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## EUROPEAN QUALIFYING EXAMINATION 2002

### PAPER B CHEMISTRY

This paper comprises:

- \* Annex 1  
Description of the Application 2002/B(C)/e/1-11
- \* Annex 2  
Communication 2002/B(C)/e/12-13
- \* Annex 3  
Document D 1 (State of the Art) 2002/B(C)/e/14-15
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## Annex 1 (the application)

### DESCRIPTION OF THE APPLICATION

Our invention relates to wall tiles and in particular to a glaze for such tiles. Tile glazes are made by mixing a powdered pre-melted precursor (a frit) with powdered minerals and if required a pigment. This mixture is applied to the tile surface and fired to give the desired surface finish. We have developed a new frit for tile glazing, which is particularly useful for interior wall tiles. Using our frit an interior wall tile can be produced using a single firing step. The tile glazes enable us to produce tiles which combine an attractive appearance with good wear resistance and acid resistance.

It has been common practice to produce interior wall tiles by a double firing process. This conventional process includes the steps of forming a green tile (i.e. a raw, unfired tile), a first firing (biscuit firing), cooling, glazing, and a secondary firing (gloss firing).

Interior wall tiles are produced by double firing because they require a thick glaze. Gases are generated when green tiles are fired as the result of the thermal decomposition of carbonate minerals and the combustion of organic substances. The presence of a molten or partially molten thick glazed layer will prevent the free passage of these gases, giving rise to bubbles in the glaze layer and an unacceptable appearance of the final tile.

The gas generation depends on the firing conditions. If the green tile is heated slowly so that a thermal equilibrium exists between the green tile and the furnace atmosphere, gases will cease to be generated at a furnace temperature of between 700 and 800°C. The typical commercial furnaces (e.g. a roller hearth kiln), however raise the temperature rapidly and in this case a thermal gradient exists in the green tile. In a roller hearth kiln gases are still generated at furnace temperatures in excess of the initial softening and melting point of a standard glaze (ca. 1000°C). Thus the presence of a thick glaze during the firing of a green tile leads to bubbles being present in the final glaze.

This drawback is absent in the double firing system, because the body to which the glaze is applied is in a form which can release no gases. Hence even a very thick glaze layer is free of bubbles. Thus it is possible to produce interior wall tiles with a high quality smooth glazed surface. Obviously, however, the requirement to fire the tiles twice is associated with considerable cost.

The tile glazes must also be wear and acid resistant since otherwise they will rapidly become damaged during routine household cleaning.

10 According to one aspect of the present invention, a frit for a tile glaze has the following components:

SiO <sub>2</sub> :	55 to 65 wt%
Al <sub>2</sub> O <sub>3</sub> :	10 to 18 wt%
CaO:	18 to 25 wt%
15 Alkali metal oxides:	0.5 to 4 wt%
ZrO <sub>2</sub> :	0 to 10 wt%
B <sub>2</sub> O <sub>3</sub> :	0 to 2 wt%
MgO, BaO, SrO, and ZnO:	0 to 10 wt% in total
Other oxides, chlorides or sulfates:	up to 3 wt%.

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According to another aspect of the present invention, a tile glaze is composed of 100 parts by weight of the following components (a) to (i) and 0 to 15 parts by weight of pigment.

(a) 50 to 90 parts by weight of a frit of the following composition:

SiO <sub>2</sub>	55 to 65 wt%
25 Al <sub>2</sub> O <sub>3</sub>	10 to 18 wt%
CaO	18 to 25 wt%
Alkali metal oxides	0.5 to 4 wt%
ZrO <sub>2</sub>	0 to 10 wt%
B <sub>2</sub> O <sub>3</sub>	0 to 2 wt%
30 MgO, BaO, SrO, and ZnO	0 to 10 wt% in total
Other oxides, chlorides or sulfates	up to 3 wt%

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- (b) Feldspar: 8 to 25 parts by weight  
(c) Clay: 0.5 to 10 parts by weight  
(d) Zirconium silicate: 0 to 20 parts by weight  
(e) Quartz: 0 to 10 parts by weight  
5 (f) Alumina: 0 to 5 parts by weight  
(g) Titania: 0 to 10 parts by weight  
(h) Barium carbonate: 0 to 10 parts by weight  
(i) Zinc oxide: 0 to 5 parts by weight
- 10 According to a further aspect of the present invention, a method for producing interior wall tiles comprises applying to a green tile a glaze composed of 100 parts by weight of said components (a) to (i) and 0 to 15 parts by weight of a pigment, drying and firing the glazed body.
- 15 Embodiments of the present invention will now be described by way of example only:
- The frit of the present invention contains less alkali metal oxides and  $B_2O_3$  than frits used to make conventional glazed tiles; therefore, it decreases in viscosity very slowly when heated above its softening point. A tile glaze made using this frit consequently does not  
20 flow to cover the entire surface of the tile until it is heated to far above its softening point. This means that gases released from a green tile body can pass through a glaze based on the present frit without causing bubbles to remain in the final glazed tile.
- The following is a detailed description of each component and preferred embodiments of  
25 the frit of the present invention.

The frit of the present invention contains  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  as its major constituents. The components are primarily responsible for the high softening point of the frit. They form a network of aluminosilicate glass in the final glaze.

5 The frit contains alkali metal oxides (abbreviated as  $\text{R}_2\text{O}$  hereinafter) and  $\text{CaO}$  which promote vitrification.

According to the present invention, the frit comprises 55 to 65 wt% of  $\text{SiO}_2$ , 10 to 18 wt% of  $\text{Al}_2\text{O}_3$ , 18 to 25 wt% of  $\text{CaO}$ , and 0.5 to 4 wt% of  $\text{R}_2\text{O}$ . These ranges ensure that the frit has softening properties which avoid bubbles in the glaze but which at the same time  
10 ensure that the glaze completely melts to cover the tile.

Excellent results have been obtained when the frit contains 60 to 64 wt%  $\text{SiO}_2$ , 12 to 16 wt%  $\text{Al}_2\text{O}_3$ , 19 to 23 wt%  $\text{CaO}$ , and 1 to 3 wt%  $\text{R}_2\text{O}$ .

The frit may optionally contain as one of the alkali metal oxides  $\text{Li}_2\text{O}$ . The presence of  $\text{Li}_2\text{O}$   
15 ensures that the glaze has a very smooth surface. The content of  $\text{Li}_2\text{O}$  should preferably be 0.5 to 1.5 wt%. With less than 0.5 wt%, it does not contribute to the smoothness of the glazed surface; and with more than 1.5 wt%, it can result in pinholes in the glazed surface. The frit of the present invention may contain  $\text{B}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{SrO}$ , and  $\text{BaO}$ , according  
20 to need. These oxides however lower the softening point of the frit, and if present at a concentration which is too high bubbles may form. Thus  $\text{B}_2\text{O}_3$  must be present at less than 2 wt%, especially less than 1 wt%.  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ , and  $\text{ZnO}$  are each preferably present at less than 5 wt%, especially less than 3 wt%. The total amount of  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ , and  $\text{ZnO}$  must be 10 wt% or less.

The frit of the present invention may optionally contain 10 wt% or less of  $\text{ZrO}_2$  to impart a  
25 hiding power to the glaze (ie to ensure that the glaze is opaque and covers up the colour and roughness of the tile).

The frit of the present invention may further contain other oxides (e.g.,  $\text{BaO}$ ), chlorides, and sulfates. The total amount of these compounds must be less than 3 wt%, preferably less than 1 wt%.

The frit of the present invention can be produced by mixing standard frit raw materials, melting them, followed by cooling and crushing the resulting mixture. For example, the production process may include crushing the raw materials, melting the powder at 1300-1500 °C for 1 to 1.5 hours, followed by quenching and crushing, typically in a ball mill.

The tile glaze of the present invention is composed of 100 parts by weight of components (a) (the frit) to (i) mentioned above, and 0 to 15 parts by weight of pigment.

Feldspar (b) and clay (c) raise the melting point of the glaze. For the glaze of the present invention to have an adequate melting point, the content of feldspar should be 8 to 25 parts by weight, preferably 15 to 21 parts by weight, and the content of clay (e.g., kaolin) should be 0.5 to 10 parts by weight, preferably 2 to 4 parts by weight.

Zirconium silicate (d) imparts a hiding power to the glaze. The content of zirconium silicate should be 0 to 20 parts by weight, preferably 10 to 15 parts by weight.

Quartz (e) alumina (f), titania (g), barium carbonate (h), and zinc oxide (i) control the melting point of the glaze and the gloss of the glazed surface. Their content should be 0 to 10 parts by weight for quartz, 0 to 5 parts by weight for alumina, 0 to 10 parts by weight for titania, 0 to 10 parts by weight for barium carbonate, and 0 to 5 parts by weight for zinc oxide.

The pigment is added, if necessary, to improve the appearance of the glazed surface of tile. Any pigment used for tiles is acceptable for this purpose. The amount of the pigment is 0 to 15 parts by weight per 100 parts by weight of the total amount of components (a) to (i).

The tile glaze of the present invention is prepared by suspending the components (a) to (i) and the pigment in water or alcohol. A suspending agent is usually used in this step. The tile glaze is made by adding all the solid components, 30 to 45 parts by weight of water and 0.05 to 0.50 parts by weight of suspending agent for 100 parts by weight of the component mixture to a ball mill and ball milling the mixture. The resulting tile glaze suspension is the tile glaze slip.

The tile glaze slip is subsequently applied to pre-formed green tiles in such an amount that the glaze thickness after drying will be 0.1 to 2 mm, preferably 0.3 to 1 mm. The application of the glaze may be performed in any manner. Once the tile glaze slip has been applied to the green tile bodies, the tile bodies are dried and then fired. The firing should preferably be performed by means of a roller hearth kiln. The best quality tiles are obtained when the firing temperature is 1170 to 1220 C. The fired tile is removed from the roller hearth kiln and is ready for shipment after packaging.

The invention will be described in more detail with reference to the following examples and comparative examples, in which experiments were carried out with green tile bodies measuring 10 x 10 x 0.5 cm which were produced from a ball-milled mixture composed of 45 parts by weight of agalmatolite, 40 parts by weight of clay, 10 parts by weight of limestone, and 5 parts by weight of chamotte. The firing in all the examples was performed in a 25 metre long roller hearth kiln through which the tiles were conveyed at a speed of 1.0 m/min. The maximum temperature in the firing zone was kept at 1190°C.

### Example 1

A frit was prepared. The chemical composition of the frit is shown in table 1. Seventy parts by weight of this frit was mixed with 15 parts by weight of feldspar (b), 2 parts by weight clay (c), and 13 parts by weight of zirconium silicate (d), no pigment was used. The resulting mixture was ball-milled together with 33 parts by weight of water and 0.20 parts by weight of suspending agent. Thus there was obtained a glaze slip. This glaze slip was applied to the above-mentioned green tile bodies in such an amount that the glaze thickness after drying was 0.6 mm. After drying, the glazed bodies were fired. Thus there were obtained interior wall tiles of high quality having a smooth, thick, glossy glaze layer free of bubbles. The tile glaze was also wear and acid resistant.

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### Examples 2 to 8

5 Frits having the compositions as detailed in table 1 were prepared in the same manner as in example 1, except that the amounts of raw materials were changed and additional raw materials (boron oxide, magnesia, and zinc oxide) were used. The frit was made into a glaze slip and the glaze slip was applied to the green bodies, followed by drying and firing, in the same manner as in example 1.

10 The interior wall tiles obtained had the same excellent surface appearance and properties as those produced in example 1.

### Comparative Examples 1 to 3

15 The procedure as in example 1 was repeated except that the composition was changed as shown in table 1. All of the resulting tiles suffered from bubbles in the glaze layer.



Table 1 Composition of the Frits (all the figures are parts by weight of the frit):

Example	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Alkali Metal Oxides R <sub>2</sub> O	ZrO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	Sum of MgO, SrO, ZnO and BaO	Bubbles Formed
1	61.4	15.1	23.0	0.5	-	-	-	No
2	61.4	14.0	22.6	1.0	-	-	1.0	No
3	63.4	12.0	19.6	2.0	-	1.0	2.0	No
4	57.5	12.2	19.6	1.7	8.5	-	-	No
5	60.0	16.0	18.5	2.0	-	1.5	1.0	No
6	58.0	14.0	24.0	3.0	-	-	1.0	No
7	61.0	14.0	20.0	3.0	-	-	2.0	No
8	59.8	12.6	21.6	2.0	-	-	4.0	No
Comp. 1	60.0	12.0	20.0	7.0	-	1.0	-	Yes
Comp. 2	53.0	19.0	18.0	3.0	-	2.0	3.0	Yes
Comp. 3	68.0	6.0	23.0	2.0	-	1.0	-	Yes

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Examples 9 to 14 and Comparative Examples 4 to 6

Glazes were prepared in the same manner as in example 1. The frit of example 2 was combined with feldspar, clay, pigment and the other components as shown in Table 2.

- 5 Pigment was used at 5 parts per 100 parts of the tile glaze. The pigment was a standard commercially available manganese and cobalt based mixture which produces tiles with a wine red coloured glaze. The glazes were applied to green tiles, followed by drying and firing.
- 10 In examples 9 to 14, there were obtained interior wall tiles of high quality having a smooth, thick, glossy glaze layer free of bubbles and with a good wear and acid resistance. In contrast, in comparative examples 4 to 6, bubbles were generated in the glaze during firing.

Table 2 Composition of the tile glaze (all figures are parts by weight of the glaze)

Example	Frit	Feldspar	Clay	Zirconium silicate	Quartz	Alumina or Titania	Barium Carbonate	Zinc Oxide
9	68	17	2	13	-	-	-	-
10	60	21	2	13	-	-	-	4
11	55	20	2	13	10	3 (alumina)	-	-
12	80	15	5	-	-	-	-	-
13	60	20	2	10	-	8 (titania)	-	-
14	55	20	2	10	4	2 (alumina)	7	-
Comp. 4	95	3	2	-	-	-	-	-
Comp. 5	70	-	5	10	15	-	-	-
Comp. 6	70	-	5	-	-	15	-	5

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## Claims

1. A frit for a tile glaze consisting of:

SiO <sub>2</sub> :	55 to 65 wt%
Al <sub>2</sub> O <sub>3</sub> :	10 to 18 wt%
CaO:	18 to 25 wt%
Alkali metal oxides:	0.5 to 4 wt%
ZrO <sub>2</sub> :	0 to 10 wt%
B <sub>2</sub> O <sub>3</sub> :	0 to 2 wt%
MgO, BaO, SrO, and ZnO:	0 to 10 wt% in total,
other oxides, chlorides or sulfates:	up to 3 wt%.

2. Tile glaze consisting of 100 parts by weight of the following components (a) to (i) and 0 to 15 parts by weight of pigment.

(a) Frit as defined in claim 1:	50 to 90 parts by weight
(b) Feldspar:	8 to 25 parts by weight
(c) Clay:	0.5 to 10 parts by weight
(d) Zirconium silicate:	0 to 20 parts by weight
(e) Quartz:	0 to 10 parts by weight
(f) Alumina:	0 to 5 parts by weight
(g) Titania:	0 to 10 parts by weight
(h) Barium carbonate:	0 to 10 parts by weight
(i) Zinc oxide:	0 to 5 parts by weight

3. A method for producing wall tiles comprises applying to a green tile a glaze composed as defined in claim 2, drying and firing the glazed tile.

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## **Annex 2 (COMMUNICATION)**

- 1) Document 1, which represents prior art in the sense of Article 54(3) and (4) EPC for all the contracting states, discloses a frit which is novelty destroying for claim 1 (see paragraph 4 and claim 1).
  - 1.1) Document 2 discloses frits, tile glazes and methods which are novelty destroying for the subject-matter of claims 1-3 (Articles 52(1), 54(1) and 54(2) EPC) (see claim 1, example).
- 2) If the applicant wishes to maintain the application, new claims should be filed which take the above objections into account. Care should be taken to ensure that the new claims comply with the requirements of the EPC in respect of novelty, inventive step, clarity and if necessary unity (Articles 54, 56, 84 and 82 EPC). The applicant should also ensure that any amendments do not introduce subject-matter which extends beyond the content of the application as originally filed (Article 123(2) EPC).
- 3) In the letter of reply, the difference between the new claims and the state of the art as well as its significance should be identified. In addition the invention should be presented in such a way that the technical problem being solved in view of the state of the art, the solution proposed to this problem, as well as the position of the applicant in respect of inventive step (Rule 27(1)(c) EPC and Guidelines C-IV, 9.5) can be clearly understood.
- 4) An independent claim must specify all the technical features necessary to define the invention (Guidelines C-III, 4.4). Thus each independent claim must contain all the technical features essential to the solution of the problem on which the invention is based.

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- 5) In order to facilitate the examination as to whether the new claims contain subject matter which extends beyond the content of the application as filed, the applicant is requested to indicate precisely where in the application documents any amendments proposed find a basis (Article 123(2) EPC, Guidelines E-II, 1 and C-VI, 5,4).
  
  - 6) It is suggested that the adaptation of the description to any new claims be postponed until the Examining Division indicates that a set of claims is allowable.

**Annex 3 (DOCUMENT 1, prior art in the sense of Articles 54(3) and (4) for all the contracting states)**

This invention relates to a glazed alumina ceramic and to a frit suitable for making the glaze.

5 Ceramics are being increasingly used in electronic applications. It has recently been determined that the thermal properties of alumina ceramics make them ideal candidates for the thermal head for a printer or a fax receiver. Thermal heads are however required to have one very smooth surface and it is not economically viable to polish an alumina ceramic to the degree of smoothness now required.

10 The problem addressed by the present invention is thus to provide an alumina ceramic with a very smooth surface by an economical method. The solution proposed to this problem is to glaze a surface of the alumina ceramic using the frit composition defined below. It has surprisingly been found that by using this frit it is possible to produce a glazed surface having the required smoothness without degrading the thermal properties  
15 of the alumina ceramic.

The frit used has the following composition:

20	SiO <sub>2</sub> :	from 63 to 65 wt%
	Al <sub>2</sub> O <sub>3</sub> :	from 12 to 14 wt%
	ZrO <sub>2</sub> :	from 1 to 5 wt%
	CaO:	from 15% to 20 wt%
	Alkali metal oxides:	0,5 to 4 wt%
	ZnO:	up to 5 wt%
25	B <sub>2</sub> O <sub>3</sub> :	up to 5 wt%

Additional oxides may be present at up to 5 wt%

### Example

100 parts by weight of a granulated frit having the following composition:  $\text{SiO}_2$ : 64 wt%;  $\text{Al}_2\text{O}_3$ : 12 wt%;  $\text{ZrO}_2$ : 2 wt%;  $\text{CaO}$ : 19.5 wt%,  $\text{Li}_2\text{O}$ : 1 wt% and  $\text{B}_2\text{O}_3$ : 1.5 wt% was placed in a ball mill. 33 parts by weight of water and 1.5 parts by weight ethyl cellulose were added and the mixture was milled until it formed a flowable paste.

The glass frit paste was applied by screen printing to a surface of a pre-fired alumina ceramic to give a uniform coating. The paste layer was dried at  $120^\circ\text{C}$  and then fired at  $1400^\circ\text{C}$  so as to ensure that the glaze melted and covered the surface of the alumina. The resulting alumina plate was covered with a very uniform glaze layer 0.1 mm thick.

The thermal properties of the glazed alumina and the smoothness of the glazed surface were tested. The thermal properties and the smoothness were found to be excellent and thus the product was ideally suited for use as a thermal head for a fax receiver or a printer.

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### **Claims**

1. A frit having the following composition:

$\text{SiO}_2$ :	from 63 to 65 wt%
$\text{Al}_2\text{O}_3$ :	from 12 to 14 wt%
$\text{ZrO}_2$ :	from 1 to 5 wt%
$\text{CaO}$ :	from 15% to 20 wt%
Alkali metal oxides:	0,5 to 4 wt%
$\text{ZnO}$ :	up to 5 wt%
$\text{B}_2\text{O}_3$ :	up to 5 wt%
Additional oxides:	up to 5 wt%

2. An alumina ceramic body characterised in that, at least one surface of the body is glazed with a frit of the composition of claim 1.

3. The use of the alumina ceramic body of claim 2 as a thermal head for a fax receiver or a printer.



#### **Annex 4 (DOCUMENT 2 illustrative of the state of the art)**

Our invention relates a glaze for interior wall tiles. Tile glazes are made by mixing a powdered pre-melted precursor (a frit) with powdered minerals and if required a pigment. This mixture is applied to the tile surface and fired to give an attractive tile with a surface which is hard wearing and resistant to acidic household cleaning agents. We have developed a tile glaze which fulfils all of these requirements. The tile glaze can be produced using a single firing step.

Glazed tiles which are produced using a single firing step (ie the firing of the green tile occurs simultaneously with the melting of the glaze) often either suffer from a poor appearance of the glaze due to the presence of bubbles or are not sufficiently wear and acid resistant. We have developed a tile glaze for a single firing process able to combine an attractive appearance with good a wear resistance and acid resistance.

The tile glaze of the present invention has the following composition:

100 parts by weight of the following components (a) to (i) and 0 to 15 parts by weight of pigment.

(a) 50 to 90 parts by weight of a frit of the following composition:

SiO <sub>2</sub>	55 to 65 wt%
Al <sub>2</sub> O <sub>3</sub>	10 to 18 wt%
CaO	18 to 25 wt%
Alkali metal oxides	0.5 to 4 wt%
ZrO <sub>2</sub>	0 to 10 wt%
B <sub>2</sub> O <sub>3</sub>	0 to 2 wt%
MgO, BaO, SrO, and ZnO	0 to 10 wt% in total

- (b) Feldspar: 8 to 25 parts by weight  
(c) Clay: 0.5 to 10 parts by weight  
(d) Zirconium Silicate: 0 to 20 parts by weight  
(e) Quartz: 0 to 10 parts by weight  
5 (f) Alumina: 0 to 5 parts by weight  
(g) Titania: 0 to 10 parts by weight  
(h) Barium carbonate: 0 to 10 parts by weight  
(i) Zinc oxide: 0 to 5 parts by weight
- 10 The tile glaze of the present invention has the following features. It is composed of 100 parts by weight of component (a) (the frit) and components (b) to (i) mentioned above, and 0 to 15 parts by weight of pigment.
- According to the present invention, the frit (a) comprises 55 to 65 wt% of  $\text{SiO}_2$ , 10 to 18  
15 wt% of  $\text{Al}_2\text{O}_3$ , 18 to 25 wt% of  $\text{CaO}$ , and 0.5 to 4 wt% of  $\text{R}_2\text{O}$  (alkali metal oxides) optionally along with other oxides. These ranges ensure that the frit has softening properties which avoid bubbles in the glaze but which at the same time ensure that the glaze completely melts to cover the tile.
- 20 The frit may optionally contain as one of the alkali metal oxides  $\text{Li}_2\text{O}$ . The presence of  $\text{Li}_2\text{O}$  ensures that the glaze has a very smooth surface. The content of  $\text{Li}_2\text{O}$  should preferably be 0.5 to 1.5 wt%. With less than 0.5 wt%, it does not contribute to the smoothness of the glazed surface; and with more than 1.5 wt%, it can result in pinholes in the glazed surface. The frit of the present invention may contain  $\text{B}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{ZnO}$ ,  $\text{SrO}$ , and  $\text{BaO}$ , according  
25 to need. These oxides however lower the softening point of the frit and if present at a concentration which is too high bubbles may form. Thus  $\text{B}_2\text{O}_3$  must be present at less than 2 wt%, especially less than 1 wt%.  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ , and  $\text{ZnO}$  are each preferably present at less than 5 wt%, especially less than 3 wt%. The total amount of  $\text{MgO}$ ,  $\text{BaO}$ ,  $\text{SrO}$ , and  $\text{ZnO}$  must be 10 wt% or less.
- 30 The frit of the present invention may optionally contain 10 wt% or less of  $\text{ZrO}_2$  to impart a hiding power to the glaze.

The components (b) to (i) when present at concentrations inside the ranges indicated ensure that the glaze is sufficiently hard wearing and acid resistant as well as contributing to the attractive appearance of the glaze.

- 5 The tile glaze of the present invention is prepared by suspending the components (a) to (i) and if required the pigment in water or alcohol. A suspending agent is usually used in this step. The tile glaze is made by adding all the solid components, 30 to 45 parts by weight of water and 0.05 to 0.50 parts by weight of suspending agent for 100 parts by weight of the component mixture to a ball mill and ball milling the mixture. The resulting tile glaze  
10 suspension is the tile glaze slip.

The tile glaze slip is subsequently applied to pre-formed green tile bodies in such an amount that the glaze thickness after drying will be 0.1 to 2 mm, preferably 0.3 to 1 mm. The application of the glaze may be performed in any manner. Once the tile glaze slip has  
15 been applied to the green tile bodies, the tile bodies are dried and then fired. The firing should preferably be performed by means of a roller hearth kiln. The fired tile is removed from the roller hearth kiln and is ready for shipment after packaging.

The invention will be described in more detail with reference to the following examples and  
20 comparative examples, in which experiments were carried out with green tile bodies measuring 10 x 10 x 0.5 cm which were produced from a ball-milled mixture composed of 45 parts by weight of agalmatolite, 40 parts by weight of clay, 10 parts by weight of limestone, and 5 parts by weight of chamotte. The firing in all the examples was performed in a 25 metre long roller hearth kiln through which the tiles were conveyed at a  
25 speed of 1.0 m/min. The temperature in the firing zone was kept at 1190°C.

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### Example

Seventy parts by weight of a frit having the following composition (57.5 wt% of  $\text{SiO}_2$ , 12.2 wt% of  $\text{Al}_2\text{O}_3$ , 19.6 wt% of  $\text{CaO}$ , 1.7 wt% of  $\text{R}_2\text{O}$  and 8.5 wt%  $\text{ZrO}_2$ ) was mixed with  
5 15 parts by weight of feldspar, 2 parts by weight clay, and 13 parts by weight of zirconium silicate. The resulting mixture was ball-milled, together with 33 parts by weight of water and 0.20 parts by weight of suspending agent. Thus there was obtained a glaze slip. This glaze slip was applied to the above-mentioned green tiles in such an amount that the glaze thickness after drying was 0.6 mm. After drying, the glazed tiles were fired.  
10 Thus there were obtained interior wall tiles of high quality having a smooth, thick, glossy glaze layer free of bubbles. The wear resistance and the acid resistance of the tile were measured in accordance with the Standard DIN xxxyyy and were determined to have a rating of 5 or above (good).

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**Claim**

1. Tile glaze consisting of 100 parts by weight of the following components (a) to (i) and 0 to 15 parts by weight of pigment.

(a) 50 to 90 parts by weight of a frit of the following composition:

SiO <sub>2</sub>	55 to 65 wt%
Al <sub>2</sub> O <sub>3</sub>	10 to 18 wt%
CaO	18 to 25 wt%
Alkali metal oxides	0.5 to 4 wt%
ZrO <sub>2</sub>	0 to 10 wt%
B <sub>2</sub> O <sub>3</sub>	0 to 2 wt%
MgO, BaO, SrO, and ZnO	0 to 10 wt% in total

- (b) Feldspar: 8 to 25 parts by weight  
(c) Clay: 0.5 to 10 parts by weight  
(d) Zirconium silicate: 0 to 20 parts by weight  
(e) Quartz: 0 to 10 parts by weight  
(f) Alumina: 0 to 5 parts by weight  
(g) Titania: 0 to 10 parts by weight  
(h) Barium carbonate 0 to 10 parts by weight  
(i) Zinc oxide: 0 to 5 parts by weight

**Annex 5 (Letter from the applicant)**

Dear Sir,

We have carefully studied the communication and the most relevant document 2. We decided to perform some further experiments in order to compare the tile glaze exemplified in document 2 with that made in examples of our application. The tiles of our examples 1-3 and the tile made in accordance with the example in document 2 were manufactured exactly as indicated in our application and document 2 respectively. The wear resistance and the acid resistance of these tiles were measured in accordance with the Standard No. DIN xxxyyy. The wear resistance and acid resistance were each rated from 1-10 in accordance with this standard. A value of 5 or above is considered to be good. A value of 8 or above is excellent.

Example	Firing Temperature	Wear Resistance	Acid Resistance	Bubbles Observed
1	1190°C	8	8	No
2	1190°C	9	7	No
3	1190°C	7	9	No
Example of Document 2	1190°C	5	6	No

The excellent results shown above are however only obtained when the tiles are fired at a temperature between 1170°C and 1220°C.

We hope that these results are of use when drafting a response to the communication.

Yours faithfully

Mr. T Layer  
BathFitz Inc.