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OPAQUING AGENTS MAINLY COMPRISING ZIRCONIA AND PROCESS FOR PREPARING SAME

Maxime Paquet, St. - Maure - des - Fosses, and Jacques Ourisson, Paris, France; vested in the Alien Property Custodian

No Drawing. Application filed May 24, 1939

The invention relates to novel opaquing agents which are applicable, in particular, to the manufacture of vitrified enamels, and a process for preparing same.

Said opaquing agents mainly comprise zirconium compounds and are prepared from natural zircon (zirconium silicate) or similar starting materials containing zirconia and silica and are utilizable for opaquing vitrified enamels in general, but more particularly enamels for cast-iron and hard enamels, having a relatively high melting point, which are used in the pottery industry for coating the surface of bricks, tiles, earthenware, stoneware, porcelain, etc.

Endeavours have been made to use zircon for opaquing enamels by introducing it when the frit is fused. In fact, zircon used in sufficient quantity imparts a certain opaqueness to frits. But in order to obtain a suitable opacity, which moreover is not that which can be obtained with zirconia it is necessary to add such large proportions of zircon that they are no longer compatible with the other properties of the enamel, a fact which limits the application of this process.

For this reason, products which are more or less enriched and have a higher ZrO_2 content, are generally prepared from zircon. This practice offers drawbacks, in particular owing to the costly chemical treatment required for eliminating the silica, a fact which limits its use.

Finally it has been proposed to prepare from natural zircon well-defined products such as basic zirconium silico-borate, alkaline silico-zirconates, double silicates of zirconium and magnesium, or of zirconium and zinc, etc. so as to involve the zirconium in a chemical compound which is more efficacious than zircon for opaquing frits. But such well-defined compounds, which can only be obtained under very specific conditions and at high temperature, have their sphere of use limited by the relative proportions of the components, necessarily due to their nature as a well-defined product, and by their particular properties, such as their crystalline structure for example.

The present invention enables these drawbacks to be avoided and permits of the preparation by a simple and economical method, from natural or previous enriched zircon, of opaquing agents which are quite comparable, as regards their efficacy in certain enamels, to good quality purified zirconia, while only introducing into the enamel substances which usually form part of their compositions.

The invention consists in calcining ground natural zircon in the presence of fluxes, at a suitable temperature which in practice is between 850° and 1300° C. with substances capable of decomposing it so as to form a substantially colourless amorphous vitreous substance which is slightly fusible or is very viscous at the temperature of preparation of the enamels for which these opaquing agents are intended, and in which vitreous substance zirconium compounds are engaged, such in particular as zirconia or undissolved zircon.

The substances which have given the best results for this manufacture are magnesium and aluminum oxides which produce, with the zircon, vitreous substances which are but slightly fusible. It is also possible to use the oxides of zinc, calcium, barium or compounds of these oxides which are capable of producing same during reaction.

The tables (J. Amer. Ceramic Soc. (1938)—16 to 10, Figures Nos. 36, 37, 39, 43, 45) give the following values for the melting point of the eutectics of the various oxides with silica:

	Degrees centigrade
SiO_2-MgO -----	1543
$SiO_2-Al_2O_3$ -----	1545
SiO_2-CaO -----	1432
SiO_2-ZnO -----	1436
SiO_2-BaO -----	1370

and it has been observed that in a general manner, the results obtained are better as the melting point of the possible eutectic is higher.

It would appear, without the inventor's considering this hypothesis as final, that the vitrified substance obtained is a solid solution in silica of zirconia ZrO_2 and of the oxide used, MgO for example. In this solid solution, there is, in the dispersed state, either zirconia ZrO_2 or zircon (SiO_2, ZrO_2) according to the operating conditions.

In order to lower the temperature of treatment, fluxes are added which are intended to enable the vitreous substances to form at a relatively low temperature, said vitreous substance remaining however very viscous, such as the compounds of the alkali metals and in particular: KCl , KNO_3 , Na_2CO_3 , K_2SO_4 , borax, KF , or again cryolite, etc. or their mixtures, or again substances having the same action, which consists in ensuring contact between the powders by the local formation of fusible compounds at a temperature

adjacent that at which the operation is being effected.

It should be observed on the other hand that instead of starting from ground natural zircon, it is possible to use similar compounds, containing ZrO_2 and SiO_2 , which are natural or treated, or enriched in ZrO_2 by means of a previous treatment.

As regards the relative proportions of the ingredients of the mixture, these may be varied within wide limits; however the best results have been obtained by taking, for one molecule of zircon to be treated, 0.2 to 2.0 molecules of additional substance, such as MgO or Al_2O_3 , and preferably between 0.4 and 1.0 molecule.

The quantity of flux to be used is less than that of the previously mentioned ingredients of the mixture, and depends on its activity. It will be about 0.1 to 1 molecule of flux per molecule of additional substance such as MgO or Al_2O_3 . The best results have been obtained by taking for example:

	Molecules
MgO or similar compound.....	0.6 to 0.9
K_2O or similar compound.....	0.4 to 0.1

It has been observed that cryolite is a very active flux, and that in a general manner the compounds of potassium are preferable to those of the other alkali metals.

It is also possible usefully to add fluorides, chlorides, borates, boric acid, these substances exerting a favorable action on the colour of the product obtained, and contingently also on its opaquing power.

The temperature of calcination will be such that there is a beginning of agglomeration or even a beginning of partial fusion according to a phenomenon similar to clinkerization, and will usually be between 850° and 1300° C. The duration will vary with the temperature. Satisfactory products can be obtained at very different temperatures if the duration of the calcination is made to operate in the reverse direction to the temperature. For example, calcining may be effected for 48 hours at 900° C. or for 2 hours at 1200° C.

The progress of the reaction during calcination can be followed by means of chemical tests.

For example, if the zircon is calcined by the process described in the presence of magnesia, it is found that as the reaction progresses, the magnesia can no longer be extracted by means of a concentrated solution of ammonium chloride. It is found at the same time, that relatively to its initial value, the silica has as gradually increasing solubility in hydrofluoric acid, and may become totally soluble therein.

If a mixture containing zircon and alumina is calcined, the same gradually increasing solubility of the silica occurs as the reaction progresses.

Similar tests enable the calcination to be followed in the other cases.

It has been found that in order to obtain a satisfactory product, it is necessary for an appreciable fraction of the zircon used to have reacted, but it is not necessary for the whole of the zircon to have been decomposed, so that the product obtained may contain a certain amount of unattached zircon, which is visible under the microscope and can be identified by its X-ray spectrum.

The following examples illustrate the preparation of the products which are the object of the invention.

Example 1

Take:	Kgs.
Zircon	1.000
Al_2O_3	275
Cryolite	150
Na_2CO_3	150

Intimately mix and calcine for 16 hours at 900° C. Allow to cool. If treated with hydrofluoric acid it is found that about 90% of the mass dissolves and that the residue only contains very little silica.

Example 2

Mix:	Kgs.
Zircon	1.000
MgO	110
Al_2O_3 in the form of hydrated alumina.....	135
Cryolite	165

The mixture is ground into a thin paste in water, is dried and calcined for two hours at 1220° C.

The product obtained is compact and white. It is allowed to cool and ground in water.

Example 3

Intimately mix by moist grinding:	Kgs.
Zircon	1.000
MgO	200

Add to the paste a solution containing:

	Kgs.
$MgCl_2 \cdot 6H_2O$	50
Na_2CO_3	100

The mixture is made homogeneous, dried and calcined for two hours at 1200° C. then poured into water, ground and dried.

In this example, Na_2CO_3 may be replaced by 50 to 100 Kgs. of KNO_3 or $NaNO_3$.

Example 4

Intimately mix by moist grinding:	Kgs.
Zircon	1.000
Magnesia	220
Cryolite	150

Add to the paste a solution containing:

	Kgs.
Na_2CO_3	75

Dry and calcine for 24 hours at 900° C. then allow to cool.

It is found that nearly all the magnesia has become insoluble in a concentrated solution of ammonium chloride.

If the product is treated with hydrofluoric acid, it is found that about 90% dissolves and that the residue only contains a few per cent of silica.

Such opaquing agents suitably ground may be used for enamels in general and even for enamels for earthenware, since the freed zirconium compound it contains is protected from dissolving by the slightly fusible or infusible vitrified substance in which it is engaged.

These products are directly utilizable as opaquing agents for vitrified enamels, but more particularly for enamels suitable for cast-iron, into which they are introduced during the fusion, or as an addition in the mill for enamels for pottery. They behave therein in the same manner as zirconia (ZrO_2) used in the same manner, and give, in the same proportion as ZrO_2 , similar and in certain cases greater opaquing effects.

The opaquing agents thus obtained comprise a zirconium compound engaged or dispersed in a vitreous mass mainly comprising silica, zirconia, and a substance such as MgO or Al₂O₃, optionally with alkali oxide or salts. Said vitreous mass is slightly fusible and protects the free zirconium compound from being quickly dissolved when it is being used for pottery manufacture. The vitreous part does not give any spectrum so that X-ray examination only shows a diagram of the free zirconium compound such as spotty zircon, on which is often superposed a diagram of lines of crystallized ZrO₂ either in the baddelyte form,

or in the tetragonal form, or in both forms at once.

In the case in which the additional substance is magnesia, a considerable fraction of same has become insoluble in a concentrated solution of ammonium chloride.

The silica of the starting material has undergone a transformation that has made it more soluble in hydrofluoric acid than the silica of the initial material.

MAXIME PAQUET.
JACQUES OURISSON.