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(12) UK Patent Application (19) GB (11) 2 093 014 A

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(21) Application No 8204318

(22) Date of filing  
15 Feb 1982

(30) Priority data

(31) 3105531

(32) 16 Feb 1981

(33) Fed Republic of Germany  
(DE)

(43) Application published  
25 Aug 1982

(51) INT CL<sup>3</sup> C04B 43/02

(52) Domestic classification  
C1J  
10 12 13 14 2 9 X

(56) Documents cited  
None

(58) Field of search  
C1J  
C3N

(71) Applicant  
Didier-Werke AG  
Lessingstrasse 16-18  
D-6200 Wiesbaden  
Federal Republic of  
Germany

(72) Inventors  
Axel Eschner  
Hermann Stein  
Morteza Nazirizadeh  
Klaus Kreuls

(74) Agents  
Kilburn and Strode  
30 John Street  
London WC1N 2DD

(54) **Process for the manufacture of ceramic fibre containing, heat-resistant or refractory compositions.**

(57) A process for the manufacture of a heat-resistant or refractory composition includes mixing 100 parts by weight ceramic fibres with 10 to 40 parts by weight water and then adding in 5 to 20 parts by weight clay and/or other common refractory additives, optionally with up to 10 parts by weight solid organic bonding agent. 0.5 to 4 parts by weight of an organic bonding agent in solution and 1 to 8 parts by weight of a phosphate bonding agent, calculated as P<sub>2</sub>O<sub>5</sub> are then mixed in. The composition may be used in its damp state or it may be dried and granulated and used as an additive to refractory materials or in fibre spraying compositions.

ERRATUM

SPECIFICATION NO 2093014A

Front page Heading 72 Inventors *for* Klaus Kreuls *read* Klaus Kreuels

THE PATENT OFFICE

15 November 1982

Bas 93286/4

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## SPECIFICATION

**Process for the manufacture of ceramic fibre containing, heat-resistant or refractory compositions**

5 The invention relates to a process for the manufacture of ceramic fibre containing heat-resistant or refractory compositions, which may be in granulated form, and to the compositions or granulates manufactured in accordance with the process and to their use. 5

Heat insulating ceramic fibre bodies comprising refractory fibres and either organic or inorganic bonding agent having either low strength and high compressibility or high values for their strength, density and constancy of shape are known. Thus DE-AS 12 74 490 describes a combustion chamber for furnaces which is made by forming out a fibre composition mixed with bonding agent and in which the concentration of bonding agent decreases over the cross-section of the chamber wall. Clays, alkaline silicates, aluminium phosphate, colloidal silica with a proportion by weight of 5 to 35, optimally 10% are disclosed as a suitable bonding agent. Such fibre bodies are, however, not suitable for subjection to high loads due to the fact that one wall surface is hard and compact whilst the opposing wall surface is soft and flexible. 10

In the process disclosed in DEENAS 27 32 387 a mineral fibre plate prebonded with an organic plastics bonding agent is supposed to be strengthened by soaking with an aqueous slurry of a bonding clay and subsequent tempering. Furthermore, fibre spraying compositions are disclosed in DE-AS 26 18 813 which, in addition to a large proportion of inorganic fibres and a low proportion of bonding agent or other inorganic additives, additionally contain a chemical additive binder, whereby these fibre spraying masses also contain 5 to 20% by weight of an oil to avoid dust formation. When using these fibre spraying compositions it is specifically stated that the inorganic fibres, e.g. rock wool, are used in a loosened state. 15

It is an object of the present invention to provide a process for the manufacture of ceramic fibre containing, heat-resistant or refractory compositions, optionally in the form of a granulate, which can be used as the main component in fibre spraying compositions or as an additive in the manufacture of refractory compositions or moulded refractory articles and has particularly advantageous properties. If the mass is present in damp form it can also be used as such. 20

According to the present invention there is provided a process for the manufacture of heat-resistant or refractory compositions including the following steps:

a) 100 parts by weight ceramic fibres are mixed with 10 to 40 parts by weight water, b) 5 to 20 parts by weight clay and/or  $\text{Al}_2\text{O}_3$  and/or  $\text{SiO}_2$  and/or aluminium hydroxides and/or magnesia and/or titanium dioxide and/or chromium oxide and 0 to 10 parts by weight solid organic bonding agent are added to the mixture produced in step a) and mixed in, c) 0.5 to 4 parts by weight of an organic bonding agent, calculated as solid material, in solution and 1 to 8 parts by weight of a phosphate bonding agent, calculated as  $\text{P}_2\text{O}_5$ , are added to the mixture produced in step b) and mixed in, 25

The damp composition may be used as such or it may be dried and then granulated. 30

The invention relates also to the use of granular, heat-resistant or refractory materials manufactured in accordance with the process, in particular in fibre spraying compositions or as an additive in the manufacture of refractory compositions or refractory moulded articles.

The ceramic fibres used in the inventive process can be all the usual fibres of this type, e.g. rock wool or fibres based on aluminium silicate preferably with a particularly high  $\text{Al}_2\text{O}_3$  content in the region of 45 to 95% by weight. Naturally mixtures of different ceramic fibres can also be used. The fibres are however, preferably based on  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  with at least 40% by weight  $\text{Al}_2\text{O}_3$  and are preferably capable of being used at temperatures in excess of  $1100^\circ\text{C}$ . This will in general exclude inorganic fibres based on, for instance, basalt, slag and glass and natural asbestos fibres whose use temperature is below  $1100^\circ\text{C}$ , but such fibres may be used as a subsidiary component in addition to those whose use temperature is above  $1100^\circ\text{C}$ . 35

When delivered, ceramic fibres are generally in the form of a loose wool which, however, is partially strongly compressed. For the manufacture of the compositions in accordance with the invention these fibres are advantageously used in loosened form thus enabling a better bonding of the fibres by the bonding agent and an excellent wetting of the surface of the fibres by liquids in very low concentration. For loosening the fibres, mixing units with rapidly rotating mixer heads, so called impact mixers, can be used, whereby the large agglomerates present in the delivery state of the fibres are loosened without the fibres being thereby unacceptably strongly crushed. 40

The clay used in the process can be a conventional clay or a special bonding clay, e.g. bentonite. This clay is preferably used in an amount of 5 to 20 parts by weight to 100 parts by weight of the ceramic fibres, advantageously 8 to 15 parts by weight clay are used. 45

As an alternative or an addition to the clay one or more of  $\text{Al}_2\text{O}_3$  and/or  $\text{SiO}_2$  and/or magnesia and/or titanium dioxide and/or chromium oxide, all of which are preferably used in very finely divided form, and/or aluminium hydroxides can be added. The use of these 50

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components is known in the refractory field. The term "very finely divided" used here is to be understood to mean that the components are present in finely ground or in colloidal state. The very finely divided refractory materials preferably have a grain size of less than 50  $\mu\text{m}$ , more preferably less than 10  $\mu\text{m}$ . Particularly when using such materials in colloidal state, such as colloidal  $\text{SiO}_2$  or colloidal aluminium oxide, it is possible to use only small quantities of bonding agent, namely close to the lower threshold value of 1.5 parts by weight of an organic bonding agent and 1 part by weight of a phosphate bonding agent. The use of approximately the same parts by weight of phosphate bonding agent and methyl cellulose as organic bonding agent is particularly preferred. It is also particularly advantageous to use a mixture of clay and one or more of the other finely divided refractory components referred to above, whereby the quantity of these other finely divided refractory components is commonly 1 to 3 parts by weight with the remainder being clay, so that altogether the quantity given in the main claim of 5 to 20 parts by weight refractory components is added.

In the process in accordance with the invention an organic bonding agent is used, and for this purpose all the organic bonding agents commonly used in this field can be used, for instance methyl cellulose, sulphite lye or waste or molasses. These organic bonding agents are commonly added in the form of a solution in water or also partially in solid form, which is particularly the case for the use of methyl cellulose. Since a total of 0.5 to 14 parts by weight of the organic bonding agent are used with 100 parts by weight of ceramic fibres and since methyl cellulose is commonly added in the form of a 5% solution, because higher percentage solutions are too viscous, the quantity of water introduced by the addition of the organic bonding agent in solution may be too great so that, particularly in the case of methyl cellulose, up to 50% by weight of this organic bonding agent is preferably added in solid form.

Additionally 1 to 8 parts by weight and preferably 2 to 6 parts by weight of a phosphate bonding agent are used in the process in accordance with the invention, the given quantities in parts by weight referring to  $\text{P}_2\text{O}_5$  in the bonding agent. A suitable phosphate bonding agent is sodium polyphosphate with a degree of polymerisation of  $n \geq 4$  and preferably with a degree of polymerisation of 6 to 10. This sodium polyphosphate is commonly used in dissolved form. A further suitable phosphate bonding agent is monoaluminium phosphate which is a commercially available product both in solid ground form and also as an aqueous solution, in particular as a 50% by weight solution. The phosphate bonding agent can either be added altogether in the form of a solution or the phosphate bonding agent can be added partially in dissolved and partially in solid form.

In the process the ceramic fibres are mixed in a mixer, commonly a drum mixer or a plough-share mixer, with 10 to 40 parts by weight to 100 parts by weight of ceramic fibres and the water is conveniently sprayed on.

Altogether up to 100 parts by weight water may be added in the process in accordance with the invention, partially in step a) and partially in step c) on the addition of the organic bonding agent in dissolved form and the phosphate bonding agent, if the latter should also be added in dissolved form.

After mixing to a homogeneous state the clay and/or the other refractory components referred to above, which are preferably present in dry finely divided form, are added to the mixture in the mixer and also homogeneously mixed in. In this step the clay and/or the other very finely divided refractory components referred to above remain adhering to the surface of the dampened fibres. Solid organic bonding agent is also optionally added in this step.

The solution of the organic bonding agent is then added to the mixture and also the phosphate bonding agent. The solid inorganic bonding agent, if added, may be added to the mixture simultaneously with the solution of the organic bonding agent or after the addition of this bonding agent.

Subsequently all the components are homogeneously mixed again which can take up to a further 30 minutes.

The composition obtained thereby can be used as such, e.g. delivered to the user as a stamping composition filled in drums.

Alternatively, this damp mass can, however, be converted into a fibre granulate as is described in more detail below. After the homogeneous mixing the finished mixture is dried, commonly at temperatures above 100°C, e.g. 110°C to 180°C. The drying time is advantageously 2 to 24 hours.

Subsequently the solid cake obtained is comminuted to the desired grain size in a conventional comminution device, e.g. a hammer mill or a roller crusher. The comminution preferably occurs to a maximum grain size of 8 mm, advantageously 6 mm, however it is also possible to set a maximum grain size of 2 or 3 mm in accordance with the intended use of the material. It is also possible, depending on the intended use, to sieve out desired grain size fractions from the granulated material.

The granular material obtained by the inventive process is found to have a density of 0.12 to 0.50 g/cm<sup>3</sup> and has a total porosity of the order of 95 to 80%. By reason of the high

proportion of organic bonding agent in the granular material it has a low density, i.e. the effect of the density increase, which is brought about by the addition of clay and/or the other finely divided refractory components, is entirely counteracted or substantially compensated for. When the granular material is used, i.e. as soon as it is brought to a high temperature, e.g. above 500°C, the organic bonding agent contained in it burns out completely or partially, depending on the temperature reached, so that a product is obtained which is still porous and which has particularly good thermal insulation properties.

A further advantage of the granular material obtained by the inventive process resides in that after the complete or partial burning out of the organic bonding agent the elastic properties of the ceramic fibres in the individual grains remain so that a material to which the granular material has been added exhibits partially elastic properties since the individual grains themselves remain elastic. This is achieved due to the fact that in the inventive process firstly the clay and/or the finely divided refractory components are added to the dampened fibres and only then is the phosphate bonding agent added so that this phosphate bonding agent remains substantially on the surface of the fibre particles which are quasi-enveloped with clay so that in the interior of the grain a core remains containing either no or very little phosphate bonding agent so that the fibres themselves remain elastic.

The granular material obtained in accordance with the inventive process can, as described above, be used with particular advantage in fibre spraying compositions. When so used, the material is either fed in dry form to a spraying nozzle at the head of which it is mixed with water and optionally further bonding agents or additives or a slurry of the granular material is produced with water and optionally further additives and sprayed. Such further additives can be, for instance, hydraulically setting bonding agents such as Portland cement or high alumina cement. Furthermore, ceramic fibres and water can also be sprayed together with such a granulate in accordance with the invention.

The use of the granular material in accordance with the invention in fibre spraying composition results in the advantage that these fibre spraying compositions require less water than conventional fibre spraying compositions when spraying, and the water saving can amount to up to 50%.

The damp composition in accordance with the invention that is to say the undried mixture, can be used particularly advantageously as an elastic and resilient expansion joint filling composition. This is particularly advantageous when placed between the bricks of a rotary tube oven, since the composition retains partially elastic properties at the use temperatures. A further advantage is that the ceramic fibres are not damaging to the health in contrast to the asbestos fibers frequently used in such expansion joint materials.

When used as an expansion joint filler, the composition is advantageously packed in the desired thickness, e.g. 2 to 8 mm thickness, between plastics foils and can be inserted as a plastic layer with the foils enveloping it as an intermediate layer, i.e. an expansion joint filling, when brick lining a furnace. For this purpose one can use, for instance, an endless roll of the plastic layer of the composition packed between plastics foils from which the desired length can be cut off or one can use prefabricated individual packages of fixed dimensions of the composition packed between the plastics foils or welded in them.

The invention will now be described in more detail with reference to the following specific examples.

Two different types of ceramic fibre were used in the Examples, namely fibres A and B, which had the following chemical composition:  
Fibres A)  $\text{Al}_2\text{O}_3 = 47\%$ ;  $\text{SiO}_2 = 53\%$ ;  
Fibres B)  $\text{Al}_2\text{O}_3 = 95\%$ ;  $\text{SiO}_2 = 5\%$ .

#### Examples 1 to 3

The following compositions were made up, the quantities being parts by weight.

Example	1	2	3	
Fibres A	100	100	100	
H <sub>2</sub> O	30	15	40	
Bentonite	10	—	15	
$\text{Al}_2\text{O}_3$	5	5	—	
$\text{TiO}_2$	—	2	1	
Solid methyl cellulose	4	—	3.5	
Solid waste	—	5	—	
Sulphite waste solution, 10% by wt.	—	2	—	

<i>Example</i>	<i>1</i>	<i>2</i>	<i>3</i>	
Methyl cellulose solution, 5% by wt.	0.5	—	3	
5 Solid monoaluminium phosphate	4	—	8	5
Solid sodium polyphosphate	—	2.5	—	

Firstly the ceramic fibres were put into an Eirich mixer and the given quantities of water were sprayed on to them and mixed in for 10 minutes. Subsequently the bentonite, the  $\text{Al}_2\text{O}_3$  or  $\text{TiO}_2$ , and the solid methyl cellulose or the solid sulphite waste were added to the mixture and mixed in for a further 8 minutes. After this the given quantities of sulphite waste or methyl cellulose to which the finely divided solid phosphate bonding agent had been added were sprayed into the mixer and mixed in for a further 10 minutes.

The crumbly mixture obtained was removed from the mixer and that of Examples 1 and 2 was dried for 6 hours at  $120^\circ\text{C}$  and subsequently comminuted in a roller crusher to a maximum grain size of 4 mm whilst that of Example 3 was used as an undried plastic composition, for which purpose it was flattened out into a plastic layer 5 mm thick which was packed in plastics foil. Such a plastic layer packed in plastics foil could be used successfully as an expansion joint filling material between fired bricks in rotary tube ovens in the delivery of such rotary tube ovens.

The properties determined on the product of the Examples were as follows:

<i>Example</i>	<i>1</i>	<i>2</i>	<i>3</i>	
Weight per unit volume, $\text{g}/\text{cm}^3$	0.22	0.14	0.40	

#### Examples 4 to 6

The method of examples 1 to 3 was repeated but loosened ceramic fibres B were used. The loosening of the fibres was effected in an impact mixer (of the type made by Drais). The fibres were treated in the rapidly rotating mixer equipped with knife heads for 5 minutes. The loosened fibres B were then transferred into an Eirich mixer, in which the further components corresponding to the composition of Examples 1 to 3 were added.

A fibre granulate was produced from the products of Examples 4 and 5 whilst the product of Example 6 was used as a stamping composition.

The properties determined on the products were as follows:

<i>Example</i>	<i>4</i>	<i>5</i>	<i>6</i>	
Weight per unit volume, $\text{g}/\text{cm}^3$	0.25	0.17	0.45	

#### CLAIMS

1. A process for the manufacture of heat-resistant or refractory compositions including the following steps:

- 100 parts by weight ceramic fibres are mixed with 10 to 40 parts by weight water,
- 5 to 20 parts by weight clay and/or  $\text{Al}_2\text{O}_3$  and/or  $\text{SiO}_2$  and/or aluminium hydroxides and/or magnesia and/or titanium dioxide and/or chromium oxide and 0 to 10 parts by weight solid organic bonding agent are added to the mixture produced in step a) and mixed in,
- 0.5 to 4 parts by weight of an organic bonding agent, calculated as solid material, in solution and 1 to 8 parts by weight of a phosphate bonding agent, calculated as  $\text{P}_2\text{O}_5$ , are added to the mixture produced in step b) and mixed in.

2. A process as claimed in Claim 1 in which the clay is bentonite.

3. A process as claimed in Claim 1 or Claim 2 in which the ceramic fibres are in loosened form.

4. A process as claimed in any one of Claims 1 to 3 in which the organic bonding agent is methyl cellulose.

5. A process as claimed in any one of claims 1 to 3 in which the organic bonding agent is sulphite waste or molasses.

6. A process as claimed in any one of the preceding claims in which the phosphate bonding agent is monoaluminium phosphate or sodium polyphosphate in dissolved and/or solid form.

7. A process as claimed in any one of the preceding claims in which the mixture produced in step c) is dried and then granulated.

8. A process for the manufacture of a heat-resistant or refractory composition substantially as specifically herein described with reference to any one of Examples 1 to 6.

9. A heat-resistant or refractory composition manufactured by a process as claimed in any one of Claims 1 to 8.

10. The use of granular, heat-resistant or refractory composition as claimed in Claims 7 and 9 in fibre spraying compositions.

11. The use of a granular, heat-resistant or refractory composition as claimed in Claims 7 and 8 as an additive in heat-resistant or refractory components which, in use, are subjected to stress.

12. The use of a damp composition manufactured by a process as claimed in any one of  
5 Claims 1 to 7 as an expansion joint filling material.

13. The use of a composition as claimed in Claim 12 in which the composition is in the form of a plastic layer packed in plastic foil.

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Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon) Ltd.—1982.  
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

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