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(54) **Slurry compositions for cast molding purposes, a method of molding cast moldings wherein these slurry compositions are used, and sinters wherein these moldings have been fired.**

(57) Redispersible resin powder in an amount of 0.5 - 20 parts by weight, and water, are added to, and mixed with, 100 parts by weight of the base material for cast molding purposes, such as base material for porcelain purposes and base material for ceramic purposes, and so it is possible to prepare slurry compositions in which the redispersible resin powder is dispersed uniformly in a very stable manner, and since the slurry composition is cast molded, cast moldings which have especially good mechanical strength, thickening rates and mold release properties, for example, are molded.

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Industrial Field of Application

This invention concerns slurry compositions for especially cast molding purposes, a method of molding cast moldings wherein these slurry compositions are used, and sinters wherein these molding have been fired.

Prior Art

Conventionally, with cast molding in the molding of porcelain and ceramics, the cast moldings have been formed by adding suitable amounts of water and deflocculating agents, for example, to the prescribed base materials and preparing a slurry, pouring this into a casting mold, such as a plaster mold which takes up water, thickening the slurry along the inner surface of the mold by the uptake of water by the mold, and removing the cast molding from the mold after thickening. The final molding has then been obtained from the cast molding by processes such as drying, pre-baking, glazing, firing and cutting etc., but when such a method is used the cast molding itself must have a mechanical strength such that it can be handled in the finishing process and in transportation, for example, and it must also be easily removed from the mold.

For this reason, when manufacturing porcelain in the past, the mechanical strength needed for processing has been imparted by including kawazume clay or kibushi clay, for example, in the base material. However, the mechanical strength of the moldings has been inadequate in large and thin moldings with the conventional base for porcelain purposes, and manufacture has been very difficult.

Furthermore, it has not been possible to mold cast moldings of adequate mechanical strength with just the base for ceramic purposes in practice when manufacturing ceramics.

A method wherein aqueous resin emulsions are added to the porcelain base material or ceramic base material and a ceramic slurry is prepared and cast molded has been proposed as means of resolving these past difficulties (see Japanese Patent H3-64465), and methods wherein water-soluble binders or aqueous resin emulsions are added to the ceramic base material and a ceramic slurry is prepared and cast molded have been proposed (see Japanese Patent H4-32155 and Japanese Patent Kokai H5-104509).

Problems to be Resolved by the Invention

The methods of resolution mentioned above enable the strength of the cast moldings to be increased by the addition of an aqueous resin emulsion or a water-soluble binder, but they have the following disadvantages.

(1) Firstly, the aqueous resin emulsions and water-soluble binders have water, for example, pre-added in view of their nature, and they are added to slurried base material for porcelain purposes or base material for ceramic purposes to prepare the slurry, and so foam is formed during stirring and mixing, and then the mechanical strength of the slurry composition for cast molding is liable to be reduced.

(2) Secondly, the density difference between the base material for porcelain purpose or the base material for ceramic purposes and the aqueous resin emulsion, for example, is considerable and so separation is liable to occur, a uniformly dispersed slurry is not formed and so cracks are liable to form in the cast molding.

(3) Thirdly, the aqueous resin emulsion or water-soluble binder permeates into the casting mold itself when the slurry is being dewatered at the time of cast molding, and separation from the mold becomes difficult.

(4) Fourthly, the resin fraction of the aqueous resin emulsion coagulates in the surface layer part of the cast molding and it is liable to become tacky, and the surface finishing properties with cast moldings such as wide flat plates become poor and, moreover, when such cast moldings are being subjected to enforced drying, the drying of the inner part is delayed by the formation of a film due to surface drying, and warping and cracking, for example, are liable to occur.

As a result of thorough research carried out with a view to resolving the abovementioned past problems, the inventors have discovered that cast moldings which have excellent mechanical strength, thickening rate and mold release properties, for example, can be obtained by adding redispersible resin powder to base material and water, and preparing a slurry composition in which this is uniformly dispersed in a stable manner by mixing, and the invention is based upon this discovery.

Means of Resolving These Problems

The first invention of this application is a slurry composition especially for cast molding purposes, characterized in that 0.5 - 20 parts by weight of redispersible resin powder, and water, are added to, and mixed with, 100 parts by weight of the prescribed base material for cast molding purposes, such as porcelain base material or ceramic base material.

The second invention of this application is a method of molding cast moldings, characterized in that the abovementioned slurry composition is cast molded.

The third invention of this application is a sinter, characterized in that a molding which has been cast molded according to the abovementioned method is fired.

The known porcelain raw materials, such as feldspar, silica, pottery stone, kaolin and clay for example, can be used for the porcelain base material in this present invention, and the known ceramic raw materials, such as alumina, zirconia, silica, ferrite, silicon carbide, silicon nitride or saialon for example, can be used for the ceramic base material. These porcelain base materials and ceramic base materials can each be used individually, or they can be used in a suitable formulation, as required. Below, the prescribed base materials for cast molding purposes, such as porcelain base materials and ceramic base materials for example, are referred to simply as the base material.

Furthermore, a so-called redispersible resin powder which has been obtained by spray drying for example a poly(vinyl acetate), vinyl acetate copolymer or acrylic resin-based emulsion is used for the redispersible resin powder. The glass transition temperature of this redispersible resin powder is preferably -5°C or above, from the viewpoint of ideal film formation on molding, and in those cases where it is below -5°C it is liable to undergo cohesion and attachment and, conversely, if the glass transition temperature is too high then the film formation on molding is liable to become inadequate, and so a glass transition temperature of $0 - 20^{\circ}\text{C}$ is preferred. Moreover, in those cases where a redispersible resin which has a high glass transition temperature is used, the drying temperature may be raised or the time may be increased, or a plasticizer or a film forming promoter may be added. Furthermore, the amount of redispersible resin powder which is added to the base material differs according to the type of base material, the type of redispersible resin powder and the characteristics of the sinter which is to be manufactured, for example, but it is generally 0.5 - 20 parts by weight. In those cases where the amount of redispersible resin powder which is added is less than 0.5 parts by weight with respect to the base material, the mechanical strength of the moldings becomes inadequate, and in those cases where it exceeds 20 parts by weight the mechanical strength is good, but the shrinkage on firing is considerable, and not only is the fall in the strength of the sinter considerable and removal from the mold when carrying out the cast molding treatment difficult, but the characteristics of the base material are liable to be diminished.

These redispersible resin powders are available commercially with trade names such as, for example, Sumikafurekksu (registered trademark) RP-100S and RP-110 (manufactured by Sumitomo Kagaku Kogyo K.K., Akuronarru (registered trademark) DS-6029 and DS-6031 manufactured by the Mitsubishi Yuka Baadeisshe K.K., and Movinyl (registered trademark) DM200, DM289, 843, SA and E45 manufactured by Hoechst Kasei K.K.

Furthermore, in addition, water is preferably added as a dispersing agent in such a way that the slurry solid fraction content is 65 - 80 percent by weight. Moreover, apart from water, inorganic deflocculating agents such as caustic soda, sodium silicate and water glass, organic deflocculating agents such as diethylamine, di-n-propylamine and pyridine, protective colloids such as humic acid, tannic acid and lignin, and pulverization promoters such as stearic acid, oleic acid and naphthenic acid, can be added, as required.

The slurry is prepared by adding the prescribed amount of redispersible resin powder to the base material and adding the water and deflocculating agent, as required, and pulverizing with a known type of pulverizing machine, such as a ball mill or a tube mill for example, to $0.1 - 10\text{ }\mu\text{m}$. At this time, the redispersible resin powder is a powder and so when compared with a conventional aqueous resin emulsion, foaming does not occur, and the separation which accompanies any difference in density from the base material, and re-coagulation, do not occur, and it is uniformly dispersed in a very stable manner, and a slurry of the correct viscosity is prepared ideally. Furthermore, the redispersible resin powder is uniformly dispersed in a stable manner and so the prepared slurry can be stored as a slurry. Moreover, the base material and water may be formed into a slurry and the redispersible resin powder may be added to, and mixed with, this slurry, but since it is difficult to disperse, much time is required for dispersion, and warping and cracking are liable to occur at the time of casting, and so the base material and the redispersible resin powder are preferably formed into a slurry at the same time.

The slurry obtained is poured into a casting mold, such as a plaster mold for example, using the known method, and a casting mold is molded and, after thickening along the inner surface of the mold by the mold taking up water, it is removed from the mold. At this time, as has been described above, a slurry of this present invention is such that, because the redispersible resin powder is uniformly dispersed in a very stable manner, the mechanical strength of the cast molding is of course considerable, and the thickening rate is also appropriate, and the molding can be removed from the mold very smoothly and easily. An especially marked effect is seen in the mold release of thin moldings. Furthermore thin, light and large cast moldings can be molded easily and not just the cast moldings of the conventional forms.

The casting mold which has been removed from the mold is subjected to an appropriate drying treatment and then fired using the known methods, and a sinter is formed. At this time, the slurry which forms the cast molding has a form in which the redispersible resin powder is uniformly dispersed in a stable manner and so there is no risk at all of warping or cracking occurring during the drying treatment or during the firing treatment.

Illustrative Examples

Examples of the invention are described below, but the invention is not limited by these examples.

Examples 1 - 6 and Comparative Examples 1 - 4

Redispersible resin powder, or aqueous resin emulsion (represented as a solid fraction) was added to a base material on the basis of the formulation proportions shown in Table 1, sodium silicate was added along with the water, and the whole was mixed in a ball mill to prepare a slurry.

The slurries which had been prepared were poured into plaster molds of two types of length 500 mm and width 500 mm, and of depth 2 mm or 5 mm, and cast moldings were obtained on standing for 1 hour, after which the moldings were removed from the mold and dried for 24 hours at normal temperature and then for 24 hours at 110 °C. An evaluation of warping and cracking during this process was made on the basis of the standards indicated below. The results are shown in Table 2.

Mold Release Properties

- O: Released easily from the mold.
- A: Some sticking to the plaster mold but could be released.
- x: Stuck to the plaster, mold cracks etc. formed and it was difficult to remove from the mold.

Warping and Cracking

- O: No warping or cracking at all, or virtually none at all.
- x: Warping and cracking occurred.

Furthermore, cast moldings were obtained in the same way by pouring the abovementioned slurries into plaster molds of length 110 mm, width 15 mm and depth 6 mm, leaving to stand for 1 hour and removing the moldings from the molds, and then drying for 24 hours at 20 °C and then for 24 hours at 110 °C. Next, the cast moldings were heated gradually to 1230 °C over a period of 5 hours and then fired for 1 hour at 1230 °C. After this, they were left to stand and cooled for 4 hours and sinters were obtained. The flex strengths after drying at 20 °C before firing, after drying at 110 °C and after firing, and the shrinkage factors during firing and the water uptakes were measured using the methods indicated below. The results are shown in Table 2.

Flex Strength: The flex strength was measured in accordance with JIS R1601-81.

Shrinkage Factor (Wt = weight)

$$\text{Shrinkage Factor (\%)} = \frac{110 \text{ mm} - \text{Lenth after firing (mm)}}{110 \text{ mm}} \times 100$$

Water Uptake

$$\text{Water Uptake (\%)} = \frac{\text{Wt after 3 hrs in water at } 80^{\circ}\text{C} - \text{Wt after drying}}{\text{Wt after Drying}} \times 100$$

Moreover, the weight after 3 hours in water at 80°C was measured by removing the sample from the water and wiping of the surface water. Furthermore, the weight after drying was the weight after standing for 24 hours at 20°C - 65% after drying.

Effect of the Invention

According to this present invention, as indicated above, 0.5 - 20 parts by weight of redispersible resin powder, and water, are added to, and mixed with, 100 parts by weight of the prescribed base material for cast molding purposes, such as base material forporcelain purposes and base material for ceramic purposes, and so a slurry composition in which the redispersible resin powder is dispersed uniformly in a very stable manner can be prepared. Furthermore, the slurry composition in which the redispersible resin powder has been dispersed uniformly in a stable manner is cast molded and so it is possible to mold cast moldings which have exceedingly good mechanical strength, thickening rates and mold release properties for example. Furthermore, since it is possible to mold cast moldings of which the mechanical- strength is greatly improved, as mentioned above, it is possible to manufacture sinters which are thin, light or large when compared to the products of the conventional form.

Table 1

5			1	1	1	1	1	1	2	2	2	2
	3	4*1	50	50	50	50	50	-	50	50	50	-
		5*2	50	50	50	50	50	100	50	50	50	100
	6	7	A*3	A	A	A	B*4	A	-	C*5	A	D*6
10		8	0,5	1,0	5,0	20,0	5,0	5,0	-	5,0	25,0	2,0
	9		37	37	39	45	39	32	37	37	47	32
	10		0,2	0,2	0,2	0,2	0,2	-	0,2	0,2	0,2	-
	11*7		-	-	-	-	-	1,0	-	-	-	1,0
15	12*8		-	-	-	-	-	-	-	-	-	0,1

KEY 1: Example, 2: Comparative Example, 3: Base Material, 4: Base Material for Porcelain Purposes*1 (parts by weight), 5: Base Material for Ceramic Purposes*2 (parts by weight), 6: Resin Added 7: Type, 8: Amount Added (parts by weight), 9: Water, 10: Sodium Silicate (parts by weight), 11: Dispersing Agent*7 (parts by weight), 12: Anti-foaming agent*8 (parts by weight)

*1: "High Grade Porcelain Base" (containing about 20% plastic minerals) manufactured by K.K. Miyao Company Limited.

*2: "Almina AMS-9" manufactured by Sumitomo Kagaku Kogyo K.K.

*3: Acrylic resin based redispersible resin powder "Akuronaaru DS-6031" (glass transition point 10°C) manufactured by Mitsubishi Yuka Baadeisshe K.K.

*4: Poly(vinyl acetate) based redispersible resin powder "Sumikafurekkusu RP-100S" (glass transition point 0°C) manufactured by Sumitomo Kagaku Kogyo K.K.

*5: Acrylic resin based aqueous resin emulsion "Akuronarru YJ-3042D" (glass transition point 2°C) manufactured by Mitsubishi Yuka Baadeisshe K.K.

*6: Paraffin based aqueous resin emulsion "Makuseron A" (glass transition point 5°C) manufactured by Nakagyo Yushi K.K.

*7: "Serunaa D-305" manufactured by Nakagyo Yushi K.K.

*8: "Nopukoo NXZ" manufactured by Sannopuko K.K.

Table 2

	1	1	1	1	1	1	1	1	1	1	2	2	2	2
3	2 mm*	0	0	0	0	0	0	0	0	0	x	x	x	x
	5 mm*	0	0	0	0	0	0	0	0	0	0	x	x	Δ
5	2 mm*	0	0	0	0	0	0	0	0	0	0	x	0	0
	5 mm*	0	0	0	0	0	0	0	0	0	0	x	0	0
6	7	30,1	40,2	77,3	95,6	64,5	30,5	23,9	33,5	109,9	20,8			
	8	34,2	45,7	91,1	121,5	72,5	-	25,7	12	-	-			
	9	919	973	919	853	903	107	898	13	710	125			
10		6,9	7,1	7,7	8,8	8,4	-	7,5	-	10,2	-			
11		6,3	6,2	6,2	7,3	6,6	-	5,7	-	8,3	-			

KEY 1: Example, 2: Comparative Example, 3: Mold Release Properties, 4: Thickness, 5: Warping and Cracking, 6: Mechanical Strength (kgf/cm²), 7: After drying at 20 °C, 8: After drying at 110 °C, 9: After firing, 10: Shrinkage Factor (%), 11: water Uptake (%), 12: Cracks formed, confirmation impossible., 13: As above.

Claims

- 5 **1.** Slurry composition characterized in that 0.5 - 20 parts by weight of redispersible resin powder, and water, are added to, and mixed with, 100 parts by weight of base material especially for cast molding purposes, such as porcelain base material or ceramic base material.
- 10 **2.** Method of molding cast moldings, characterized in that a slurry composition disclosed in Claim 1 is cast molded.
- 15 **3.** Sinter, characterized in that a molding which has been cast molded according to the method disclosed in Claim 2 is fired.

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