Published May 11, 1943 Serial No. 387,359

ALIEN PROPERTY CUSTODIAN

METHOD FOR THE PRODUCTION OF CERAMIC GOODS

Emil Klingler, Korntal, Germany; vested in the Alien Property Custodian

No Drawing. Application filed April 7, 1941

Ceramic goods containing fluxing or binding materials with preponderant content of alumina are known as also goods without addition of real fluxing or binding material. It is known that the products of the first mentioned kind are preferably produced by known pressing methods. In opposition hereto the ceramic goods of the last mentioned kind are produced almost only by casting. It is further known, that the production of ceramic goods from pure alumina by casting is relatively expensive or at least more expensive than the production of pressed products containing sintering means. Notwithstanding, cast ceramic goods free from fluxing or binding materials have been adopted in the technics for the reason that the properties of the pure alumina, for instance the heat conducting capability of the same, the capability of electric insulation and so forth are found in highest perfection in such products and in many instances differ only little from the values obtainable solely by the alumina. In opposition hereto, these so-called alumina properties are toned down more or less by the addition of the fluxing material according to the kind and/or the quantity of the fluxing or binding material employed, also if in these products the alumina forms the preponderant constituent.

It has been further ascertained that stones for sparking plugs cast for instance from pure alumina supply, as regards stability against change of temperature, not only not better but even worse values than insulators which contain fluxing or binding material and consist for instance of 95% alumina and 5% magnesium metasilicate. This result, which at first seems to be surprising, could be explained in the course of further experiments almost with certainty in so far as the reduced stability against change of temperature of the stones cast from pure alumina, compared with the stability of the sparking plug stones containing fluxing or binding material, seems to be in any connection with the numerous fine fissures, so-called hair fissures, having been observed in the structure. Whether the fissures in the comparison pieces are due more or less to the extraordinarily high burning temperatures and/or to the almost completely lacking of the fluxing material and/or to the special method of production and the like could not be explained with security in the frame of the experiments carried out up to the present.

The present invention relates to a method for manufacturing by pressing ceramic goods the content of alumina of which amounts, after the ceramic burning, to more than 98% and their percentage of fluxing material is below 1%. The content remaining for the 100% is to be divided to the impurities existing in the alumina from the beginning and having probably been added in the course of manufacture.

According to the invention the unshaped bodies necessary for the production of the ceramic goods with such a high content in alumina are obtained by a dry pressing of the alumina. It is known, that pure alumina cannot be pressed in dry state. In order therefore to be able to carry out the dry pressing with pure alumina for the purpose of the production of unshaped bodies according to the invention, the pure alumina must first be transformed into a state adapted to be pressed in dry condition. This can be attained according to the invention in the following manner:

Pure alumina with a content of 99.4 to 99.7% Al_2O_3 is finely ground in dry state. Rubbered mills with grinding balls of pure corundum are preferably employed herefor. The alumina flour thus obtained is then treated with diluted acid, the employed quantity of which depends on its kind. It is for instance advisable, to employ, when hydrochloric acid is used, for 100 kgs alumina flour 7.7 liters diluted hydrochloric acid. Instead of hydrochloric acid also any other inorganic or organic acid suitable for the purpose may be used, but according to the results obtained up to the present the hydrochloric acid supplies the best values. The hydrochloric acid is especially advantageous also as regards economy.

It is known that the alumina is decomposed or activated by the added acid. In which measure this takes place depends as well on the concentration of the acid which is employed and on its electrolytic dissociation degree as on the fineness of the alumina flour. Of decisive importance for the activation of the alumina is, however, chiefly the time during which the acid acts upon the alumina. The transformation of the alumina, practically insoluble in water and diluted acids, into a more or less strong colloidal, which means not genuine solution—in the present instance by way of aluminium chloride to the aluminium oxidehydrate—is a timely reaction which gradually occurs only after the acid has acted for days onto the alumina flour.

On the activation of the alumina, already known as such, follows, according to the invention, immediately the hydrolysis of the alumina by strong dilution of the slime, for instance in the proportion 1:2. The colloidal, diluted solution is then evaporated preferably at a timely distance, according to the invention, until the condensed residue can be pulverised easily. The pulverized alumina is then well pressable in dry state without further addition of plastic substances or of substances which become plastic at the pressing. From the unshaped bodies pressed at dry state the shaped bodies ready for burning are then produced, if necessary by separate treatment, and then burnt at temperatures of about 1800° C.

There has been ascertained, however, that at the re-crystallisation of the alumina, which according to the invention is pressable in dry state during the ceramic burning—the re-crystallisation proceeding seems to be initiated also with this pure alumina same as with cast bodies, according to the ascertained facts, by little impurities for instance of iron compounds—some of the crystals grow excessively on the cost of others. As hereby the properties of the burnt body are unfavorably influenced, it is not only advisable, but even necessary, to use a sintering agent for the more rapid sintering of the alumina adapted to be pressed at dry state. Such sintering agents are known. For the alumina pressable at dry state iron chloride has proved to be especially suitable as sintering agent, which suitably is added to the alumina with the hydrochloric acid, or is formed by treatment with hydrochloric acid of the alumina containing some metallic iron. It is not excluded that the iron chloride at the simultaneous addition of the acid also assists catalytically the activating of the alumina, but it participates with certainty in the hydrolysis proceeding of the alumina. Hereby a very fine and chiefly also uniform distribution of the sintering agent in the alumina pressable at dry state is positively attained. The extremely fine distribution of the sintering agent has an advantageous effect at the ceramic burning with relation to a more uniform re-crystallisation of the alumina.

The ceramic goods produced according to the invention with addition of iron chloride as sintering agent consist after the ceramic burning of crystallized alumina with little additions of iron compounds (below 1%). The iron compounds convert, as a rule, with the usual impurities of the alumina mostly to iron aluminium silicates. The by far greatest portion of the iron chloride used as sintering agent is, however, sublimated off or evaporated during the ceramic burning.

The alumina pressable at dry state sintered with the little fluxing material percentage supplies products, which very advantageously differ from the ceramic goods produced of pure cast alumina, although they correspond in their composition in general to these, as also from the ceramic goods containing more binding material with preponderant basis of alumina. This is valid especially for the stability against sudden change of temperature.

The sintering agents employed up to the present in the ceramics were always materially different from the portion of the ceramic goods, which had to be sintered. It has further been found, that the alumina pressable at dry state and produced according to the invention can be further improved by an additional material of similar material composition as it has itself. Crystallised corundum, i. e. molten alumina with 99.5 to 99.7% Al_2O_3 content is a sintering agent materially similar to alumina pressable at dry state. Herefor it is however necessary that the crystallised corundum is added in finest ground state to the alumina pressable at dry state according to the invention and also preferably intimately admixed with the same. This is preferably effected by stirring the corundum flour into the condensed alumina residues and in the presence of little quantities of iron compounds. The corundum, however, can also be added to the already pulverised residue. The quantity of the sintering agent of similar kind added to the alumina which according to the invention is pressable at dry state may amount up to 50 weight percent.

The most finely ground corundum, if employed according to the invention, acts at the ceramic burning of the shaped bodies as crystallisation agent in the alumina pressable at dry state produced according to the invention and most intimately mixed with the corundum flour as sintering material. By the fineness of the ground corundum many crystallisation germs are thus produced within the ceramic mass. This is favorable, as by the great number of crystallisation germs an essentially more rapid re-crystallisation of the alumina pressable at dry state is attained and chiefly an irregular growing of individual crystals on the expense of others is prevented. Beyond this, the corundum crystals as such exert already a considerable solidifying effect upon the structure of the burnt ceramic goods. It has further been found, that the pressing capability of the alumina pressable at dry state is not only not impaired by the addition of the most finely ground corundum but on the contrary quite considerably improved, as also besides this the working facility of the condensed alumina is additionally quite considerably facilitated.

The addition of the finest ground corundum with simultaneous presence of small quantities of $FeCl_3$ has, however, also the unexpected advantage, that the burning time of the shaped bodies can be shortened, under circumstances even with slight lowering of the maximum burning temperature.

The ceramic goods produced according to the invention from pure alumina pressable at dry state, with or without employment of finest ground corundum as sintering agent, are free from fissures in their structure according to the observations which have been made. These goods have also in the highest degree the properties of the pure alumina, such as their good heat conductability, their electric isolation capability and so forth. They show, however, chiefly a maximum stability against change of temperature, especially a maximum stability against sudden change of temperature. Such ceramic masses which can be pressed as according to the invention are especially suitable for the production of such ceramic articles, the use of which supposes a high stability at temperature change, as is the case for instance in insulators for sparking plugs.

By the method according to the invention it is now also possible to dry-press pure alumina without addition of plastic substances or of substances which become plastic at the pressing. By the method according to the invention ceramic goods can be produced as far as necessary practically without a percentage of iron compounds, as far at least as the unavoidable polluting of the pure alumina by iron compounds is left out of consideration the relative proportion of which even can be easily increased by the technical method. But even these small quantities of iron compounds are considerably reduced at the ceramic burning by evaporation or sublimation. The lower the iron constituent is in the burnt body, the greater will be the electric insulation capability of the same. It has been ascertained that this insulation capability in goods produced according to the invention from alumina made pressable in dry state with employment of finest ground corundum as sintering agent exceeds, as regards number, all known values of goods of similar composition produced otherwise.

EMIL KLINGLER.