Patented Nov. 24, 1942 2,303,304

UNITED STATES PATENT OFFICE

2,303,304

METHOD OF MAKING ZIRCON REFRACTORIES

Henry M. Schleicher, Elizabeth, and Steve Kopin, Carteret, N. J., assignors of one-half to Scovill Manufacturing Company, Waterbury, Conn., a corporation of Connecticut and one-half to United States Metal Refining Company, Carteret, N. J., a corporation of New Jersey

No Drawing. Application April 14, 1941, Serial No. 388,439

10 Claims. (Cl. 25—156)

This invention relates to zircon refractories and more especially to zircon shapes and method of making same. The invention is especially useful as applied to slip cast zircon shapes.

The production of zircon refractories in which the zircon particles have been bonded by the use of phosphoric acid is known in the prior art. It has also been proposed to produce such zircon refractories by slip casting to the desired shape.

We have found that in slip casting zircon shapes the phosphoric acid content of the slip is appreciably reduced by the slip action and the bonding action is therefore materially lessened. We have discovered that after zircon shapes have been slip cast and bonded with the thus reduced phosphoric acid content, the bonding action may be enhanced and the hardness of the shapes increased to the desired degree by subsequent treatment of the shapes after the original firing. We have further discovered that phosphoric acid may even be eliminated from the slip entirely and a primary or partial bond be otherwise effected, and after the initial firing of the shape a secondary bonding and hardening may be effected by suitable treatment; with many beneficial advantages.

An object of the invention is to provide a method of hardening a previously fired and initially bonded zircon body.

Another object of the invention is to provide an improved method of bonding a slip cast zircon body.

Another object of the invention is to provide an improved bonded zircon body and method of producing the same.

The invention consists in the novel methods and steps thereof hereinafter described and the resulting product. With the above and other objects and advantages in contemplation, the invention is hereinafter described and more particularly defined in the accompanying claims.

In the presently preferred form of the invention we have produced relatively small zircon shapes, by slip casting, in the following manner:

Milled zircon and china clay, in the relative proportions by weight of 96% zircon and 4% clay, are thoroughly mixed in relatively dry condition; and water is added to produce a slip with a preferred density of about 1.66, this density apparently giving the maximum density of the resultant shapes. The shapes are then slip-cast in the customary manner; the molds or forms being suitably made of 30–40 parts of pottery plaster and 70–60 parts of water, by weight, it being noted that the plaster-water ratio is rather critical, and is considerably different from that generally used in clay pottery work, where the range is about 60–57 parts plaster to 40–43 parts water. Also forms may be advantageously employed when made according to the invention described and claimed in Henry M. Schleicher copending application Serial No. 388,437, filed on even date herewith. After the shapes have been slip-cast they are carefully dried at 180–200° F., and are baked at 400–600° F., and are fired at 2300° F., heating slowly when cast in pottery plaster molds in the customary manner, the shapes are removed as soon as they have compacted enough to stand handling, and before they have been heated over 200° F.; since a greater temperature is detrimental to the usual pottery plaster mold if it is to be re-used. After the shapes have been fired they are then trimmed or cut as necessary or desired to produce the desired finished shape. They are then treated, such as by soaking in 85% orthophosphoric acid for a period of the order of 30 minutes, drained, dried and again fired at 2300° F. or higher. The treatment with phosphoric acid is preferably carried to the extent of impregnating the shape with about 0.23 pound of 85% orthophosphoric acid per pound of shapes, where the wall thickness is about ¼". The above formula, utilizing milled zircon, produces superior smoothness and maximum whiteness; and has been used with great success in producing refractory bushings utilized in the casting of commercial copper. The relative proportions of zircon and clay have been successfully used over the range 94 to 96% zircon and 6 to 4% china clay.

For a more general use, as where relatively larger shapes are desired, or where smoothness is not a factor, grain zircon could be included and the formula would then become: 0–47% grain zircon; 96–47% milled zircon and 4–6% china clay.

The following formula has also been used successfully: 94% milled zircon; 4% china clay and 2% aluminum hydroxide.

While a mixture of zircon and china clay will not withstand as high a temperature as zircon bonded with phosphoric acid, we have found that 4% china clay gives a sufficient primary or initial bonding action and shapes made of the zircon-clay mixture when tested at temperatures up to 2500° F. did not apparently deform. However after baking or after baking and firing the zircon-clay shapes are soft enough to permit cutting or trimming while still presenting sufficient strength and hardness to withstand han-

dling. The final acid treatment and re-firing greatly increases the bond of the zircon particles and enhances the strength and hardness; rendering the articles at least as hard and strong as articles consisting of zircon bonded with phosphoric acid.

As compared with previously known bonded zircon shapes, such as those consisting of zircon particles bonded with phosphoric acid, the foregoing preferred form of the invention presents the following advantages in connection with slip-castings:

1. Slip-casting proceeds faster; due to the fact that the absorption rate will be greater for water alone than for the more viscous solution of phosphoric acid.

2. Many more (5 times or more) castings can be made in a mold—where it is a simple mold from which the shape may be stripped in the usual manner without destroying the mold or form. This is because the acid seems to deteriorate the plaster mold in some way so that the absorption rate diminishes rapidly; and a mold can be used only for 3 or 4 castings (with the zircon-acid mix), as compared to 20 or more castings for the zircon-clay-water mix.

3. After the first firing the shapes are soft enough to permit cutting or trimming without difficulty. The castings produced by this method are strong and firm enough to stand handling in stripping and subsequent heating. It is not necessary to trim the casting during the drying or baking stage because the shape is made stronger after the first firing but still lends itself well to any cutting operation.

4. The articles are considerably whiter; which is an advantage where a strongly reflecting surface is desired.

5. The articles have a better surface texture.

6. The method is better adapted to large scale production.

While the previously described embodiment of the invention is the presently preferred form, i. e. where phosphoric acid is eliminated from the mix and clay is utilized in the mix; certain aspects of the invention may be beneficially employed in conjunction with the utilization of a mix free from clay and in which phosphoric acid is used as the bonding agent. As previously indicated, such mixtures have been used in bonded zircon articles; wherein the phosphoric acid has been employed to effect the bond between the zircon particles. Likewise phosphoric acid has been similarly used with zircon and the addition of zirconia and/or other ingredients. For example, it has been proposed to utilize phosphoric acid and zircon in a mixture in which the phosphoric acid calculated as phosphorus pentoxide (P_2O_5) equals approximately 6% by weight of the mixture. With this proportion of phosphoric acid, or even with a substantially greater proportion, we have found that the slip-casting action robs the mixture of acid to an extent where the finished fired product is not sufficiently strong and hard for many purposes. However, by applying the subsequent treatment after firing, similar to the treatment hereinabove described, the slip-cast shape may be made to attain the desired hardness and strength. The following is given by way of example for carrying out this modified process.

0 to 47 parts by weight grain zircon; 94 to 47 parts by weight of milled zircon and 6 parts by weight of P_2O_5 (as 85% orthophosphoric acid) are mixed together and water is added to the consistency of heavy cream and the mixture is digested by heat or aging; and is then brought to the desired consistency by adding water or by evaporation of excess water, as necessary, to produce a suitable mixture for slip casting. The mixture is then slip-cast in the usual manner, or as described and claimed in the said copending application. The dried, baked and fired shapes are thereafter treated with phosphoric acid, as previously described, to the extent of approximately .23 lb. per lb. of shape for shapes having a wall thickness of about ¼". After the shapes have been preliminarily fired they may be trimmed or brought to the desired finished shape, far more easily than after the subsequent treatment and refiring to produce the ultimate bonding and final hardness and strength.

Having thus described our invention with particularity with reference to the preferred method of carrying out the same and the product resulting therefrom, and having referred to certain modifications thereof, it will be obvious to those skilled in the art, after understanding the invention, that other changes and modifications may be made therein without departing from the spirit and scope of the invention, and it is aimed that the appended claims should cover such changes as come within the scope of the invention.

What we claim is:

1. Method of making a ceramic body which comprises preparing a slip containing zircon and china clay in the relative proportions by weight of 94 to 96% zircon and 6 to 4% china clay and water, slip-casting said body, drying, baking and firing said body, impregnating said fired body with phosphoric acid and thereafter again firing said body.

2. Method of making a ceramic body which comprises preparing a slip containing zircon and china clay in the relative proportions by weight of the general order of 96% zircon and 4% china clay and water, slip-casting said body, removing the casting from its form, heating said body slowly to about 600° F., firing at about 2300° F., impregnating the said shape with 85% orthophosphoric acid and again heating to a temperature of the order of 2300° F.

3. Method of making a ceramic body which comprises preparing a slip containing zircon and china clay in the relative proportions by weight of 94 to 96% zircon and 6 to 4% china clay and water to produce a density of the order of 1.66, slip-casting said body to the approximate shape desired, removing the casting from its form, drying at 180–200° F., baking at 400–600° F., firing slowly to a relatively higher temperature, finishing said body to the desired shape, soaking the said shape in 85% orthophosphoric acid and again firing at approximately 2300° F.

4. Method of making a slip cast bonded zircon shape which comprises mixing 94 to 96 parts by weight of zircon with 6 to 4 parts by weight of china clay, adding water sufficient to produce a slip of the desired density, slip-casting said shape, removing said shape from said form, drying said shape at 180–200° F., baking the same at about 400–600° F., firing said shape to a temperature of the order of 2300° F., thereafter soaking said shape in 85% orthophosphoric acid until said acid has been absorbed by said shape in the relative proportion of approximately 0.23 pound of acid per pound of shape, and then drying said shape and firing to at least 2300° F.

5. Method of making a highly refractory ce-

ramic body which comprises initially bonding zircon with china clay in the form of a fired body, said zircon and china clay being in the relative proportions by weight of 94–96% of zircon and 6–4% of china clay, applying to said fired body phosphoric acid, and subsequently firing said body at a relatively high temperature.

6. Method of making a highly refractory ceramic body which comprises mixing together 94–96% zircon and 6–4% china clay with water and forming a body from said mix, firing said body, treating said fired body by impregnation with 85% orthophosphoric acid and subsequently firing the same at a temperature of the order of 2300° F.

7. Method of making a highly refractory ceramic body which comprises mixing together 94–96% zircon and 6–4% china clay with water and forming a body from said mix, firing said body, treating said fired body by soaking the same with 85% orthophosphoric acid for a period of time of the general order of 30 minutes, draining excess acid from said body, drying said body and subsequently firing the same at a temperature of the order of 2300° F.

8. Method of making a highly refractory ceramic body which comprises mixing together 94–96% zircon and 6–4% china clay with water and forming a body from said mix, firing said body, treating said fired body by causing the same to be impregnated with 85% orthophosphoric acid in the proportionate amount of approximately .23 pound of said acid per pound of body weight and subsequently firing the same at a relatively high temperature.

9. Method of making a highly refractory ceramic body which comprises forming a fired body consisting substantially entirely of zircon and china clay in the relative proportions of 94–96% zircon and 6–4% china clay, the zircon in said body being partially bonded by said china clay, impregnating said partially bonded body with phosphoric acid, drying said body and firing at a relatively high temperature, thereby to greatly enhance the bonding of said zircon and increase the hardness of said body.

10. In a method of producing refractory bushings such as are utilized in the casting of copper, the steps which consist in preliminarily bonding zircon with clay in the relative proportions by weight of approximately 94–96% of zircon and 6–4% of clay into a relatively soft body of approximately desired shape, said preliminary bonding including firing said body, trimming said body to the desired shape, impregnating said fired and shaped body with phosphoric acid, and subsequently firing said body at a relatively high temperature.

HENRY M. SCHLEICHER.
STEVE KOPIN.