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(54) Title: CALCIUM SULPHATE-BASED PRODUCTS

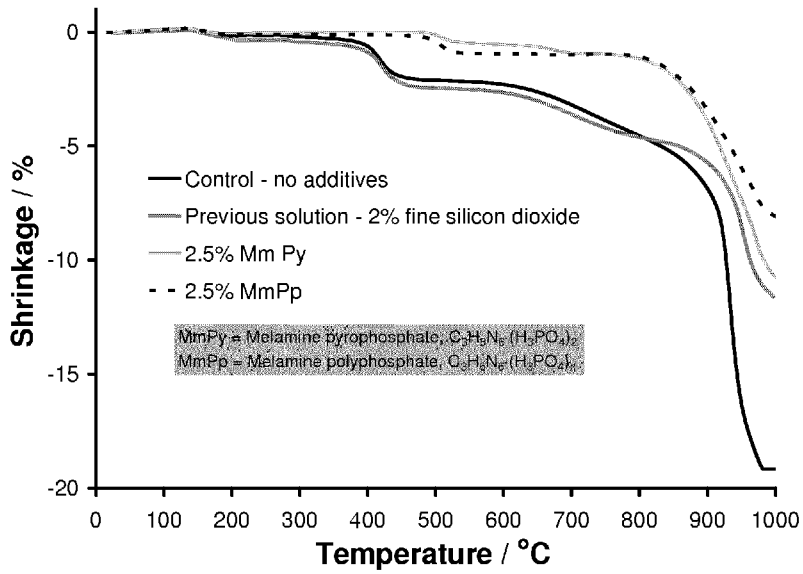

Figure 3

(57) Abstract: This invention relates to improved high temperature resistant calcium sulphate-based products e.g. gypsum wallboard products and, in particular, to products having reduced shrinkage at high temperatures. The invention provides calcium sulphate-based product comprising gypsum and a shrinkage resistance additive. The shrinkage resistance additive is melamine polyphosphate or melamine pyrophosphate.

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))*

CALCIUM SULPHATE-BASED PRODUCTS

This invention relates to improved high temperature resistant calcium sulphate-based products and, in particular, to calcium sulphate-based products having reduced shrinkage at high temperatures.

BACKGROUND

Calcium sulphate-based products are widely used in the construction of buildings, for example, to form internal partitions (using wallboard, also known as dry wall, gypsum board or plaster board) and ceilings or to encase ducts (e.g. ventilation ducts) within buildings.

Calcium sulphate-based products such as wallboard are typically formed by drying an aqueous slurry of the hemihydrate of calcium sulphate ($CaSO_4.½\ H_2O$), also known as calcined gypsum or stucco, between two sheets of lining paper or fibreglass matting. As the slurry dries and the calcined gypsum is hydrated, a hard, rigid core of gypsum (calcium sulphate dihydrate - ($CaSO_4.2H_2O$)) sandwiched between the lining sheets/mats is formed.

When wallboard or ceiling tiles are exposed to high temperatures such as those experienced in a building fire or those experienced by wallboards used for encasing ducts carrying high temperature fluids, the water of crystallization contained within the gypsum is driven off to yield the anhydrite of calcium sulphate. Initially, this has the advantage that heat transfer across the wallboard/ceiling tile is reduced thus helping to contain the heat emanating from ducting or generated during a building fire. However, at temperatures around 400-450°C, the initially formed AIII phase anhydrite (also known as γ-$CaSO_4$ or "soluble" anhydrite) converts to the AII phase (or "insoluble" anhydrite) and this phase change results in shrinkage of the wallboard/tile i.e. a loss of dimensional stability. This shrinkage (which may be around 2% of the wallboard's/tile's length or width, or around 6% of the wallboard's volume) often causes the wallboards to pull away from their supporting structures. This is

obviously undesirable. It can leave ducts exposed to high temperatures. Furthermore, in situations where wallboard is used for internal partitions and a fire breaks out, shrinkage can leaves gaps exposing rooms adjacent to the fire source to the effects of the heat/fire. Gaps also allow ingress of oxygen into the fire source thus fuelling the fire and negating the effects of any fire doors.

At higher temperatures (in excess of 600°C), the insoluble anhydrite goes on to sinter resulting in large reductions in wallboard volume. This results in extreme shrinkage which eventually causes collapse of the internal walls/ceilings/duct casings as they are no longer held by their supporting structures.

Efforts have been made to improve the heat resistance of calcium sulphate-based products such as wallboard in an attempt to reduce shrinkage.

It is known e.g. from EP0258064 to use micro silica as an additive in the gypsum core of wallboard to reduce shrinkage.

However, these additives only have an effect at temperatures greater than 600°C i.e. they do not resist the shrinkage of the board at lower temperatures and linear shrinkage of more than 10% is still seen as temperatures around 1000°C.

It is known from WO99/08979 and WO00/06518 to add sodium trimetaphosphate (STMP), sodium hexametaphosphate (SHMP) or ammonium polyphosphate (APP) to a calcium sulphate wallboard core to improve strength, sag resistance and shrinkage during drying. No effect of these additives on shrinkage during exposure to high temperatures is recorded. The trimetaphosphate ions and APP were found to accelerate the rate of hydration of calcined gypsum thus decreasing the set time for the wallboard core.

WO2012/069826 discloses use of aluminium and ammonium phosphate additives for enhancing fire resistance of calcium sulphate-based products. Ammonium polyphosphate (APP) was found to reduce hydration time of the calcined gypsum and accelerate setting time.

Calcium sulphate-based products are also used to cast metal objects. Calcium sulphate moulds are heated to 700-900°C prior to being filled with molten metal. It is important to control high temperature shrinkage of such calcium sulphate-based moulds to ensure that the moulds do not leak and to ensure that the cast metal products are not warped.

A preferred aim of the present invention is to provide an improved heat resistant calcium sulphate-based product having reduced shrinkage after heat exposure e.g. when in contact with ducting, during a building fire or during casting of metal products. Such an improved heat resistant product may have particular use as wallboard or panels for forming internal partitions in buildings, ceiling tiles, wallboard or panels for encasing ventilation/smoke extraction ducting, joint filler materials for joining wallboard/panels/tiles or for moulds for use in metal product casting.

SUMMARY OF THE INVENTION

Accordingly, in a first aspect, the present invention provides a calcium sulphate-based product comprising gypsum and a shrinkage resistance additive wherein the shrinkage resistance additive is melamine polyphosphate or melamine pyrophosphate.

Melamine polyphosphate is $C_3H_6N_6 \cdot (H_3PO_4)_n$ where n is greater than 2. Melamine pyrophosphate is $C_3H_6N_6 \cdot (H_3PO_4)_n$ where n is two.

The inventors have found that including melamine polyphosphate (MPP) or melamine pyrophosphate in the calcium sulphate based products e.g. the gypsum core of a wallboard reduces shrinkage of the wallboard when the board is exposed to high temperatures. Unlike micro silica which only has an effect above 600°C, MPP/melamine pyrophosphate begins to have an effect around 350°C where it undergoes an endothermic decomposition (to yield phosphoric acid) and thus acts as a heat sink. The MPP also acts to increase the temperature at which the transition from the soluble to insoluble calcium sulphate anhydrite occurs thus allowing the product to resist the shrinkage arising from the phase change until higher temperatures (around 800°C) are reached.

The term "calcium sulphate-based product" may include wallboards (with or without liners) (with or without fibrous reinforcement), tiles (e.g. ceiling tiles), duct encasement panels, joint filler materials (e.g. for joining adjacent wallboards/tiles/panels etc.) and moulds for casting metal products.

The calcium sulphate–based product may be a composite product e.g. it may be a wallboard having a gypsum matrix core (containing the shrinkage resistance additive) sandwiched between two liners (e.g. paper liners or fibreglass matting).

The term "gypsum" is intended to refer predominantly to calcium sulphate dihydrate ($CaSO_4.2H_20$).

MPP is used as the shrinkage resistance additive in preferred embodiments. Unlike APP which has been found to accelerate the setting of the hemihydrate (calcined gypsum) to the dihydrate (gypsum) of the gypsum, it has been found that MPP does not cause any acceleration. Acceleration of the setting is undesirable because it restricts the possible addition level and gives the production plant less control over their processes. In fact, MPP has been found to cause a slight retardation of the setting.

Preferably, the MPP/melamine pyrophosphate shrinkage resistance additive is included in an amount from 0.1 to 20 wt%, preferably 1 to 10wt%, more preferably 1 to 5 wt% and most preferably 2 to 5 wt%.

Preferably, the calcium sulphate-based product does not contain glass fibres. The glass fibres are typically used form a mechanical network within the gypsum which helps maintain the structural integrity of the product after exposure to heat. However, the present inventors believe that the inclusion of MPP/melamine pyrophosphate may reduce shrinkage by such an amount that the structural integrity can be maintained without using glass fibres.

The calcium sulphate-based product may contain additives such as accelerators to off-set the slight retardation of the set time observed for MPP. The accelerators may be, for example, freshly ground gypsum having an additive of sugar or surfactant. Such accelerators may include Ground Mineral NANSA (GMN), heat resistant accelerator (HRA) and ball milled accelerator (BMA). Alternatively, the accelerator may be a chemical additive such as aluminium sulphate, zinc sulphate or potassium sulphate. In certain cases, a mixture of accelerators may be used, e.g. GMN in combination with a sulphate accelerator. As a further alterative, ultrasound may be used to accelerate the setting rate of the slurry, e.g. as described in US2010/0136259.

In a second aspect, the present invention provides a method of forming a calcium sulphate-based product by drying an aqueous slurry comprising calcined gypsum and shrinkage resistance additive wherein the shrinkage resistance additive is melamine polyphosphate or melamine pyrophosphate.

The term “calcium sulphate-based product” may include wallboards (with or without liners) (with or without fibrous reinforcement), tiles (e.g. ceiling tiles), duct encasement panels, joint

filler materials (e.g. for joining adjacent wallboards/tiles/panels etc.) and moulds for casting metal products.

The calcium sulphate–based product may be a composite product e.g. it may be a wallboard having a gypsum matrix core (containing the shrinkage resistance additive) sandwiched between two liners (e.g. paper liners or fibreglass matting). In this embodiment, the method comprises drying an aqueous slurry comprising calcined gypsum and MPP between two liners (e.g. paper liners or fibreglass matting).

The term "calcined gypsum" is intended to refer predominantly to calcium sulphate hemihydrate ($CaSO_4.2H_2O$) but may also encompass any other calcium sulphate compound having a lower bound water content than calcium sulphate dihydrate (e.g. calcium sulphate anhydrite).

Preferably, the MPP/melamine pyrophosphate shrinkage resistance additive is included in the slurry in an amount from 0.1 to 20 wt%, preferably 1 to 10wt%, more preferably 1 to 5 wt% and most preferably 2 to 5 wt%.

The preferred shrinkage resistance additive is MPP. This has been found not to accelerate the setting time of calcined gypsum, unlike APP.

The calcium sulphate-based product preferably contains no glass fibres. The glass fibres are typically used to form a mechanical network within the gypsum which helps maintain the structural integrity of the product after exposure to heat. The present inventors believe that the addition of MPP/melamine pyrophosphate reduces high temperature shrinkage to such an extent that the glass fibres are no longer necessary. Therefore, preferably, the method comprises drying an aqueous slurry comprising gypsum and MPP/melamine pyrophosphate in the absence of inorganic (glass) fibres.

The method may comprise adding glass matting to the slurry prior to drying. The slurry is typically dried in a mould. The matting may be added by laying it onto the surface of the slurry after some or all of the slurry has been added to the mould or it may be laid in the bottom of the mould before the slurry is added. If the matting is laid in the base of the empty mould or laid on the surface of the slurry of the full mould then the matting will rest at the surface of the gypsum core. If it is added to the mould when only some of the slurry has been added, it will be embedded within the gypsum core.

The calcium sulphate-based product may contain additives such as accelerators. The accelerators may be, for example, freshly ground gypsum having an additive of sugar or surfactant. Such accelerators may include Ground Mineral NANSA (GMN), heat resistant accelerator (HRA) and ball milled accelerator (BMA). Alternatively, the accelerator may be a chemical additive such as aluminium sulphate, zinc sulphate or potassium sulphate. In certain cases, a mixture of accelerators may be used, e.g. GMN in combination with a sulphate accelerator. In these embodiments, the method comprises drying an aqueous slurry comprising gypsum, MPP/melamine pyrophosphate and accelerator, optionally between two liners as discussed above. Glass matting may also be included (as discussed above) along with the accelerator.

In a third aspect, the present invention provides the use of melamine polyphosphate/melamine pyrophosphate as an additive in a gypsum matrix for reducing shrinkage in a calcium sulphate-based product during heat exposure.

Preferably, the MPP/melamine pyrophosphate is used as an additive for reducing shrinkage in a composite wallboard having a gypsum core (containing MPP/melamine pyrophosphate) sandwiched between two liners (e.g. paper liners or fibreglass matting).

Preferably, an amount of from 0.1 to 20 wt%, preferably 1 to 10wt%, more preferably 1 to 5 wt% and most preferably 2 to 5 wt% MPP/melamine pyrophosphate is used to reduce shrinkage in the product.

DESCRIPTION OF THE DRAWINGS

Figure 1 shows a graph of area shrinkage for the control and MPP samples after heating to 1000°C and subsequent cooling;

Figure 2 shows a graph of linear shrinkage for the control and MPP samples during heating to 1000°C; and

Figure 3 shows a graph of linear shrinkage for the control, MPP and melamine pyrophosphate samples during heating to 1000°C

EXPERIMENTAL

The following examples are given by way of illustration only.

Control sample 1

1500g of stucco was blended with 0.1wt% (relative to the weight of the stucco) ground gypsum accelerator (GMN – Ground mineral NANSA) and added to 1350g of water at 40°C. This was mixed for 10 seconds in a large Waring blender and the resulting slurry was poured 100 x 50 x 11mm and 200 x 200 x 12.5mm brass moulds to harden. The thumb set was less than 10 minutes. The thumb set is taken by depressing a thumb end onto a portion of the setting gypsum. The time is recorded when sufficient strength is attained such that an impression can no longer be made in the setting gypsum. After leaving the samples to hydrate for an hour, they were transferred to an oven at 40°C and left to dry overnight (at least 12 hours).

Control sample 2

1500g of stucco was blended with 0.1wt% ground gypsum accelerator. 0.5wt% (based on the weight of the stucco) (i.e. 7.5g) Johns Manville glass fibres were dispersed in 1350g of water at 40°C for 10 seconds and then the dry blend was added. This was mixed for 10 seconds in a large Waring blender and the resulting slurry was poured 100 x 50 x11mm and 200 x 200 x 12.5mm brass moulds to harden. The thumb set was less than 10 minutes. After leaving the samples to hydrate for an hour, they were transferred to an oven at 40°C and left to dry overnight (at least 12 hours).

MPP sample 1

1500g of stucco was blended with 0.3wt% (based on the weight of stucco) ground gypsum accelerator. 2.5wt% MPP (based on weight of stucco) was dispersed in 1350g of water at 40°C for 10 seconds and then the dry blend was added. This was mixed for 10 seconds in a large Waring blender and the resulting slurry was poured 100 x 50 x 11mm and 200 x 200 x 12.5mm brass moulds to harden. The thumb set was less than 10 minutes. After leaving the samples to hydrate for an hour, they were transferred to an oven at 40°C and left to dry overnight (at least 12 hours).

MPP sample 2

1500g of stucco was blended with 0.3wt% (based on the weight of stucco) ground gypsum accelerator. 0.5% Johns Manville glass fibres and 2.5wt% MPP (based on weight of stucco) were dispersed in 1350g of water at 40°C for 10 seconds and then the dry blend was added. This was mixed for 10 seconds in a large Waring blender and the resulting slurry was poured 100 x 50 x11mm and 200 x 200 x12.5mm brass moulds to harden. The thumb set was less than 10 minutes. After leaving the samples to hydrate for an hour, they were transferred to an oven at 40°C and left to dry overnight (at least 12 hours).

MPP sample 3

1500g of DSG Stucco was blended with 0.5wt% (based on the weight of stucco) ground gypsum accelerator. 5wt% MPP (based on weight of stucco) was dispersed in 1350g of water at 40°C for 10 seconds and then the dry blend was added. This was mixed for 10 seconds in a large Waring blender and the resulting slurry was poured 100 x 50 x11mm and 200 x 200 x12.5mm brass moulds to harden. The thumb set was less than 10 minutes. After leaving the samples to hydrate for an hour, they were transferred to an oven at 40°C and left to dry overnight (at least 12 hours).

MPP sample 4

1500g of DSG Stucco was blended with 0.5wt% (based on the weight of stucco) ground gypsum accelerator. 0.5% Johns Manville glass fibres and 5wt% MPP (based on weight of stucco) were dispersed in 1350g of water at 40°C for 10 seconds and then the dry blend was added. This was mixed for 10 seconds in a large Waring blender and the resulting slurry was poured 100 x 50 x11mm and 200 x 200 x12.5mm brass moulds to harden. The thumb set was less than 10 minutes. After leaving the samples to hydrate for an hour, they were transferred to an oven at 40°C and left to dry overnight (at least 12 hours).

	Control 1	Control 2	MPP 1	MPP 2	MPP 3	MPP 4
Calcined gypsum/g	1500	1500	1500	1500	1500	1500
Water/g	1350	1350	1350	1350	1350	1350
Accelerator/g	1.5	1.5	4.5	4.5	7.5	7.5
Glass Fibres/g	-	7.5	-	7.5	-	7.5
MPP/g	-	-	37.5	37.5	75	75

Table 1 – Summary of MPP Samples

Melamine pyrophosphate sample 1

2.5wt% melamine pyrophosphate (based on weight of stucco) was dispersed in 140mL of tap water for 5 minutes using an Ultra-Turrax high shear mixer and then 200g of stucco was added. This was mixed by hand for 1 minute and the resulting slurry was formed into 12.5 mm diameter gypsum cylinders. They were transferred to an oven at 40°C and left to dry overnight (at least 12 hours).

For comparison with this melamine pyrophosphate, gypsum cylinders a) as above but with no melamine pyrophosphate, b) as above but with 2.5 wt% MPP instead of melamine pyrophosphate and c) as above but with no melamine pyrophosphate and 2.0wt% (based on weight of stucco) micro silica. The results of the comparison are discussed below and shown in Figure 3.

Area Shrinkage

For each of the 100 x 50 x 11 mm samples, the initial measurements (length and width) were recorded and then the samples heated to around 1000°C over 120 mins (at 20°C/min up to around 200°C and thereafter at a steadily and slowly decreasing rate). After cooling, the sample's dimensions were re-measured. The area shrinkage was calculated as the difference between the initial area of the sample and the heat treated sample and is shown in Figure 1.

It can be seen that all samples containing MPP showed a considerable reduction in area shrinkage compared to the control samples containing no MPP. The reduction in shrinkage is achieved with as little as 2.5 wt% MPP. Indeed, doubling the amount of MPP to 5wt% does not show a significant further reduction in area shrinkage.

The samples were inspected for cracks and the results are shown below in Table 2.

	Observations
Control sample 1	Numerous visible cracks – some very wide - sample disintegrated
Control sample 2	Numerous visible cracks
MPP sample 1	A couple of very fine cracks
MPP sample 2	A couple of very fine cracks
MPP sample 3	A couple of very fine cracks
MPP sample 4	A couple of very fine cracks

Table 2 – Observations after heating to 1000°C

Linear Shrinkage

The linear shrinkage of the 200 x 200 x12.5mm samples was measured using a ceramic rod attached to a linear displacement transducer. The samples were supported by other ceramic rods and the heated in a furnace to 1000°C at an initial rate of around 44°C/min up to around 600°C and then at a steadily and slowly decreasing rate (in line with ISO 834). The results are shown in Figure 2.

It can be seen that the linear shrinkage at 1000°C is reduced to around 5% for all samples containing MPP. The biggest reduction in linear shrinkage was seen in the samples containing 5% MPP.

Figure 3 shows the linear shrinkage results for melamine pyrophosphate. It can be seen that the reduction in shrinkage is comparable to that obtained with the MPP i.e. a shrinkage of around 10% compared to around 19% for the control sample (with no melamine pyrophosphate).

CLAIMS

1. A calcium sulphate-based product comprising gypsum and a shrinkage resistance additive wherein the shrinkage resistance additive is melamine polyphosphate or melamine pyrophosphate.

2. A product according to claim 1 wherein the shrinkage resistance additive is provided in an amount from 0.1 to 20 wt%.

3. A product according to claim 2 wherein the shrinkage resistance additive is provided in an amount from 2 to 5wt%.

4. A product according to any one of claims 1 to 3 comprising substantially no glass fibres.

5. A product according to any one of the preceding claims further comprising an accelerator.

6. A product according to any one of the preceding claims wherein the product is a wallboard, panel, tile, joint filler material or mould for metal casting.

7. A product according to claim 6 wherein the product is a composite wallboard comprising a core of the gypsum and shrinkage resistance additive sandwiched between two liners.

8. A method of forming a calcium sulphate-based product by drying an aqueous slurry comprising calcined gypsum and a shrinkage resistance additive wherein the shrinkage resistance additive is melamine polyphosphate or melamine pyrophosphate.

9. A method according to claim 8 wherein the aqueous slurry contains melamine polyphosphate in an amount from 0.1 to 20wt%.

10. A method according to claim 9 wherein the aqueous slurry contains melamine polyphosphate in an amount from 2 to 5wt%.

11. A method according to any one of claims 8 to 10 wherein the aqueous slurry comprises substantially no glass fibres.

12. A method according to any one of claims 8 to 11 wherein the aqueous slurry the further comprises an accelerator.

13. A method according to any one of claims 8 to 11 wherein the product is a wallboard, tile, panel, joint filler material or mould for casting metal.

14. A method according to claim 13 wherein the product is a composite wallboard and the method comprises drying the aqueous slurry between two liners.

15. Use of melamine polyphosphate or melamine pyrophosphate as an additive in a gypsum matrix for reducing shrinkage in a calcium sulphate-based product during heat exposure.

16. Use according to claim 15 wherein the calcium sulphate-based product is a wallboard, tile, panel, joint filler material or mould for casting metal.

17. Use according to claim 15 or 16 wherein an amount of from 0.1 to 20 wt% of the additive is used for reducing shrinkage.

18. Use according to claim 17 wherein an amount of from 2 to 5 wt% of the additive is used for reducing shrinkage.

19. Calcium sulphate-based product substantially as any one embodiment herein described.

20. Method of forming a calcium sulphate-based product substantially as any one embodiment herein described.

21. Use of melamine polyphosphate or melamine pyrophosphate substantially as any one embodiment herein described.

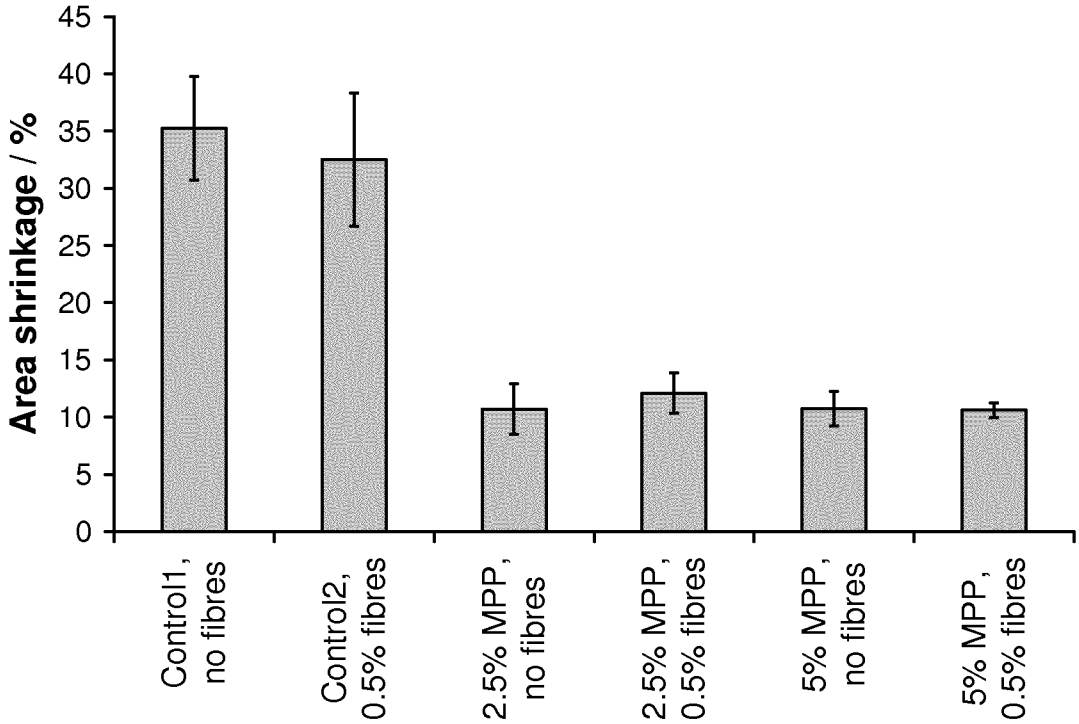
Area shrinkage / %
45
40
35
30
25
20
15
10
5
0
Control1, no fibres
Control2, 0.5% fibres
2.5% MPP, no fibres
2.5% MPP, 0.5% fibres
5% MPP, no fibres
5% MPP, 0.5% fibres

Figure 1

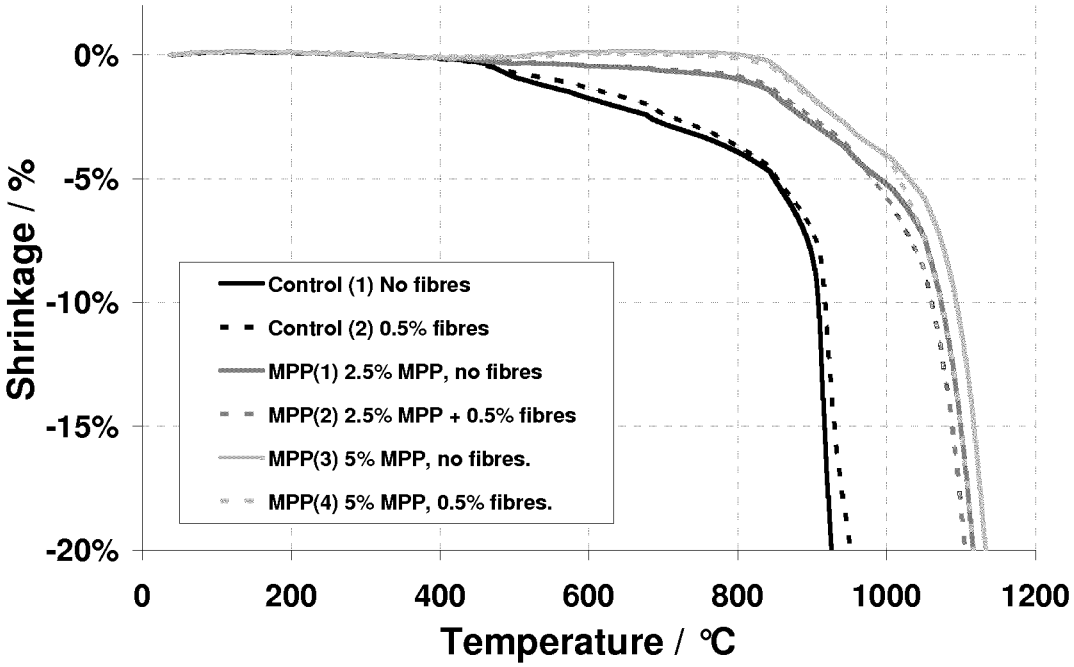
0%
-5%
-10%
-15%
-20%
Shrinkage / %
0
200
400
600
800
1000
1200
Temperature / ℃
Control (1) No fibres
Control (2) 0.5% fibres
MPP(1) 2.5% MPP, no fibres
MPP(2) 2.5% MPP + 0.5% fibres
MPP(3) 5% MPP, no fibres.
MPP(4) 5% MPP, 0.5% fibres.

Figure 2

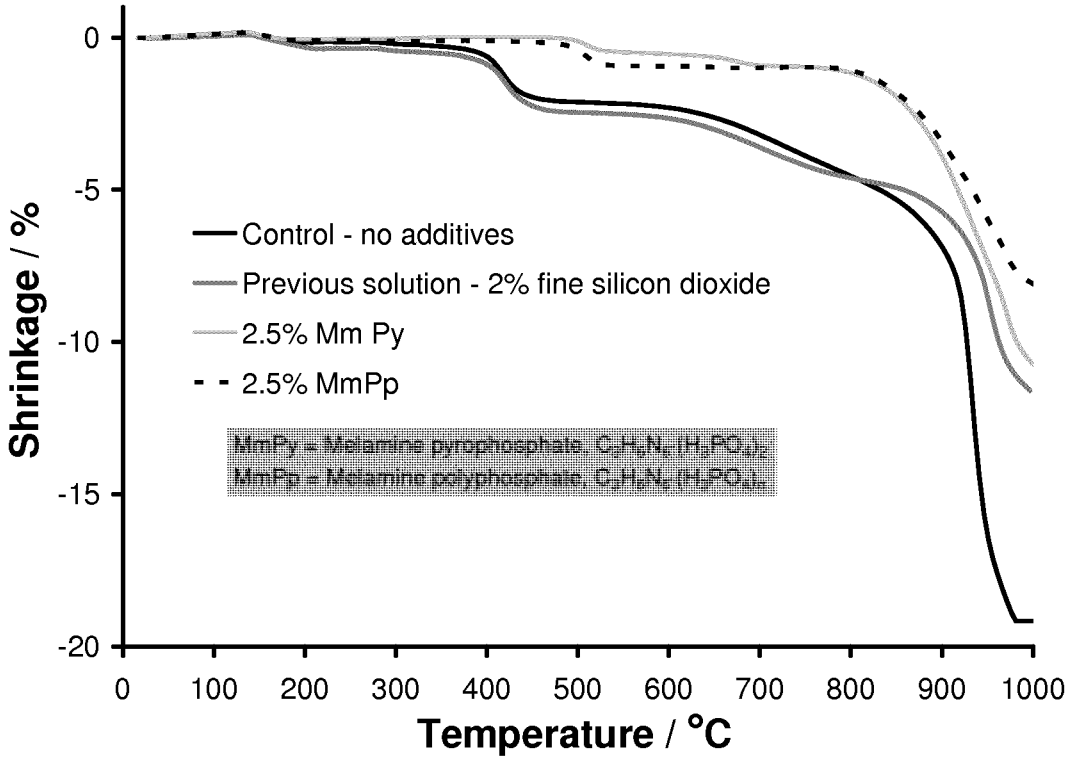
0
-5
-10
-15
-20
Shrinkage / %
0
100
200
300
400
500
600
700
800
900
1000
Temperature / °C
Control - no additives
Previous solution - 2% fine silicon dioxide
2.5% Mm Py
2.5% MmPp
MmPy = Melamine pyrophosphate, $C_3H_9N_6(H_3PO_4)_2$
MmPp = Melamine polyphosphate, $C_3H_9N_6(H_3PO_4)_n$

Figure 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/077315

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B28/14
ADD. C04B103/63 C04B111/00 C04B111/28

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B C09D C08K C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data, COMPENDEX, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 201356 Thomson Scientific, London, GB; AN 2013-B14612 XP002723965, & CN 102 746 651 A (SUZHOU YUDU MEDICAL APPLIANCE CO LTD) 24 October 2012 (2012-10-24) abstract -----	1,2,4,8, 9,11
X	US 2008/171231 A1 (LOPEZ RICHARD A [US] ET AL) 17 July 2008 (2008-07-17) page 1, line 2 - page 2, line 29; claims 1-20; figure 1; examples 1-7; tables I,II page 3, line 17 - page 4, line 17 page 4, line 25 - page 12, line 13 ----- -/--	1-21

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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A	WO 2008/045217 A2 (UNITED STATES GYPSUM CO [US]) 17 April 2008 (2008-04-17) paragraphs [0019] - [0025], [0035] - [0037]; example 2	1-21

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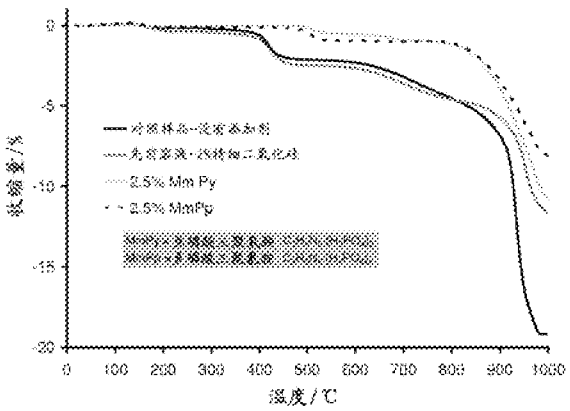
(54)发明名称

基于硫酸钙的产品

(57)摘要

本发明涉及改善的耐高温性的基于硫酸钙的产品，例如石膏墙板产品，具体地，涉及在高温下具有减少的收缩量的产品。本发明提供了包含石膏和抗收缩添加剂的基于硫酸钙的产品。所属抗收缩添加剂是三聚氰胺聚磷酸或三聚氰胺焦磷酸。



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1. 一种基于硫酸钙的产品，包含石膏和抗收缩添加剂，其中所述抗收缩添加剂是三聚氰胺聚磷酸或三聚氰胺焦磷酸。

2. 根据权利要求 1 所述的产品，其中，所述抗收缩添加剂的量为 0.1wt％～ 20wt％。

3. 根据权利要求 2 所述的产品，其中，所述抗收缩添加剂的量为 2wt％～ 5wt％。

4. 根据权利要求 1 至 3 中任一项所述的产品，基本上不包含玻璃纤维。

5. 根据前述权利要求中任一项所述的产品，进一步包含促进剂。

6. 根据前述权利要求中任一项所述的产品，其中，所述产品是墙板、面板、瓦块、接缝填料或用于金属铸造的模具。

7. 根据权利要求 6 所述的产品，其中，所述产品是复合墙板，其包含夹在两个内衬之间的所述石膏和抗收缩添加剂的芯部。

8. 一种通过干燥水性浆料形成基于硫酸钙的产品的方法，所述水性浆料包括煅烧的石膏和抗收缩添加剂，其中所述抗收缩添加剂是三聚氰胺聚磷酸或三聚氰胺焦磷酸。

9. 根据权利要求 8 所述的方法，其中，所述水性浆料包含 0.1wt％～ 20wt％的三聚氰胺聚磷酸。

10. 根据权利要求 9 所述的方法，其中，所述水性浆料包含 2wt％～ 5wt％的三聚氰胺聚磷酸。

11. 根据权利要求 8 至 10 中任一项所述的方法，其中，所述水性浆料基本上不包含玻璃纤维。

12. 根据权利要求 8 至 11 中任一项所述的方法，其中，所述水性浆料进一步包含促进剂。

13. 根据权利要求 8 至 11 中任一项所述的方法，其中，所述产品是墙板、瓦块、面板、接缝填料或用于铸造金属的模具。

14. 根据权利要求 13 所述的方法，其中，所述产品是复合墙板，并且所述方法包括干燥在两个内衬之间的所述水性浆料。

15. 三聚氰胺聚磷酸或三聚氰胺焦磷酸作为石膏基质中的添加剂用于减少基于硫酸钙的产品在热暴露期间的收缩量的用途。

16. 根据权利要求 15 所述的用途，其中，所述基于硫酸钙的产品是墙板、瓦块、面板、接缝填料或用于铸造金属的模具。

17. 根据权利要求 15 或 16 所述的用途，其中，0.1wt％～ 20wt％所述添加剂用于减少收缩量。

18. 根据权利要求 17 所述的用途，其中，2wt％～ 5wt％所述添加剂用于减少收缩量。

19. 基本上如本文所描述的任何一种实施方式的基于硫酸钙的产品。

20. 基本上如本文所描述的任何一种实施方式的形成基于硫酸钙的产品的方法。

21. 基本上如本文所描述的任何一种实施方式的三聚氰胺聚磷酸或三聚氰胺焦磷酸的用途。

基于硫酸钙的产品

[0001] 本发明涉及改善的耐高温性的基于硫酸钙的产品，具体地，涉及在高温下具有减少的收缩量的基于硫酸钙的产品。

背景技术

[0002] 基于硫酸钙的产品广泛用于构建建筑物，例如，形成室内隔断（使用墙板，也称为清水墙、石膏板或灰泥板）和天花板或包裹建筑物中的管道（例如通风管道）。

[0003] 基于硫酸钙的产品如墙板通常通过干燥在两个衬纸板或玻璃纤维垫之间的硫酸钙的半水合物（$CaSO_4 \cdot 1/2H_2O$），也称为煅烧的石膏或灰泥的水性浆料而形成。随着浆料干燥和煅烧的石膏被水化，形成夹在内衬板／衬垫之间的硬的、刚性石膏（硫酸钙二水合物－（$CaSO_4 \cdot 2H_2O$））的芯部。

[0004] 当墙板或天花板瓦块（tile）暴露于高温，比如在建筑火灾中经历的高温或用于包裹携带高温流体的管道的墙板经受的高温时，石膏中包含的结晶水被驱出，产生硫酸钙的硬石膏。起初，这具有如下优势，即横跨墙板／天花板瓦块的传热降低，因此有助于包含从管道系统散发的热或建筑火灾期间所产生的热。但是，在约400-450℃的温度下，起初形成的AIII相硬石膏（也称为 γ-$CaSO_4$或“可溶性”硬石膏）转化成AII相（或“不溶的”硬石膏），该相变导致墙板／瓦块的收缩，即尺寸稳定性的损失。该收缩（其可能是墙板／瓦块的长度或宽度的约2％，或墙板体积的约6％）通常使得墙板远离它们的支撑结构。这显然是不希望的。其可使得管道暴露于高温。此外，在墙板用于室内隔断并爆发火灾的情况下，收缩可留下空隙，使得与火源邻近的房间暴露于热／火的影响。空隙也使得氧进入火源，因此使得火燃烧并且使任何防火门失效。

[0005] 在更高的温度（超过600℃）下，不溶解的硬石膏烧结，导致墙板体积大大缩小。这导致极大的收缩量，其最终造成内墙／天花板／管道套管的坍塌，因为它们不再被它们的支撑结构保持。

[0006] 已经努力改善基于硫酸钙的产品如墙板的抗热性以试图减少收缩。

[0007] 例如，由EP0258064已知，使用微细二氧化硅作为墙板石膏芯的添加剂以减少收缩。

[0008] 但是，这些添加剂仅在大于600℃的温度下有效，即它们在更低的温度不抵抗收缩并且当温度为约1000℃时仍可见大于10％的线性收缩。

[0009] 由WO99/08979和WO00/06518已知，添加三偏磷酸钠（STMP）、六偏磷酸钠（SHMP）或多磷酸铵（APP）至硫酸钙墙板芯材中以在干燥期间改善强度、抗下垂性和收缩。记录了在暴露于高温期间这些添加剂对于收缩无效。发现三偏磷酸离子和APP加速煅烧的石膏水合的速度，因此减少了墙板芯的固化时间。WO2012/069826公开了铝磷酸盐和铵磷酸盐添加剂用于增强基于硫酸钙的产品的耐火性的用途。发现多磷酸铵（APP）减少煅烧的石膏的水合时间和加速固化时间。

[0010] 基于硫酸钙的产品也用于铸造金属物体。在硫酸钙模具被填充熔融的金属之前，将其加热至700-900℃。重要的是，控制这样的基于硫酸钙的模具的高温收缩，以确保模具

不渗漏且确保铸造的金属产品不弯曲。

[0011] 本发明优选的目标是提供改进了耐热性的基于硫酸钙的产品，其在热暴露之后，例如当接触管道时、在建筑火灾期间或在金属产品的铸造期间具有减少的收缩。这样的改进的耐热产品可以具有特定的用途，用作形成建筑物中室内隔断墙板或面板、天花板瓦块、用于包裹通风设备 / 抽风管道的墙板或面板、用于结合墙板 / 面板 / 瓦块的接缝填料材料或用于金属产品铸造的模具。

发明内容

[0012] 因此，在第一方面，本发明提供了基于硫酸钙的产品，其包含石膏和抗收缩添加剂，其中所述抗收缩添加剂是三聚氰胺聚磷酸或三聚氰胺焦磷酸。

[0013] 三聚氰胺聚磷酸是 $C_3H_6N_6-(H_3PO_4)n$，其中 n 大于 2。三聚氰胺焦磷酸是 $C_3H_6N_6\cdot(H_3PO_4)n$，其中 n 是 2。

[0014] 本发明人已经发现在基于硫酸钙的产品中，例如墙板的石膏芯中包括三聚氰胺聚磷酸 (MPP) 或三聚氰胺焦磷酸，当所述板暴露于高温时减少墙板的收缩。不像仅在 600℃之上起作用的微细二氧化硅，MPP/ 三聚氰胺焦磷酸在约 350℃下开始起作用，其经历吸热分解（产生磷酸）并且因此起到吸热器的作用。MPP 也用于升高发生从可溶的至不溶的硫酸钙硬石膏的转变的温度，因此使得产品抵抗源于相变的收缩，直到达到更高的温度（约 800℃）。

[0015] 术语“基于硫酸钙的产品”可以包括墙板（有或没有内衬）（有或没有纤维增强）、瓦块（例如天花板瓦块）、管道包裹面板、接缝填料（例如用于结合相邻的墙板 / 瓦块 / 面板等）和用于铸造金属产品的模具。

[0016] 基于硫酸钙的产品可以是复合产品，例如其可以是具有夹在两个内衬（例如衬纸或玻璃纤维垫）之间的石膏基质芯（包含抗收缩添加剂）的墙板。

[0017] 术语“石膏”旨在主要指硫酸钙二水合物 ($CaSO_4\cdot 2H_2O$)。

[0018] 在优选的实施方式中，MPP 用作抗收缩添加剂。不像被发现加速从石膏的半水合物（煅烧的石膏）到石膏的二水合物（石膏）的固化的 APP，已经发现 MPP 不造成任何加速。固化的加速是不希望的，因为其限制可能的添加水平，并且在它们的过程中生产设施较不易控制。事实上，已经发现 MPP 造成固化的稍微迟缓。优选地，所包括的 MPP/ 三聚氰胺焦磷酸抗收缩添加剂的量为 0.1wt％至 20wt％，优选地 1wt％至 10wt％，更优选地 1wt％至 5wt％，最优选地 2wt％至 5wt％。

[0019] 优选地，基于硫酸钙的产品不包含玻璃纤维。玻璃纤维通常用于形成石膏的机械网络，其有助于维持产品在暴露于热之后的结构完整性。但是，本发明人认为以这样的量包括 MPP/ 三聚氰胺焦磷酸可以减少收缩使得不使用玻璃纤维能够保持所述结构完整性。

[0020] 基于硫酸钙的产品可以包含添加剂如促进剂以弥补 MPP 所观察到的固化时间的稍微迟缓。所述促进剂可以是，例如，具有添加剂糖或表面活性剂的新鲜研磨的石膏。这样的促进剂可包括研磨的矿物质 NANSA(GMN)、耐热促进剂 (HRA) 和球磨的促进剂 (BMA)。可选地，所述促进剂可以是化学添加剂，比如硫酸铝、硫酸锌或硫酸钾。在某些情况下，可以使用促进剂的混合物，例如，与硫酸盐促进剂结合的 GMN。作为进一步的选择，超声可以用于加速浆料的固化速度，例如，如在 US2010/0136259 中所描述的。

[0021] 在第二个方面，本发明提供了通过干燥水性浆料形成基于硫酸钙的产品的方法，所述水性浆料包括煅烧的石膏和抗收缩添加剂，其中抗收缩添加剂是三聚氰胺聚磷酸或三聚氰胺焦磷酸。

[0022] 术语“基于硫酸钙的产品”可以包括墙板（有或没有内衬）（有或没有纤维增强）、瓦块（例如天花板板材）、管道包裹面板、接缝填料（例如用于结合相邻的墙板 / 瓦块 / 面板等）和用于铸造金属产品的模具。

[0023] 基于硫酸钙的产品可以是复合材料产品，例如，其可以是具有夹在两个内衬（例如衬纸或玻璃纤维垫）之间的石膏基质芯的墙板（包含抗收缩添加剂）。在该实施方式中，所述方法包括干燥在两个内衬（例如衬纸或玻璃纤维垫）之间的包含煅烧的石膏和 MPP 的水性浆料。

[0024] 术语“煅烧的石膏”旨在主要指硫酸钙半水合物 ($CaSO_4 \cdot 2H_2O$)，但是也可包括比硫酸钙二水合物具有更低结合水含量的任何其他硫酸钙化合物（例如硫酸钙硬石膏）。

[0025] 优选地，所述浆料中包括的 MPP/ 三聚氰胺焦磷酸抗收缩添加剂的量为 0.1wt％至 20wt％，优选地 1wt％至 10wt％，更优选地 1wt％至 5wt％，最优选地 2wt％至 5wt％。

[0026] 优选的抗收缩添加剂是 MPP。不像 APP，已经发现其不加速煅烧的石膏的固化时间。

[0027] 基于硫酸钙的产品优选地不包含玻璃纤维。玻璃纤维通常用于形成石膏中的机械网络，其有助于维持在暴露于热之后该产品的结构完整性。本发明人认为 MPP/ 三聚氰胺焦磷酸的添加将高温收缩减少至使得玻璃纤维不再是必须的程度。所以，优选地，所述方法包括干燥在没有无机（玻璃）纤维的情况下含有石膏和 MPP/ 三聚氰胺焦磷酸的水性浆料。

[0028] 所述方法可以包括添加玻璃垫至所述浆料，然后干燥。所述浆料通常在模具中干燥。所述垫通过如下方式添加，即在一些浆料或所有的浆料已经添加至模具之后，可通过将所述垫添加在浆料的表面上；或者在添加浆料之前，可以将所述垫平铺在模具的底部。如果所述垫平铺在空模具的底部或平铺在充满模具的浆料的表面，则所述垫将会设置于石膏芯的表面。如果当仅添加一些浆料时将所述垫添加至模具，则所述垫将会嵌入石膏芯中。

[0029] 基于硫酸钙的产品可包含添加剂如促进剂。所述促进剂可以是，例如，具有添加剂糖或表面活性剂的新鲜研磨的石膏。这样的促进剂可以包括研磨的矿物质 NANSA(GMN)、耐热促进剂 (HRA) 和球磨的促进剂 (BMA)。可选地，所述促进剂可以是化学添加剂如硫酸铝、硫酸锌或硫酸钾。在某些情况下，可以使用促进剂的混合物，例如，与硫酸盐促进剂结合的 GMN。在这些实施方式，所述方法包括干燥含有石膏、MPP/ 三聚氰胺焦磷酸和促进剂的水性浆料，任选地，在两个内衬之间，如上所讨论的。也可以包括玻璃垫（如上所讨论的）以及促进剂。

[0030] 在第三方面，本发明提供了三聚氰胺聚磷酸 / 三聚氰胺焦磷酸作为石膏基质中的添加剂用于减少在热暴露期间基于硫酸钙的产品的收缩的用途。

[0031] 优选地，MPP/ 三聚氰胺焦磷酸作为添加剂用于减少具有夹在两个内衬（例如衬纸或玻璃纤维垫）之间的石膏芯（包含 MPP/ 三聚氰胺焦磷酸）的复合墙板的收缩。

[0032] 优选地，0.1wt％至 20wt％，优选 1wt％至 10wt％，更优选 1wt％至 5wt％，最优选 2wt％至 5wt％的量的 MPP/ 三聚氰胺焦磷酸用于减少所述产品的收缩。

附图说明

[0033] 图 1 显示在加热至 1000℃且随后冷却之后，对照样品和 MPP 样品的面积收缩量的图；

[0034] 图 2 显示在加热至 1000℃期间，对照样品和 MPP 样品的线性收缩量；和

[0035] 图 3 显示在加热至 1000℃期间，对照样品、MPP 和三聚氰胺焦磷酸样品线的性收缩量的图。

实施例

[0036] 仅仅通过图解的方式给出下述实施例。

[0037] 对照样品 1

[0038] 1500g 的灰泥与 0.1wt％（相对于灰泥的重量）研磨的石膏促进剂 (GMN- 研磨的矿物质 NANSA) 混合，并且在 40℃下添加至 1350g 的水。这在大的瓦林搅拌机 (Waring blender) 中混合 10 秒，并且将所得浆料倾倒至 100×50×11mm 和 200×200×12.5mm 黄铜模具中以硬化。拇指固化小于 10 分钟。通过将拇指端压在一部分固化石膏上进行拇指固化测定。当获得使得在固化的石膏上不再产生印记的足够强度时，记录时间。使样品水合一小时之后，将它们转移至 40℃的烤箱中并且干燥过夜（至少 12 小时）。

[0039] 对照样品 2

[0040] 1500g 的灰泥与 0.1wt％研磨的石膏促进剂混合。0.5wt％（基于灰泥的重量）(即 7.5g) Johns Manville 玻璃纤维分散在 40℃的 1350g 的水中 10 秒，然后添加干燥掺混物。这在大的瓦林搅拌机 (Waring blender) 中混合 10 秒，并且将所得浆料倾倒至 100×50×11mm 和 200×200×12.5mm 黄铜模具以硬化。拇指固化小于 10 分钟。使样品水合一小时后，将它们转移至 40℃的烤箱中并且干燥过夜（至少 12 小时）。

[0041] MPP 样品 1

[0042] 1500g 的灰泥与 0.3wt％（基于灰泥的重量）研磨的石膏促进剂混合。2.5wt％ MPP（基于灰泥的重量）分散在 40℃的 1350g 的水中 10 秒，然后添加干燥掺混物。这在大的瓦林搅拌机 (Waring blender) 中混合 10 秒，将所得浆料倾倒至 100×50×11mm 和 200×200×12.5mm 黄铜模具以硬化。拇指固化小于 10 分钟。使样品水合一小时之后，将它们转移至 40℃的烤箱中并且干燥过夜（至少 12 小时）。

[0043] MPP 样品 2

[0044] 1500g 的灰泥与 0.3wt％（基于灰泥的重量）研磨的石膏促进剂混合。0.5％ Johns Manville 玻璃纤维和 2.5wt％ MPP（基于灰泥的重量）分散在 40℃的 1350g 的水中 10 秒，然后添加干燥掺混物。这在大的瓦林搅拌机 (Waring blender) 中混合 10 秒，将所得浆料倾倒 100×50×11mm 和 200×200×12.5mm 黄铜模具以硬化。拇指固化小于 10 分钟。使样品水合一小时之后，将它们转移至 40℃的烤箱中并且干燥过夜（至少 12 小时）。

[0045] MPP 样品 3

[0046] 1500g 的 DSG 灰泥与 0.5wt％（基于灰泥的重量）研磨的石膏促进剂混合。5wt％ MPP（基于灰泥的重量）分散在 40℃的 1350g 的水中 10 秒，然后添加干燥掺混物。这在大的瓦林搅拌机 (Waring blender) 中混合 10 秒，将所得浆料倾倒至 100×50×11mm 和 200×200×12.5mm 黄铜模具以硬化。拇指固化小于 10 分钟。使样品水合一小时之后，将它

们转移至 40℃的烤箱中并且干燥过夜（至少 12 小时）。

[0047] MPP 样品 4

[0048] 1500g 的 DSG 灰泥与 0.5wt％（基于灰泥的重量）研磨的石膏促进剂混合。0.5％ Johns Manville 玻璃纤维和 5wt％ MPP（基于灰泥的重量）分散在 40℃的 1350g 的水中 10 秒，然后添加干燥掺混物。这在大的瓦林搅拌机 (Waring blender) 中混合 10 秒，将所得浆料倾倒至 100×50×11mm 和 200×200×12.5mm 黄铜模具以硬化。拇指固化小于 10 分钟。使样品水合一小时之后，将它们转移至 40℃的烤箱中并且干燥过夜（至少 12 小时）。

[0049]

	对照	对照 2	MPP1	MPP2	MPP3	MPP4
煅烧的石膏 /g	1500	1500	1500	1500	1500	1500
水 /g	1350	1350	1350	1350	1350	1350
促进剂 /g	1.5	1.5	4.5	4.5	7.5	7.5
玻璃纤维 /g	-	7.5	-	7.5	-	7.5
MPP/g	-	-	37.5	37.5	75	75

[0050] 表 1-MPP 样品的总结

[0051] 三聚氰胺焦磷酸样品 1

[0052] 使用 Ultra-Turrax 高速剪切混合器，2.5wt％三聚氰胺焦磷酸（基于灰泥的重量）分散在 140mL 的自来水中 5 分钟，然后添加 200g 的灰泥。这通过手动混合 1 分钟，并且将所得浆料形成为 12.5mm 直径的石膏柱。将它们转移至 40℃的烤箱中并且干燥过夜（至少 12 小时）。

[0053] 为了与该三聚氰胺焦磷酸比较，石膏柱 a) 如上所述的但没有三聚氰胺焦磷酸，b) 如上所述的但是用 2.5wt％ MPP 代替三聚氰胺焦磷酸，和 c) 如上所述的但是没有三聚氰胺焦磷酸，并且具有 2.0wt％（基于灰泥的重量）微细二氧化硅。下面讨论比较的结果并且显示在图 3 中。

[0054] 面积收缩量

[0055] 对于每个 100×50×11mm 样品，记录初始测量值（长度和宽度），然后将样品加热至约 1000℃至 120 分钟以上（以 20℃ /min 至约 200℃，其后稳定和缓慢降低速度）。冷却之后，再次测量样品的尺寸。面积收缩量计算为样品的初始面积和热处理后的样品之间的差，显示在图 1 中。

[0056] 可见，与不包含 MPP 的对照样品比较，包含 MPP 的所有样品显示面积收缩量的显著下降。以 MPP2.5wt％这样少的量就实现了收缩量的减少。的确，MPP 的量加倍至 5wt％不显示面积收缩量的显著的进一步减少。

[0057] 观察样品的裂纹，其结果显示在下面表 2 中。

[0058]

.	观察结果

对照样品 1	许多可见的裂纹 - 一些非常宽 - 样品碎裂
对照样品 2	许多可见的裂纹
MPP 样品 1	几个非常细的裂纹
MPP 样品 2	几个非常细的裂纹
MPP 样品 3	几个非常细的裂纹
MPP 样品 4	几个非常细的裂纹

[0059] 表 2- 加热至 1000℃之后的观察结果

[0060] 线性收缩

[0061] 使用连接至线性位移变换器的陶瓷棒测量 200×200×12.5mm 样品的线性收缩量。该样品由其他陶瓷棒支撑并且在熔炉中加热至 1000℃，初始速度为 44℃ /min 至约 600℃，然后以稳定和缓慢下降的速度（与 ISO 834 一致）。结果显示在图 2 中。

[0062] 可见包含 MPP 的所有样品在 1000℃时的线性收缩量减少约 5％。观察到在包含 5％ MPP 的样品中线性收缩量减少最多。

[0063] 图 3 显示了三聚氰胺焦磷酸的线性收缩量结果。可见收缩量的减少与用 MPP 所获得的收缩量相当，即与对照样品（没有三聚氰胺焦磷酸）的 19％收缩量相比，约 10％的收缩量。

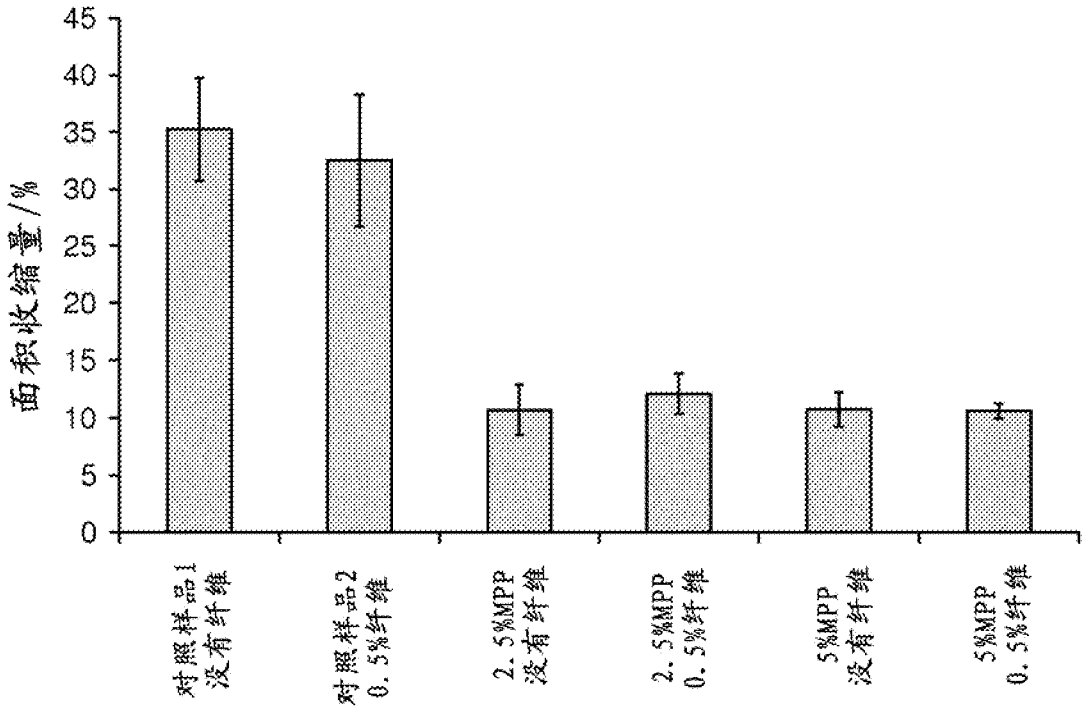
面积收缩量/%
45
40
35
30
25
20
15
10
5
0
对照样品1 没有纤维
对照样品2 0.5%纤维
2.5%MPP 没有纤维
2.5%MPP 0.5%纤维
5%MPP 没有纤维
5%MPP 0.5%纤维

图 1

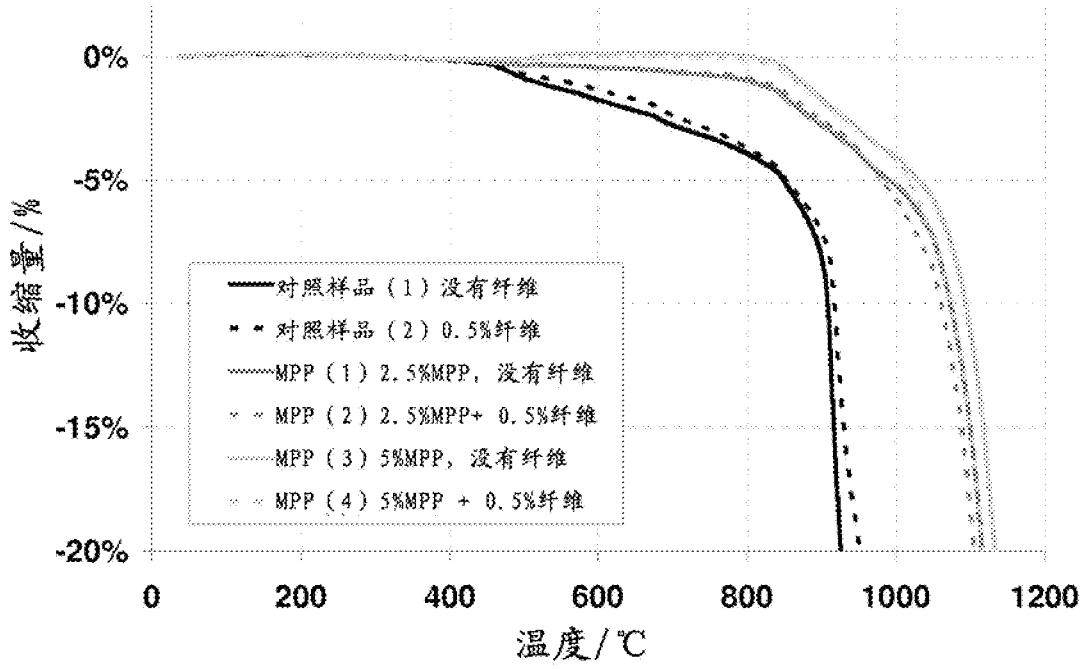
收缩量/%
0%
-5%
-10%
-15%
-20%
0
200
400
600
800
1000
1200
温度/℃
对照样品（1）没有纤维
对照样品（2）0.5%纤维
MPP（1）2.5%MPP，没有纤维
MPP（2）2.5%MPP+ 0.5%纤维
MPP（3）5%MPP，没有纤维
MPP（4）5%MPP + 0.5%纤维

图 2

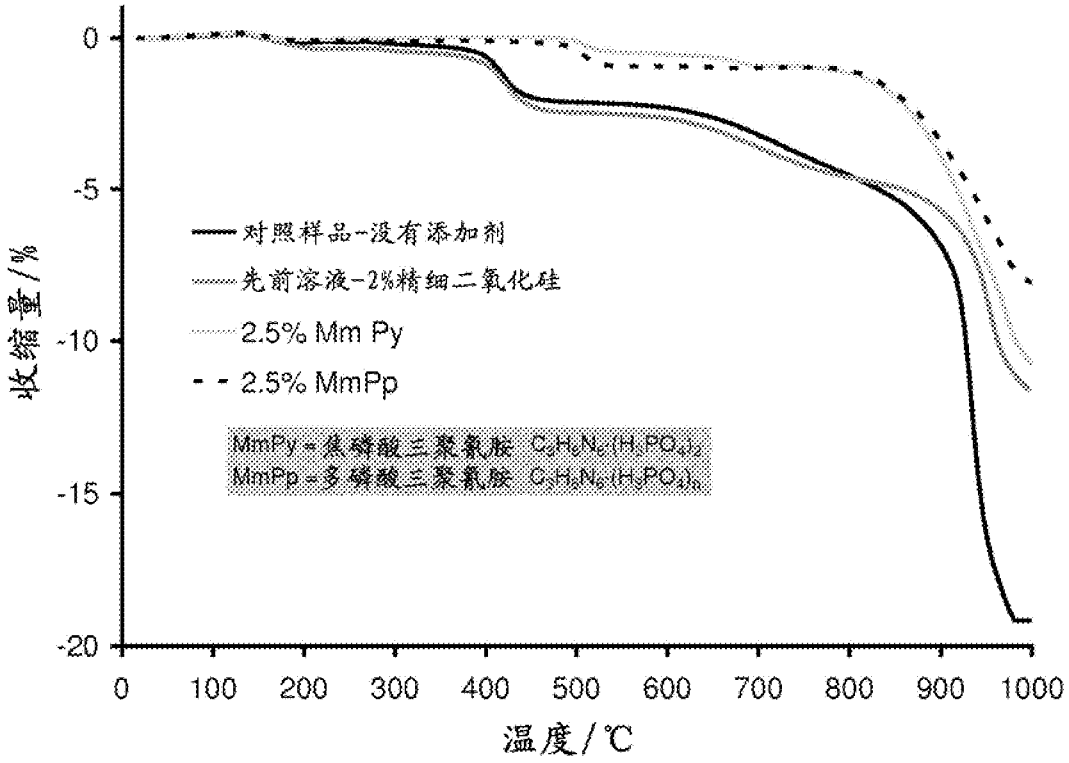
0
-5
-10
-15
-20
收缩量/%
0
100
200
300
400
500
600
700
800
900
1000
温度/℃
对照样品-没有添加剂
先前溶液-2%精细二氧化硅
2.5% Mm Py
2.5% MmPp
MmPy = 焦磷酸三聚氰胺 $C_3H_6N_6(H_4P_2O_7)_2$
MmPp = 多磷酸三聚氰胺 $C_3H_6N_6(H_3PO_4)_n$

图 3

Abstract

This invention relates to improved high temperature resistant calcium sulphate-based products e.g. gypsum wallboard products and, in particular, to products having reduced shrinkage at high temperatures. The invention provides calcium sulphate-based product comprising gypsum and a shrinkage resistance additive. The shrinkage resistance additive is melamine polyphosphate or melamine pyrophosphate.