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(54) **Formázatlan tűzálló anyag, eljárás egy földnedves formázatlan tűzálló anyagnak az előállítására, valamint a formázatlan tűzálló anyag alkalmazása**

Az európai szabadalom ellen, megadásának az Európai Szabadalmi Közlönyben való meghirdetésétől számított kilenc hónapon belül, felszólalást lehet benyújtani az Európai Szabadalmi Hivatalnál. (Európai Szabadalmi Egyezmény 99. cikk(1))

A fordítást a szabadalmas az 1995. évi XXXIII. törvény 84/H. §-a szerint nyújtotta be. A fordítás tartalmi helyességét a Szellemi Tulajdon Nemzeti Hivatala nem vizsgálta.

Description

The invention relates to an unformed refractory material, to a method of producing an earth-moist, unformed refractory material, and to use of the unformed refractory material.

Unformed refractory materials, also known as refractory masses, are made of a mixture comprising a refractory base component and binder.

Unformed refractory materials are used in particular as building compositions, repair and maintenance compositions and as mortar. Building, repair and maintenance compositions are used in particular for the construction, repair and maintenance of the internal linings of vessels for steel production, for example units for the smelting or treatment of molten steel.

US 5,954,872 discloses a refractory concrete, comprising a refractory component and a binding agent component in the form of an acid-basic-binder, which solidifies under an exothermic reaction. Said refractory concrete is pre-mixed as a dry mixture and consolidated by the addition of water. Example 1 shows a dry mixture, comprising olivine as refractory component, aluminium phosphate and MgO as binding components. Water is added to the dry mixture and an exothermic consolidation reaction is generated.

Consolidation or hardening of the unformed refractory materials may proceed in various ways. For example, hydraulic systems are known in which, once water has been added, hydraulic binding leads to setting of the unformed refractory material. Ceramic binder systems are also known, with which setting proceeds by heat treatment accompanied

by sintering. "Cold curing" compositions are also known, in which consolidation proceeds by way of chemical or organic binding.

The refractory base component may comprise one or more
5 refractory substances, for example substances based on the system Al_2O_3 - SiO_2 (acidic refractory materials) or based on basic refractory materials, for example materials based on MgO .

An important field of use for unformed refractory materials
10 is the use thereof as tundish compositions or tundish wear lining compositions. For this purpose, in particular basic compositions are used, which then form the refractory inner lining of the tundish.

Cold curing compositions are also used for tundish
15 compositions. The advantage of cold curing compositions is in particular that no additional thermal energy has to be applied to initiate binding in the composition. Instead, with these composition types one or more liquid adhesive binders are regularly used, for example water glass,
20 synthetic resin and sulfur- or phenol-containing binders. However, the disadvantage of these binders is that handling both of the binders and of the unformed refractory material mixed therewith is very complex. The reason for this is in particular also the adhesive properties of the binders,
25 which may result in the machinery in which the binders, and the unformed refractory material mixed therewith, are processed becoming stuck up by the binders. For this reason, complicated and thus expensive machinery has often to be used, for example expensive mixing machines, which
30 have in addition to be regularly cleaned. In addition, some of these liquid adhesive binders constitute an odour

nuisance or are flammable or toxic, such that the machinery for handling the binders or the compositions mixed therewith has to be elaborately enclosed. Also, some of these binders have to be stored under permanently cool
5 conditions, since otherwise undesired curing or consolidation of the binder may occur before the binder has been added to the composition. Conversely, it is also sometimes necessary to heat the unformed refractory material mixed with such liquid adhesive binders in order
10 to initiate the binding reaction of the binders.

The object of the present invention is to provide a cold curing composition, i.e. an unformed refractory material usable without the use of external thermal energy, which may be used without the use of liquid adhesive binders. In
15 particular, it is intended that no liquid binders should be needed for mixing the unformed refractory material which constitute an odour nuisance or are toxic or flammable. In addition, the unformed refractory material is intended to be usable without the use of additional external thermal
20 energy, i.e. to consolidate or cure without the use of additional external thermal energy.

This object is achieved by the provision of an unformed refractory material in the form of a dry mixture with
- a refractory base component and
25 - a binder agent component, the binder agent component comprising an acid component and a basic component.

The fundamental consideration underlying the present invention is to provide such a binder agent component in the unformed refractory material, which binder comprises an
30 acidic component and a basic component. The use of such a binder component is based on the recognition that a binder

may be produced from an acidic component and a basic component solely by the addition of water (mixing water), which binder leads to consolidation or curing of the unformed refractory material.

- 5 The unformed refractory material according to the invention therefore requires mixing solely with water, in order to obtain a ready-to-use, plastic unformed refractory material. The use of liquid adhesive binders is therefore no longer necessary. The above-stated disadvantages, which
10 arise when liquid adhesive binders are used, are thus completely eliminated.

- It has emerged that such an excellent binder may be produced from a binder component composed according to the invention in that, in accordance with a preferred
15 embodiment of the invention, the binder component of the material according to the application does not comprise any further component in addition to the acidic component and the basic component (while as yet unmixed with water).

- The acid component is preferably a component which exhibits
20 an acidic action in an aqueous environment or in aqueous solution. The acid component is present in the form of at least one of the following substances: acid, salt of an acid, ester of an acid as sulphonate, sulphate or carbonate.

- 25 The unformed refractory material particularly preferably comprises an acid component in the form of at least one acid, preferably in the form of at least one weak to moderately weak organic acid, in particular in the form of a weak organic acid.

For example, an acid component may be provided in the form of at least one of the following substances: citric acid, amidosulfonic acid, malic acid, tartaric acid, formic acid, acetic acid, oxalic acid, boric acid, sodium bicarbonate,
5 lignin sulfonate, hydrogenphosphate, hydrogensulfate, sodium metaphosphate.

The above-stated acid components may be used in any desired combination as an acid component. A preferred combination of acid components is for example the combination of
10 amidosulfonic acid and boric acid.

The basic component is preferably a component which exhibits a basic action in an aqueous environment or in aqueous solution. The basic component is present in the form of at least one of the following substances: urotropin
15 (hexamethylenetetramine), calcium oxide, calcium hydroxide, sodium hydroxide, potassium hydroxide or magnesium hydroxide.

The above-stated basic components may be used in any desired combination as a basic component.

20 The above-stated acidic and basic components may be used in any desired combination as a binder component.

For example, the binder component of the unformed refractory material may comprise one of the following combinations of acidic and basic components:

25

citric acid and hydrated lime;
citric acid and calcium oxide;
sodium metaphosphate and hydrated lime;
amidosulfonic acid, boric acid and hydrated lime.

Particularly preferably, the unformed refractory material comprises an acid component in the form of at least one acid and a basic component in the form of at least one base, which react together in an acid-base reaction only when water is added. In particular, an acidic component in the form of at least one acid and a basic component in the form of at least one base may be provided, which react in an exothermic reaction, in particular an exothermic acid-base reaction, when water is added. The particular advantage of such an exothermic reaction is that, as a result of the accompanying increase in temperature, the time needed for curing of the unformed refractory material may be reduced markedly relative to the curing time of unformed refractory materials according to the prior art, in which no exothermic reaction of an acidic and a basic component may be initiated with water.

It has emerged according to the invention that a particularly advantageous course of consolidation or particularly favourable curing may be achieved for the material according to the invention in that the above-stated exothermic reaction increases the temperature of the material by at least 5°C, i.e. for example also by at least 8°C or by at least 10°C. In addition, the temperature of the material may be increased by the exothermic reaction by at most 30°C, i.e. for example also by at most 18°C. As a result of the exothermic reaction, the temperature of the material may accordingly be increased for example by 5 to 30°C, by 8 to 30°C or for example by 10 to 30°C. In other words, the acid component and the basic component of the unformed refractory material are tailored to one another in such a way that they react together once water has been added in such an exothermic reaction, in particular in an

acid-base reaction, that the temperature of the material is increased by the above-stated temperature range by this reaction. When this temperature increase takes place, curing of the unformed refractory material proceeds
5 sufficiently quickly, but not too quickly and also not with a violent reaction of the acidic and basic component with water.

The proportion of acid component in the unformed refractory material is 1.5 to 6 wt.%.

- 10 Unless otherwise stated herein, the proportions in wt.% relate in principle to the total weight of the unformed refractory material (without water).

The proportion of basic component in the material is 1 to 4 wt.%.

- 15 The acid component and the basic component of the binder component are preferably present in the unformed refractory material in such proportions that they neutralise one another completely once water has been added, thus for example they in particular react together in such a way in
20 an acid-base reaction that, once the reaction is complete, virtually no acid component and no basic component of the binder component any longer remains in the refractory material, or at most in extremely small residual quantities, for example in proportions of ≤ 1 wt.%, of
25 ≤ 0.5 wt.% or of only ≤ 0.1 wt.%.

Preferably, the acid component and the basic component of the binder component are readily water-soluble, such that these may dissolve readily in the mixing water and react together completely.

Reaction of the acid component and the basic component may be improved still further if they assume finely divided form, preferably uniformly distributed in the unformed refractory material. According to one embodiment, the acid component and the basic component of the binder component
5 assume finely divided form, preferably with an upper grain limit of 1000 μm or of 500 μm , determined to DIN 52 098.

The acid component and the basic component accordingly preferably assume a dry or flowable or pourable form in the
10 unformed refractory material.

In addition, the acid component and the basic component assume a storage-stable form in the unformed refractory material, such that the unformed refractory material (when not mixed with water) may be simply stored and transported,
15 without the acid component and the basic component (in the dry state) reacting together or with the refractory base component.

The total proportion of binder component in the unformed refractory material may be for example $\geq 1 \text{ wt.}\%$, thus for
20 example also $\geq 1.5 \text{ wt.}\%$, $\geq 2 \text{ wt.}\%$, $\geq 2.5 \text{ wt.}\%$, $\geq 3 \text{ wt.}\%$ or $\geq 3.5 \text{ wt.}\%$. The maximum quantity of binder component in the material may for example be 20 wt.%, thus for example also $\leq 18 \text{ wt.}\%$, $\leq 16 \text{ wt.}\%$, $\leq 14 \text{ wt.}\%$, $\leq 12 \text{ wt.}\%$, $\leq 10 \text{ wt.}\%$, $\leq 8 \text{ wt.}\%$ or $\leq 6 \text{ wt.}\%$. The proportion of binder component in
25 the material may accordingly lie for example in the range from 1 to 20 wt.%, thus for example also in the range from 1.5 to 16 wt.%, 1.5 to 12 wt.% or in the range from 2 to 10 wt.%.

In principle, the refractory base component of the unformed
30 refractory material may be any desired refractory base

component, in particular an inorganic refractory base component.

Preferably, the refractory base component in the unformed refractory material is a basic refractory base component,
5 preferably an MgO-based refractory base component.

A basic refractory base component may be based for example on at least one of the following substances: magnesia (in particular sintered magnesia), magnesia-spinel, doloma, olivine, limestone.

- 10 The proportion of refractory base component in the unformed refractory material may be for example ≥ 88 wt.%, thus for example also ≥ 90 wt.% or ≥ 92 wt.%. The maximum proportion of refractory base component may be for example ≤ 98.5 wt.%, thus for example also ≤ 97 wt.% or ≤ 96 wt.%.
15 Accordingly, the proportion of refractory base component in the material may accordingly lie for example in the range from 88 to 98.5 wt.%, thus for example also in the range from 90 to 97 wt.% or in the range from 92 to 96 wt.%.

- The refractory base component may be present for example in
20 a grain size of ≤ 5 mm and for example in a grain size of > 0.5 mm or > 1 mm. The refractory base component may accordingly be present for example in a grain size of > 0 to 5 mm, > 0 to 3 mm, > 0 to 1 mm, > 1 to 5 mm or > 1 to 3 mm.

- 25 The unformed refractory material (not mixed with water) preferably assumes pourable form, thus as a flowable or crumbly composition or as a dry mixture.

To produce a ready-to-use, i.e. earth-moist (plastic) composition from the unformed refractory material according

to the invention, the latter is mixed with water.
Preferably, such a quantity of water is added to the material that said material takes on an earth-moist, in particular an earth-moist, crumbly consistency. The
5 material is mixed with a quantity of water of 1 to 5 wt.%.

A method of producing an earth-moist unformed refractory material from the unformed refractory material according to the invention may for example comprise the following successive steps:

- 10 - producing the unformed refractory material described herein;
- mixing the material with 1 to 5 wt.% water to produce an earth-moist unformed refractory material.

As explained above, the unformed refractory material may be
15 mixed in particular with such a quantity of water that it takes on an earth-moist consistency.

For this purpose, the unformed refractory material may preferably be mixed with the above-stated quantities of water.

20 Water may preferably be added to the unformed refractory material in a mixer, in particular for example in a compulsory mixer or a continuous mixer, or in a spraying machine, for example a pressure sprayer, in which the water is preferably added at the end of the hose.

25 The unformed refractory material may preferably be used for template backfilling. Accordingly, the unformed refractory material mixed with water, i.e. in a plastic (earth-moist) state, may be introduced in a further step behind a template in particular immediately or shortly after mixing.

In particular, the unformed refractory material may be used for template backfilling in a tundish.

The earth-moist unformed refractory material displays extremely favourable curing behaviour. The earth-moist refractory material accordingly displays such strength after a relatively short time that it does not have to be held in shape by further auxiliary means, such as for example templates. For example, the earth-moist refractory material may be left to cure for a period of only ≥ 10 minutes, thus for example also for a period of ≥ 30 minutes or ≥ 1 hour. The maximum curing time amounts for example to ≤ 4 hours, thus for example also to ≤ 3 hours or ≤ 2 hours. The curing time accordingly amounts to for example 10 minutes to 4 hours, thus for example also 30 minutes to 2 hours.

After consolidation or curing, any auxiliary means with which the earth-moist refractory material is held in shape may be removed, for example templates may be withdrawn. The cured refractory material is then ready for use.

The unformed refractory material is also distinguished in particular in that the water may be added thereto at room temperature, i.e. the unformed refractory material does not have to be heated externally in order, once water has been added to the material, to cause the binder component to perform its binding action. Instead, in the case of the unformed refractory material according to the invention, an exothermic reaction of the acid component and the basic component may supply any increased material temperature needed once water has been added.

The unformed refractory material may in principle be used in any desired manner. Use of the unformed refractory material as a tundish composition is preferably provided. For instance, the unformed refractory material may be used
5 as a tundish composition for monolithic structures or for repairs.

The following formulations demonstrate four examples of compositions for unformed refractory materials according to the invention:

10 Example 1:

Component	Material	Proportion [wt.%]
Base component	Sintered magnesia	72
Base component	Olivine	22
Acid component	Citric acid	4
Basic component	Hydrated lime	2

Example 2:

Component	Material	Proportion [wt.%]
Base component	Sintered magnesia	73
Base component	Olivine	22
Acid component	Boric acid	1
Acid component	Amidosulfonic acid	2
Basic component	Hydrated lime	2

Example 3:

Component	Material	Proportion [wt.%]
Base component	Sintered magnesia	72
Base component	Olivine	22
Acid component	Sodium metaphosphate	4
Basic component	Hydrated lime	2

Example 4:

Component	Material	Proportion [wt.%]
Base component	Sintered magnesia	72
Base component	Olivine	24
Acid component	Sodium metaphosphate	2
Basic component	Calcium oxide	2

The unformed refractory material according to the four above-stated formulations was mixed in each case with the addition of 3 wt.% mixing water in a laboratory mixer and the following investigations of the course of setting were
5 performed:

Consolidation is determined using an apparatus to DIN-EN 1015-4 (1998) "Test methods for mortar for masonry, Part 4, Determination of consistency of fresh mortar (by plunger penetration)" at 2-minute intervals. The interval of time
10 calculated from the addition of water until a falling weight penetration depth of ≤ 1 mm is achieved is the consolidation time. The increase in temperature caused by the exothermic acid-base reaction was measured by means of a temperature sensor additionally installed in the test
15 specimen mould.

The results achieved with the test mixtures were as follows:

For Example 1:

Temperature increase: 12-26°C

20 Consolidation time: 8-14 min

For Example 2:

Temperature increase: 8-18°C

Consolidation time: 30-40 min

For Example 3:

25 Temperature increase: 14-28°C

Consolidation time: 10-16 min

For Example 4:

Temperature increase: 7-15°C

Consolidation time: 18-26 min

For testing with regard to application as a tundish composition, the same batches were produced in sufficient quantities and, after mixing with 3 wt.% mixing water, the earth-moist unformed refractory materials obtained in each
5 case were used for template backfilling in a tundish.

The consolidation times determined in this case (calculated from the addition of the mixing water to the earliest time at which it was possible to withdraw the template) and the temperature increase measured in each case were as follows:

10 For Example 1:

Temperature increase: 15-22°C

Consolidation time: 10-15 min

For Example 2:

Temperature increase: 5-18°C

15 Consolidation time: 40-50 min

For Example 3:

Temperature increase: 15-25°C

Consolidation time: 10-15 min

For Example 4:

20 Temperature increase: 10-20°C

Consolidation time: 15-25 min

Szabadalmi igénypontok:

1. Formázatlan tűzálló anyag, amelynek van
 - a. egy tűzálló báziskomponense és
 - b. egy kötőanyag komponense, ahol a kötőanyag komponens az anyaghoz viszonyítva tartalmaz
 - b1. egy savas komponenst a következő anyagoknak legalább egyikéből: sav, só és/vagy észtere egy savnak mint szulfonát, szulfát vagy karbonát, 1,5 – 6 tömeg% részarányban,
 - b2. egy bázikus komponenst a következő anyagok legalább egyikének a formájában: urotropin, kalcium-oxid, kalcium-hidroxid, nátrium-hidroxid, kálium-hidroxid, magnézium-hidroxid 1 – 4 tömeg% részarányban, és
 - c. 1 – 5 tömeg% víznek a hozzáadásával egy földnedves, porhanyós konzisztenciát kap és a kötőanyag komponensnek egy exoterm reakcióját követően megszilárdítható.
2. Az 1. igénypont szerinti anyag, amelynek a savas komponense legalább egy szerves sav formájában van jelen, amelynek erőssége gyengétől a közepesen gyengéig terjed.
3. Az 1. igénypont szerinti anyag, amelynek a savas komponense a következő savak legalább egyikének formájában van: citromsav, amidoszulfonsav.
4. Az 1. igénypont szerinti anyag, amelynél a kötőanyag komponensnek a savas komponens és a bázikus komponens mellett további kötőanyag komponense nincs.
5. Az 1. igénypont szerinti anyag, amelynek a savas komponense legalább egy sav formájában és amelynek bázikus komponense legalább egy bázis formájában van, amelyek víznek az anyaghoz való hozzáadása mellett egy sav-bázis reakcióban reagálnak.
6. Az 1. igénypont szerinti anyag, amelynek a savas komponense legalább egy sav formájában és amelynek bázikus komponense legalább egy bázis formájában van,

amelyek víznek az anyaghoz való hozzáadása mellett egy exoterm reakcióban reagálnak.

7. A 6. igénypont szerinti anyag, amelynél az exoterm reakció folytán az anyag hőmérséklete 5 – 30 °C –kal növelhető.

8. Az 1. igénypont szerinti anyag, amelynek egy bázikus tűzálló báziskomponense van.

9. Az 1. igénypont szerinti anyag, amelynek egy bázikus tűzálló báziskomponense van, amelynek alapja a következő anyagoknak legalább egyike: égetett magnézia, olivin.

10. Eljárás földnedves formázatlan tűzálló anyag előállítására, amely a következő egymás utáni lépéseket tartalmazza:

A. Egy 1. igénypont szerinti anyag előállítása;

B. Az anyagnak a bekeverése 1 – 5 tömeg% vízzel egy földnedves formázatlan tűzálló anyagnak az előállítására.