide alloy placed on the nose of the plunger which is a part of the molding die. After left standing for 1 week, the resin composition for cleaning a die and the cemented carbide alloy tip contacted therewith and placed on the nose of the plunger were observed by visual observation, and a presence or absence of discoloration was checked by visual observation and evaluated according to the following evaluation criteria:

-Evaluation criteria-

A (Excellent): No discoloration occurred on the resin composition for cleaning a die and the tip.

B (Good): Practically non-problematic, although there was slight discoloration on the

resin composition for cleaning a die or the tip.

C (Poor): Discoloration occurred on the resin composition for cleaning a die or the tip.

[0071] [Operation stability evaluation]

For operation stability in the production of the resin composition for cleaning a die, a case in which the dispersing of a cleaning agent was easy during kneading was evaluated as "good" while a case in which the dispersing of a cleaning agent during kneading was slightly difficult was evaluated as "fair".

Further, for operation stability in die cleaning, when the resin composition for cleaning a die was molded at a die temperature of 175°C, a molding pressure of 15 MPa and a molding time of 300 seconds, and the molded product was taken, in a case in which the molded product was easily integrally removed, it was evaluated as "good", while a case in which the molded product was partly separated but was removed without sticking, it was evaluated as "fair".

[0072] [Examples 2 to 9]

A resin composition for cleaning a die was obtained and was evaluated in the same manner as that in Example 1 except that the composition of the resin composition for cleaning a die in Example 1 was replaced by a combination listed in Table 1.

[0073] [Example 10]

A resin composition for cleaning a die was obtained and was evaluated in the same manner as that in Example 4 except that monomethylurea was used instead of 1,3-dimethylurea in the preparation of the resin composition for cleaning a die of Example 4.

[0074] [Example 11]

A resin composition for cleaning a die was obtained and was evaluated in the same manner as that in Example 4 except that EPT4010 (manufactured by Mitsui Chemicals, Inc., ethylene/propylene ratio = 58.4/41.6) was used as an ethylene-propylene rubber instead of EPT4021 (manufactured by Mitsui Chemicals, Inc.) in the preparation of the resin composition for cleaning a die of Example 4.

[0075] [Comparative Example 1]

A resin composition for cleaning a die was obtained and was evaluated in the same manner as that in Example 4 except that 2-aminoethanol was used instead of 1,3-dimethylurea in the preparation of the resin composition for cleaning a die of Example 4.

[0076] [Comparative Examples 2 to 4]

A resin composition for cleaning a die was obtained and was evaluated in the same manner as that in Example 1 except that the composition of the resin composition for cleaning

a die in Example 1 was replaced by a combination listed in Table 2.

[0077] [Comparative Examples 5 to 7]

A resin composition for cleaning a die was obtained and was evaluated in the same manner as that in Example 4 except that EPT4070 (manufactured by Mitsui Chemicals, Inc., ethylene/propylene ratio = 60.9/39.1), EPT3090 (manufactured by Mitsui Chemicals, Inc., ethylene/propylene ratio = 50.6/49.4), and EPT3091 (manufactured by Mitsui Chemicals, Inc., ethylene/propylene ratio = 64.5/35.5) were used as ethylene-propylene rubbers, respectively, instead of EPT4021 (manufactured by Mitsui Chemicals, Inc.) in the preparation of the resin composition for cleaning a die of Example 4.

[0078] Table 1

	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example	Example
	1	2	3	4	5	6	7	8	9	10	11	
Composition (part(s) by mass)	Ethylene-propylene rubber (A)	70	70	70	70	70	70	30	40	70	70	
	Butadiene rubber (B)	30	30	30	30	30	30	70	60	30	30	
	Inorganic filler (C)	40	40	40	35	30	29	35	35	35	40	
	1,3-Dimethylurea (D)	0.2	0.3	0.5	6	12	15	17	6	-	6	
	Monomethylurea (D)	-	-	-	-	-	-	-	-	6	-	
	2-Aminoethanol	-	-	-	-	-	-	-	-	-	-	
	Stearic acid	1	1	1	1	1	1	1	1	1	1	
	2,5-Dimethyl-2,5-di(t-butylperoxy)hexane	3.2	3.2	3.2	3.2	3.2	3.2	3.2	4	3.2	3.2	
	Ethylene/propylene ratio	55.5/44.5	55.5/44.5	55.5/44.5	55.5/44.5	55.5/44.5	55.5/44.5	55.5/44.5	55.5/44.5	55.5/44.5	58.4/41.6	
	Mooney viscosity (ML (1+4) 100°C)	62	63	63	69	77	80	81	76	88	60	
Physical properties	Durionate hardness (after curing)	86	87	85	88	91	73	74	93	79	74	
	Operation stability in production	Good	Good	Good	Good	Good	Good	Fair	Good	Fair	Good	
	Operation stability in die cleaning	Fair	Good	Good	Good	Good	Good	Good	Good	Good	Fair	
Evaluation	Cleaning property (number of shots)	4	4	4	3	3	3	4	3	4	4	
	Corrosiveness	A	A	A	A	A	A	A	A	A	A	

[0079] Table 2

		Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7
Composition (part(s) by mass)	Ethylene-propylene rubber (A)	30	100	75	25	70	70	70
	Butadiene rubber (B)	70	-	25	75	30	30	30
	Inorganic filler (C)	35	35	35	35	35	35	35
	1,3-Dimethylurea (D)	-	6	6	6	6	6	6
	Monomethylurea (D)	-	-	-	-	-	-	-
	2-Aminoethanol	6	-	-	-	-	-	-
	Stearic acid	1	1	1	1	1	1	1
	2,5-Dimethyl-2,5-di(t-butylperoxy)hexane	3.2	3.2	3.2	3.2	3.2	3.2	3.2
	Ethylene/propylene ratio	55.5/44.5	55.5/44.5	55.5/44.5	55.5/44.5	60.9/39.1	50.6/49.4	64.5/35.5
	Mooney viscosity (ML (1+4) 100°C)	74	46	59	78	93	103	101
Physical properties	Durionate hardness (after curing)	93	82	85	94	90	96	95
	Operation stability in production	Good	Fair	Good	Good	Fair	Fair	Fair
Evaluation	Operation stability in die cleaning	Good	Fair	Fair	Good	Good	Good	Good
	Cleaning property (number of shots)	5	7	5	5	6	6	6
	Corrosiveness	C	A	A	A	A	A	A

[0080] As is clear from the evaluation results in Table 1 and Table 2, the sheet-shaped resin compositions for cleaning a die according to the embodiments of the present invention could remove the stain on the inner surface of the molding die generated in the step of molding the curable resin composition with a small number of shots and thereby exhibited excellent cleaning performance. Further, deterioration of the cemented carbide alloy member on the inner surface of the molding die was suppressed.

In contrast, it is found that the resin compositions for cleaning a die according to the comparative examples could not provide sufficient cleaning performance. Particularly, the resin composition for cleaning a die shown as Comparative Example 1, in which monoethanolamine was used as the cleaning agent, was found to have a poor cleaning property as compared with the resin composition for cleaning a die according to the present invention, and further, it was found to deteriorate a member made of a cemented carbide alloy. Further, the resin composition for cleaning a die shown as Comparative Example 2, which contained no butadiene rubber, was found to have a poor cleaning property as compared with the resin composition for cleaning a die according to the present invention.

[0081] The disclosure of Japanese Patent Application No. 2011-131709 is incorporated herein by reference in its entirety.

All literatures, patent applications, and technical standards described herein are herein incorporated by reference to the same extent as if each individual literature, patent application, or technical standard was specifically and individually indicated as being incorporated by reference.

CLAIMS

1. A resin composition for cleaning a die, comprising an ethylene-propylene rubber (A), a butadiene rubber (B), an inorganic filler (C), and a urea derivative (D),
a mass ratio of a content of a constitutional unit originating from ethylene to a content of a constitutional unit originating from propylene in the ethylene-propylene rubber (A) being in a range of from 55/45 to 60/40, and
a mass ratio (A/B) of a content of the ethylene-propylene rubber (A) to a content of the butadiene rubber (B) being in a range of from 30/70 to 70/30.
2. The resin composition for cleaning a die according to claim 1, wherein the urea derivative (D) is at least one selected from the group consisting of 1,3-dimethylurea and monomethylurea.
3. The resin composition for cleaning a die according to claim 1 or claim 2, wherein a content of the urea derivative (D) is from 0.3 parts by mass to 15 parts by mass based on a total content of the ethylene-propylene rubber (A) and the butadiene rubber (B) of 100 parts by mass.
4. The resin composition for cleaning a die according to any one of claim 1 to claim 3, having a Mooney viscosity at 100°C of from 60ML (1+4) 100°C to 90ML (1+4) 100°C.
5. The resin composition for cleaning a die according to any one of claim 1 to claim 4, having durometer hardness after molding at 175°C for 5 minutes of from A70 to A100.
6. The resin composition for cleaning a die according to any one of claim 1 to claim 5, wherein the inorganic filler (C) comprises silica.