

DESCRIPTION

MOLD CLEANING/CONDITIONING RESIN COMPOSITION AND METHOD OF MOLD CLEANING/CONDITIONING

Technical Field

5 [0001]

This invention relates to a compression type resin composition for mold cleaning/conditioning which serves for both mold cleaning and mold conditioning in molding a curing resin compound, i.e., which removes mold stain while imparting release properties to the mold surface. It also relates to a mold cleaning/conditioning
10 method using the resin composition.

Background Art

[0002]

When encapsulation molding of integral circuits, etc. with a thermosetting resin such as an epoxy resin is continued for a long time, cases not infrequently occur in
15 which the inner surface of the mold is stained, and continuation of molding with such a stained mold results in contamination of the surface of the molded products or adhesion of the molded product to the mold surface, making further shots impossible. The mold should therefore be cleaned periodically, which is practiced by making a few shots with a mold cleaning resin per several hundreds of shots with a molding material thereby to
20 clean the mold.

For example, JP 52-788B proposes a method of cleaning a mold for molding a curing resin compound other than an amino resin compound, the cleaning method comprising molding an amino resin-based material in the mold. JP 52-788B discloses a mold cleaning resin composition comprising an amino resin, an organic
25 filler and/or an inorganic filler, and a release agent.

[0003]

With the ever increasing integration scale and decreasing device thickness

and the spreading use of surface mount technology in integral circuits, etc. (hereinafter referred to as IC/LSIs) fabrication, the shapes and structures of molded products have been increasingly diversified. To cope with this, fluidity of a molding compound for semiconductor encapsulation has been improved.

5 A high fluidity epoxy molding compound is liable to clog the air vent. If air vent clogging occurs, the resin compound does not flow because air is not allowed to escape. It follows that an incomplete fill occurs, making continuous molding difficult. To avoid the problem, cleaning is required. It has been difficult, however, to remove the resin compound clogging the air vent with a
10 transfer type cleaning material because the cleaning resin does not flow normally for the reason described above.

[0004]

 Cleaning operation using a mold cleaning resin composition makes the mold surface clean but, on the other hand, also removes a mold release agent from the
15 mold surface. As a result, if molding is resumed immediately after the cleaning operation, the mold exhibits extremely poor release properties. It has therefore been necessary that mold cleaning operation be followed by a shot with a mold conditioning resin composition containing a release agent to allow the release agent to ooze out onto the mold surface thereby to impart release properties to the mold
20 surface.

 The mold conditioning resin composition is adapted to transfer the release agent to the mold surface thereby to rapidly make the mold recover release properties. Conventional mold conditioning resin compositions contain, for example, an epoxy resin, a phenol resin, a curing catalyst, carnauba wax, silica, and
25 so on.

[0005]

 Because of a failure to flow into the air vent for the same reason as described above, however, the mold conditioning resin composition encounters difficulty in imparting release properties to the resin-clogged air vent.

[0006]

Patent Document 1: JP 52-788B

Disclosure of the Invention

Problem to be Solved by the Invention

5 [0007]

The present invention is contemplated to overcome the air vent clogging with a high fluidity molding compound for semiconductor encapsulation and the difficulty in cleaning and conditioning a mold with a mold cleaning/conditioning resin composition due to the air vent clogging. The present invention is also
10 contemplated to provide a mold cleaning/conditioning resin composition of compression type having both mold cleaning ability and mold conditioning ability. With the composition of the invention, the air vent portion of a molding die can be cleaned and conditioned easily, and mold cleaning and conditioning can be achieved through a single operation unlike conventional methods involving a complicated
15 two-stage operation: cleaning a mold to remove stains from the mold surface, followed by applying a mold conditioning resin composition to supply a release agent that has been removed together with the stains.

Means for Solving the Problem

[0008]

20 Aiming at solving the above problems, the present invention provides a mold cleaning/conditioning resin composition which is used in the molding of a curing resin molding compound to remove stains from the mold surface and to impart release properties to the mold surface and which contains a melamine resin and at least one metal soap-based release agent.

25 [0009]

Preferably, the mold cleaning/conditioning resin composition of the invention further contains mannitol and/or a release agent other than mannitol and a metal soap.

Effect of the Invention

[0010]

The mold cleaning/conditioning resin composition of the invention is a compression type resin composition having both a mold cleaning effect and a mold conditioning effect. It is capable of removing mold stains from not only the cavity, runner and gate but also the air vent and parting area of a mold and conditioning these parts, particularly the air vent with ease. The present invention provides means for achieving mold cleaning and conditioning through a single stage operation, eliminating the necessity of conducting the conventionally practiced, complicated two-stage operation including mold cleaning with a mold cleaning resin composition and mold conditioning with a mold conditioning resin composition.

Best Mode for Carrying out the Invention

[0011]

The mold cleaning/conditioning resin composition according to the present invention will be illustrated in detail.

The melamine resin that can be used in the invention can be prepared by known processes. For example, formaldehyde and melamine crystals are allowed to react at a molar ratio of 1:1 to 4:1, advantageously 1.5:1 to 3:1, in an aqueous solution to prepare an initial condensate aqueous solution. The reaction proceeds at a melamine crystal concentration of 20% to 60% at a reaction temperature of 70 to 100°C under a weakly alkaline condition and completes in 10 to 100 minutes. Part of the formaldehyde may be replaced with an aldehyde component other than paraformaldehyde and formaldehyde, such as an aliphatic aldehyde, e.g., acetaldehyde.

[0012]

The mold cleaning/conditioning resin composition of the invention contains a metal soap-based release agent in addition to the melamine resin.

Examples of the metal soap-based release agent include calcium stearate, zinc stearate, and zinc myristate. The amount of the metal soap-based release agent to be used ranges preferably 0.2 to 1.0 part, more preferably 0.4 to 0.8 parts

by weight, per 100 parts by weight of the melamine resin. Too small an amount of the metal soap-based release agent results in reduction of mold conditioning and cleaning effects. Use of too large an amount of the metal soap-based release agent results in reduction of cleaning effect, while exhibiting good mold conditioning effect.

[0013]

It is preferable that the mold cleaning/conditioning resin composition of the invention further contain mannitol in addition to the melamine resin and the metal soap-based release agent. Addition of mannitol enables reduction of thermal color change of the resin composition while retaining the mold conditioning effect.

The mannitol to be used is preferably D-mannitol.

When mannitol is added, the weight ratio of the metal soap-based release agent to mannitol is preferably 90:10 to 30:70, more preferably 80:20 to 40:60. Too high a weight ratio of mannitol results in poor cleaning performance.

The amount of mannitol to be added is preferably 0.2 to 1.0 part by weight, more preferably 0.3 to 0.8 parts by weight, per 100 parts by weight of the melamine resin. Too small an amount of mannitol brings about no effect of addition. Too large an amount of mannitol results in reduction of cleaning effect, while exhibiting good conditioning effect.

[0014]

It is preferred that the mold cleaning/conditioning resin composition of the invention furthermore contain a release agent other than a metal soap, in addition to the melamine resin and the metal soap release agent. Presence of a release agent other than the metal soap helps the composition exhibit the mold conditioning effect without being influenced by the release agent component contained in the epoxy molding compound.

Release agents other than metal soaps include ester types such as partially saponified montanic esters and polymeric complex esters and synthetic waxes such as modified hydrocarbon waxes and mineral oil-based synthetic waxes. Commercially available products can be used conveniently, including Licowax OP (partially saponified montanic ester from Clariant Japan), Loxiol G78 (polymeric complex ester from Cognis Japan), Ricolub H-4 (modified hydrocarbon from Clariant Japan), and Loxiol VPN881 (mineral oil-based synthetic wax from Cognis Japan). The ester type release agents and synthetic waxes described above are preferred release agents other than a metal soap. Use of release agents other than those described above may reduce the cleaning performance.

In using the release agent other than a metal soap, the weight ratio of the metal soap-based release agent to the other release agent is preferably 90:10 to 30:70, more preferably 80:20 to 40:60. Too large a proportion of the release agent other than a metal soap impairs the cleaning performance.

The amount of the release agent other than a metal soap to be added is preferably 0.02 to 0.7 parts by weight, more preferably 0.1 to 0.5 parts by weight, 100 parts by weight of the melamine resin. Addition of too small an amount of the release agent other than a metal soap produces no substantial effect. Conversely, addition of too much release agent other than a metal soap brings about good releasability but impairs the cleaning performance.

[0015]

It is preferred that the mold cleaning/conditioning resin composition of the invention furthermore contain pulp to have an improved cleaning effect. Examples of usable pulp include straw pulp, bamboo pulp, and wood pulp (soft wood pulp and hard wood pulp), each of which may be either chemical or mechanical pulp.

The pulp, if used, is preferably incorporated into the mold cleaning/conditioning resin composition in the form as impregnated with the melamine resin, the essential component of the resin composition (i.e., in the form of resin-impregnated pulp). Resin-impregnated pulp can be prepared by

impregnating pulp with a melamine-formaldehyde resin aqueous solution followed by drying. A part or the whole of the pulp may be replaced with powdered pulp, whereby the resulting resin composition will have further improved fluidity.

5 The size of the pulp is not particularly limited but usually ranges from about 5 to 1000 μm , preferably from about 10 to 200 μm . The amount of the pulp to be added is usually 5 to 70 parts by weight, preferably 20 to 60 parts by weight, per 100 parts by weight of the melamine resin. Addition of less than 5 parts of pulp produces no effect. Addition of more than 70 parts of pulp impairs the fluidity so that the resulting resin composition fails to completely fill the extremities of a mold,
10 leaving stains on the mold behind.

[0016]

It is preferred that the mold cleaning/conditioning resin composition of the invention still furthermore contain a curing catalyst. Examples of useful curing catalysts include organic acids such as phthalic anhydride, oxalic acid, sulfamic acid,
15 and p-toluenesulfonic acid; inorganic acids such as hydrochloric acid and sulfuric acid; and salts of these acids with triethylamine, triethanolamine, β -dimethylaminoethanol, 2-methyl-2-amino-1-propanol, etc. A recommended amount of the curing catalyst to be added is usually 0.05 to 1.5 parts by weight, preferably 0.1 to 1 part by weight, per 100 parts by weight of the melamine resin.

20 It is preferred for the mold cleaning/conditioning resin composition of the invention to contain at least one of the pulp and the curing catalyst.

The mold cleaning/conditioning resin composition of the invention may contain, as appropriate, a colorant such as a pigment, a fibrous filler other than pulp, a particulate, low-hardness and small-size filler, and so forth.

25 [0017]

The mold cleaning/conditioning resin composition of the invention can be prepared by any means that achieves uniform mixing of the melamine resin and the

metal soap releasing agent and other optional additives including mannitol, the releasing agent other than a metal soap, and pulp. Examples of such a mixing means include a kneader, a ribbon blender, a Henschel mixer, a ball mill, a roll mill, an automated motor, and a tumbling mixer.

5 [0018]

The curing resin molding material that can be removed from the surface of a mold with the mold cleaning/conditioning resin composition of the present invention is exemplified by an epoxy resin molding compound and a phenol resin molding compound, preferably an epoxy resin molding compound, especially the
10 one for semiconductor encapsulation. While the mold cleaning/conditioning resin composition of the invention is applicable to any mold that is used to automatically molding such a curing resin molding material, it is advantageously applied to molds made of iron, chromium, and the like.

A stained mold can be cleaned and, at the same times, conditioned to restore
15 release properties by molding the mold cleaning/conditioning resin composition in the mold. Preferred molding conditions of molding the mold cleaning/conditioning resin composition of the invention are: a mold temperature of 160° to 190°C, a molding pressure of 10 to 20 MPa, and a curing time of 2 to 3 minutes.

Examples

20 [0019]

The present invention will now be illustrated in greater detail with reference to its Examples, but it should be understood that the invention is not deemed to be limited thereto.

[0020]

25 Preparation Example 1

Four hundred and eighty parts by weight of melamine and 520 parts by weight of formalin (37% aqueous solution) were allowed to react in 350 parts by weight of water under heating in a known manner to prepare an aqueous solution of a melamine-formaldehyde resin. The resulting melamine resin aqueous solution

was kneaded with 257 parts by weight of pulp, followed by drying under reduced pressure to provide a pulp-loaded melamine-formaldehyde resin powder (melamine resin-impregnated pulp) having a resin content of about 72%.

Preparation Example 2

5 The melamine resin aqueous solution prepared in Preparation Example 1 (solid content: ca. 60 wt%) was spray dried at about 200°C to give a powdered melamine resin.

[0021]

Example 1

10 A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was mixed with 0.5 parts by weight of phthalic anhydride and 6.0 parts by weight of zinc stearate in a ball mill to prepare a mold cleaning/conditioning resin composition (designated resin composition A). Resin composition A was evaluated for mold
15 cleaning and conditioning performance in accordance with the test methods described below. The results obtained are shown in Table 1. Resin composition A exhibited excellent mold cleaning performance as shown in Table 1. When a mold having been cleaned with resin composition A but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding
20 compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with a conventional mold conditioning resin composition.

[0022]

Example 2

25 A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was mixed with 30 parts by weight of the powdered melamine resin obtained in Preparation Example 2, 30 parts by weight of powdered pulp, 0.5 parts by weight of phthalic anhydride, 2.5 parts by weight of zinc stearate, and 3.5 parts by weight of
30 calcium stearate in a ball mill to prepare a mold cleaning/conditioning resin composition (designated resin composition B). Resin composition B was

evaluated for mold cleaning and conditioning performance in the same manner as in Example 1. The results obtained are shown in Table 1. As shown in Table 1, resin composition B exhibited excellent mold cleaning performance. When a mold having been cleaned with resin composition B but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with a conventional mold conditioning resin composition.

[0023]

Test Methods

(1) Mold cleaning test

Five hundred shots of a commercially available biphenyl epoxy resin molding compound (EME-7351T, available from Sumitomo Bakelite Co., Ltd.) were made in a mold for TQFP packaging to create mold stains. The mold cleaning/conditioning resin composition was repeatedly molded in the stained mold to know the number of shots required to complete mold cleaning.

(2) Mold conditioning test

After the mold cleaning test, a commercially available biphenyl epoxy resin molding compound (EME-7351T, available from Sumitomo Bakelite Co., Ltd.) was continuously molded in the cleaned mold to examine mold release. The mold that had not been completely cleaned because of poor mold cleaning performance of the cleaning resin composition was not subjected to the mold conditioning test.

[0024]

Table 1

	Resin Composition	Mold Cleaning Performance	Mold Conditioning Performance
		Number of Shots to Complete Mold Cleaning (upper half mold/lower half mold)	
Example 1	A	5/4	good
Example 2	B	6/4	good

[0025]

Example 3

A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was
5 mixed with 0.5 parts by weight of phthalic anhydride, 3.0 parts by weight of zinc stearate, and 2.0 parts by weight of D-mannitol in a ball mill to prepare a mold cleaning/conditioning resin composition (designated resin composition C). Resin composition C was evaluated for mold cleaning and conditioning performance in the same manner as in Example 1. The results obtained are shown in Table 2. As
10 shown in Table 2, resin composition C exhibited excellent mold cleaning performance. When a mold having been cleaned with resin composition C but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with
15 a conventional mold conditioning resin composition.

[0026]

Example 4

A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was
20 mixed with 0.5 parts by weight of phthalic anhydride, 1.5 parts by weight of zinc stearate, and 3.0 parts by weight of D-mannitol in a ball mill to prepare a mold cleaning/conditioning resin composition (designated resin composition D). Resin composition D was evaluated for mold cleaning and conditioning performance in the same manner as in Example 1. The results obtained are shown in Table 2. As
25 shown in Table 2, resin composition D exhibited excellent mold cleaning performance. When a mold having been cleaned with resin composition D but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with
30 a conventional mold conditioning resin composition.

[0027]

Table 2

	Resin Composition	Mold Cleaning Performance	Mold Conditioning Performance
		Number of Shots to Complete Mold Cleaning (upper half mold/lower half mold)	
Example 3	C	5/4	good
Example 4	D	6/4	good

[0028]

5 Example 5

A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was mixed with 0.5 parts by weight of phthalic anhydride, 2.5 parts by weight of zinc stearate, and 3.5 parts by weight of Licowax OP (partially saponified montanic ester from Clariant Japan) in a ball mill to prepare a mold cleaning/conditioning resin composition (designated resin composition E). Resin composition E was evaluated for mold cleaning and conditioning performance in the same manner as in Example 1. The results obtained are shown in Table 3 below. As shown in Table 3, resin composition E exhibited excellent mold cleaning performance. When a mold having been cleaned with resin composition E but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with a conventional mold conditioning resin composition.

20 [0029]

Example 6

A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was mixed with 0.5 parts by weight of phthalic anhydride, 2.5 parts by weight of zinc stearate, and 1.0 part by weight of Loxiol G78 (polymeric complex ester from Cognis Japan) in a ball mill to prepare a mold cleaning/conditioning resin

composition (designated resin composition F). Resin composition F was evaluated for mold cleaning and conditioning performance in the same manner as in Example 1. The results obtained are shown in Table 3. As shown in Table 3, resin composition F exhibited excellent mold cleaning performance. When a mold having been cleaned with resin composition F but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with a conventional mold conditioning resin composition.

[0030]

Example 7

A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was mixed with 30 parts by weight of the powdered melamine resin obtained in Preparation Example 2, 30 parts by weight of powdered pulp, 0.5 parts by weight of phthalic anhydride, 2.5 parts by weight of zinc stearate, and 3.5 parts by weight of Licolub H-4 (modified hydrocarbon from Clariant Japan) in a ball mill to prepare a mold cleaning/conditioning resin composition (designated resin composition G). Resin composition G was evaluated for mold cleaning and conditioning performance in the same manner as in Example 1. The results obtained are shown in Table 3. As shown in Table 3, resin composition G exhibited excellent mold cleaning performance. When a mold having been cleaned with resin composition G but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with a conventional mold conditioning resin composition.

[0031]

Example 8

A thousand parts by weight of the pulp-loaded melamine-formaldehyde resin powder having a resin content of about 72% obtained in Preparation Example 1 was mixed with 30 parts by weight of the powdered melamine resin obtained in Preparation Example 2, 30 parts by weight of powdered pulp, 0.5 parts by weight of

phthalic anhydride, 2.5 parts by weight of zinc stearate, and 3.0 parts by weight of Loxiol VPN881 (mineral oil-based synthetic wax from Cognis Japan) in a ball mill to prepare a mold cleaning/conditioning resin composition (designated resin composition H). Resin composition H was evaluated for mold cleaning and conditioning performance in the same manner as in Example 1. The results obtained are shown in Table 3. As shown in Table 3, resin composition H exhibited excellent mold cleaning performance. When a mold having been cleaned with resin composition H but not having been conditioned with any mold conditioning resin composition was used to mold an epoxy molding compound for encapsulation, the mold showed equal or superior release as compared when the cleaning was followed by conditioning with a conventional mold conditioning resin composition.

[0032]

Table 3

	Resin Composition	Mold Cleaning Performance	Mold Conditioning Performance
		Number of Shots to Complete Mold Cleaning (upper half mold/lower half mold)	
Example 5	E	5/5	good
Example 6	F	5/5	good
Example 7	G	4/4	good
Example 8	H	6/6	good

Industrial Applicability

[0033]

The mold cleaning/conditioning resin composition of the present invention makes it feasible to clean the cavity and air vent of a molding die to remove the heavy stains that have become more problematical with the increasing functions of epoxy molding compounds and semiconductor devices. The resin composition of the invention also allows for imparting release properties to a molding die without a mold conditioning operation that has been required after a mold cleaning operation.

This reduces the burden and time of the very troublesome operations of mold cleaning and conditioning. Additionally, use of the compression type mold cleaning/conditioning resin composition eliminates the use of a lead frame or a dummy frame that is needed in cleaning a mold by transfer molding, which reduced the cost of mold cleaning and conditioning.

CLAIMS

1. A mold cleaning/conditioning resin composition to be used in the molding of a curing resin molding compound to remove stains from the mold surface and to impart release properties to the mold surface, the composition comprising a melamine resin and at least one metal soap-based release agent, and further comprising mannitol.
2. The mold cleaning/conditioning resin composition according to claim 1, wherein the metal soap-based release agent is present in an amount of 0.2 to 1.0 part by weight per 100 parts by weight of the melamine resin.
3. The mold cleaning/conditioning resin composition according to claim 1 or 2, wherein the mannitol is D-mannitol.
4. The mold cleaning/conditioning resin composition according to claims 1 to 3, wherein the metal soap-based release agent and the mannitol are present at a weight ratio of 90:10 to 30:70.
5. The mold cleaning/conditioning resin composition according to any one of claims 1 to 4, further comprising a release agent other than a metal soap.
6. The mold cleaning/conditioning resin composition according to claim 5, wherein the release agent other than a metal soap is an ester type release agent or a synthetic wax.
7. The mold cleaning/conditioning resin composition according to claim 6, wherein the ester type release agent is a partially saponified montanic ester or a polymeric complex ester.

8. The mold cleaning/conditioning resin composition according to claim 6, wherein the synthetic wax is a modified hydrocarbon wax or a mineral oil-based synthetic wax.
- 5 9. The mold cleaning/conditioning resin composition according to any one of claims 5 to 8, wherein the metal soap-based release agent and the release agent other than a metal soap are present in a weight ratio of 90:10 to 30:70.
- 10 10. The mold cleaning/conditioning resin composition according to any one of claims 1 to 9, further comprising at least one of pulp and a curing catalyst.
- 10 11. The mold cleaning/conditioning resin composition according to any one of claims 1 to 10, which is of compression type.
12. A mold cleaning/conditioning method comprising using the mold cleaning/conditioning resin composition according to any one of claims 1 to 11.