United States Patent Office 2,902,380
Patented Sept. 1, 1959

2,902,380

SLIP CASTING METHOD

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No Drawing. Application July 13, 1956
Serial No. 597,829

6 Claims. (Cl. 106—121)

The present invention is related to a method of preparing a magnesium oxide slurry for making slip cast ceramics and in particular a method for preparing a magnesium oxide slurry where very large or very thin wall, slip-cast pieces are required.

Prior to the present invention the preparation of slip-cast pieces of magnesium oxide has been difficult for small size castings and virtually impossible for large castings or for small castings of thin wall and/or intricate shapes. The use of water as the suspending medium for the magnesium oxide used for slip casting has not been satisfactory, as the cast pieces thus produced nearly always crack either in the mold, upon removal from the mold, or upon firing. The difficulties encountered with water suspension have been noted in the technical literature, for example, see National Bureau of Standards, Journal of Research, "The Preparation of Crucibles from Special Refractories by Slip-Casting," Thompson and Mallett, vol. 23, August 1939, page 325. The usual method for preparing the casting slurry has been to use water-free ethyl alcohol or some other organic solvent as the suspending medium of the slip.

The use of a solvent such as ethyl alcohol has a number of disadvantages. The high rate of evaporation of the alcohol makes the process quite inconvenient. The resulting "green" slip casting is very weak and must be handled with extreme care, a very undesirable feature for a production product. Further, the success of slip casting with an organic medium depends almost entirely on the skill of the person doing the casting. It is rather common for the piece to stick to the mold and skill beyond that the ordinary workman is required to produce a sound, intact casting. Because of the great weakness of such a casting, it has been virtually impossible to produce large magnesium oxide slip-cast pieces or pieces of intricate shape when using an organic solvent as a medium. Another very serious disadvantage to the use of a slurry containing organic solvent is that only fine grain, i.e., small particle sizes (magnesium oxide), may be used. This results in high shrinkage of the fired product and difficulty in holding the fired piece to a close tolerance in physical size. A further disadvantage to the use of alcohol is that it causes rapid deterioration of the mold.

In the ceramic art a common method of preparing a metal oxide slurry, other than magnesium, for slip casting is to mix the finely divided oxide with water, add acid to make the slurry acidic and then cast the slurry. This method is successful with most metal oxides but, although others have occasionally claimed practicability with magnesium oxide, it has not been successful for that particular oxide, as many skilled in the art have found and reported in the literature, as hereinbefore noted. Thus until the present invention there has been no successful means of slip casting magnesium oxide.

Preparing a magnesium oxide suspended in water by the method of the present invention yields a very strong "green" slip casting and results in a fired piece of very close dimensional tolerance. The slurry is prepared by aging the mixture of magnesium oxide and water for 24 hours, then adding a small amount of deflocculating agent. The "green" casting prepared with this slurry has so much strength that it appears that the magnesium oxide has formed a ceramic cement as a result of the chemical change in aging.

It is therefore an object of this invention to provide a method for preparing a slip casting slurry that sets to an unusually high strength when cast in a mold.

Another object of this invention is to provide a method for preparing a magnesium oxide slip slurry suspended in water and having the property of producing a high strength slip casting.

Further objects of this invention will be apparent from the following specification and appended claims.

By the method of the present invention the magnesium oxide slurry is prepared in the preferred embodiment in the following steps:

A quantity of minus 200 mesh fused magnesium oxide with 30 percent water is placed in a 1 gallon porcelain pebble mill containing a charge of 4200 grams of porcelain balls ½ to 1 inch in diameter. The pebble mill is run at a speed of 50 revolutions per minute for a period of 15 hours. This provides a quantity of magnesium oxide of mesh size minus 325. Then 3 percent additional distilled water is added to the magnesium oxide and the pebble mill is again run for about 5 minutes to thoroughly mix the slurry.

The slurry is now allowed to stand for 24 hours at an ambient temperature of about 16° C. This is the very important step in the preparation of this slurry, as during the standing the magnesium oxide combines with H_2O to form what is probably a mixture of

$$Mg(OH)_2 \cdot H_2O$$

This has a basic pH of about 11.3. After the slurry is aged for 24 hours, it is mixed with a variable speed mixer and a small amount of hydrochloric acid is added while mixing. The hydrochloric acid is prepared by mixing equal volumes of concentrated hydrochloric acid and water. The hydrochloric acid is not sufficient in quantity to make an appreciable change in the pH of the solution, thus it remains basic. Now a suitable amount of coarse grain magnesium oxide can be added and thoroughly mixed until there are no air bubbles in the slurry. The slurry is then poured in a plaster of Paris mold and cast by the usual techniques well known in the art; and as described in the N.B.S. publication referenced above. Upon removal, the cast piece can be trimmed or otherwise handled without breaking, as it has unusually high strength. It is air dried at room temperature and then fired in a suitable furnace.

In the aging process, it appears that the factor which determines that the slurry is "ready" is not the pH, but the viscosity. Experiments have shown that at 6 hours aging, the viscosity is about 65–75 centipoises, at 24 hours from 270–280 centipoises, and at 48 hours from

6000 to 9000 centipoises. It is apparent that the viscosity change is very large with a variation in time. In this case, the viscosity was measured by a model RVT-Brookfield viscometer with a No. 1 spindle run at both 10 and 20 r.p.m., with the slurry at room temperature, i. e., 21° C. The important step of this invention, therefore, is that the slurry must be aged to have a viscosity of about 275 centipoises, which can be achieved by aging for a known time.

Table A below shows the preferred composition for the magnesium oxide slip of this invention. Table B shows the permissible limits of the components of the various slip compositions usable by this invention. All weights of magnesium oxide are dry weights.

Table A

Minus 325 Mesh MgO	Minus 100 Mesh, Plus 200 Mesh MgO	Water	HCl:H_2O=1:1 By Volume
Gms. 60	*Gms.* 40	*Gms.* 20	0.0575 cc. per 100 grams of MgO.

Table B

Minus 325 Mesh MgO	Minus 100 Mesh, Plus 200 Mesh MgO	Water	HCl:H_2O=1:1 By Volume
Gms. 100–50	*Gms.* 0–75	*Gms.* 30–12	0.02 to 0.1 cc. per 100 grams of MgO.

The exact phenomenon which occurs as a result of the aging and which makes the magnesium oxide slip casting so very strong is not thoroughly understood. However, apparently the HCl acts as a deflocculent even though it is not added to the slurry in sufficient quantity to cause the slurry to be acidic. It is believed that after the magnesium hydroxide forms a portion of it is transformed to a form of a magnesium oxychloride cement. This cement probably sets when the water leaves the slurry in the mold, thus improving the "green" strength of the cast piece.

By the present invention magnesium oxide crucibles have been made of a size heretofore impossible. Thin walled intricate shapes are no problem and the results are highly reproducible and consistent. 5 liter crucibles having ⅛" thick walls are readily made. In one production run 1500 pieces were produced with less than 2 percent loss through breakage. Since coarse grain magnesium oxide may be added, the shrinkage is lower than that resulting from an organic solvent slurry. The shrinkage does not exceed 5 percent compared with the order of 20 percent by methods of the prior art. The life of the molds is essentially indefinite since the aqueous slurry of this invention does not attack the molds. Further, the quantity of molds required for a given production is not as great as in some slip casting processes, as the air drying time in the mold is only about 15 minutes and for high production rates the molds can be oven dried and in an even shorter time. The magnesium oxide aggregate particle size may vary within the ranges specified though larger particles help keep the firing shrinkage low.

The aging indicated required by the present invention in the preferred embodiment appears to depend upon certain variables and although an optimum time is indicated, the time will vary with temperature so that at lower temperatures a longer time will be required and conversely at elevated temperatures a shorter time will be required. The ball mill time is considered a part of the aging time and if the magnesium oxide is not ground in a ball mill for 15 hours a greater aging time will be required. Further embodiments of the present invention are understood to be possible and it is therefore understood that the invention is not to be limited by the specific examples but only by the appended claims.

What is claimed is:

1. The process of making an aqueous magnesium oxide slip casting slurry, which comprises adding magnesium oxide grains to water in the proportion of about 12 to about 30 grams of water per 100 grams of magnesium oxide, the size of said magnesium oxide grains being about minus 325 mesh, mixing said magnesium oxide with said water, said mixture having a pH value of about 11.3, aging said magnesium oxide in said water until said mixture has a viscosity of about 275 centipoises, and adding from about 0.02 to about 0.1 cc. of 5 N hydrochloric acid per 100 grams of magnesium oxide whereby said aged slurry may be used to prepare a high strength slip casting.

2. A process for making an aqueous magnesium oxide casting slurry which comprises aging a mixture of magnesium oxide grains and water in the proportion of about 20 grams of water per 100 grams of magnesium oxide at about 16° C. temperature until said mixture has a viscosity of about 275 centipoises, the size of said magnesium oxide grains being about minus 325 mesh, said mixture having a pH value of about 11.3, and adding from about 0.02 to about 0.1 cc. of 5 N hydrochloric acid per 100 grams of magnesium oxide.

3. A process of making a magnesium oxide slip casting slurry which comprises milling at least a portion of said magnesium oxide in water for a period of about 15 hours to a size of about minus 325 mesh, the magnesium oxide and water mixture having a pH value of about 11.3, allowing said magnesium oxide and water mixture to stand for about 24 hours at about 16° C., adding about 0.1 cc. 5 N hydrochloric acid per 100 grams of dry magnesium oxide, said water to be in the proportion of about 20 grams of water per 100 grams of magnesium oxide.

4. A process of making a magnesium oxide slip casting slurry which comprises milling at least a portion of said magnesium oxide in water for a period of about 15 hours to a size of about minus 325 mesh, the magnesium oxide and water mixture having a pH value of about 11.3, allowing said magnesium oxide and water mixture to stand for about 24 hours at about 16° C., and adding about 0.05 cc. of 5 N hydrochloric acid per 100 grams of dry magnesium oxide and finally adding an amount of magnesium oxide of grain coarser than 325 grain mesh up to about 150 percent of the weight of 325 mesh grain, said water to be in the proportion of about 20 grams of water per 100 grams of total magnesium oxide.

5. The process of making a magnesium oxide slip casting slurry comprising aging a mixture of minus 325 mesh magnesium oxide and water until said mixture has a viscosity of about 275 centipoises, said mixture having a pH value of about 11.3, adding hydrochloric acid, and adding magnesium oxide having a grain size coarser than 325 mesh within the proportion limits of about 40 to about 90 percent minus 325 mesh magnesium oxide, from about 10 to about 60 percent magnesium oxide having a grain size coarser than 325 mesh and from about 0.02 to about 0.1 cc. of 5 N hydrochloric acid per 100 grams of magnesium oxide, said water to be in the proportion of from about 12 grams to about 30 grams of water per 100 grams of total magnesium oxide.

6. The process of making a magnesium oxide slip casting slurry which comprises milling for about 15 hours at least a portion of said magnesium oxide in water in the proportion of 20 grams of water per 60 grams of magnesium oxide, said milling to produce a magnesium oxide particle size of about 325 mesh, said magnesium and water mixture having a pH value of about 11.3, allowing said magnesium and water mixture to stand

until said mixture has a viscosity of about 275 centipoises, deflocculating said mixture by adding from about 0.02 to 0.1 cc. of 5 N hydrochloric acid per 100 grams of magnesium oxide, and finally adding an amount of magnesium oxide of minus 100 mesh to plus 100 mesh up to about 150 percent of the weight of said minus 325 mesh magnesium oxide.

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