



- (51) **International Patent Classification:**  
*C04B 11/032* (2006.01) *C04B 28/14* (2006.01)
- (21) **International Application Number:**  
PCT/EP2012/075353
- (22) **International Filing Date:**  
13 December 2012 (13.12.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**  
1121 589.4 15 December 2011 (15.12.2011) GB
- (71) **Applicant:** SAINT-GOBAIN PLACO SAS [FR/FR]; 34 Avenue Franklin Roosevelt, F-92150 Suresnes (FR).
- (72) **Inventors:** MONGROLLE, Jean-Louis; 106 Chemin du Grivet, F-73000 Bassens (FR). GERMAIN, Jean-Luc; 17 Allée des Martyrs Hongrois, F-93190 Livry-Gargan (FR).
- (74) **Agent:** PUGSLEY, Victoria; 20 Staple Gardens, Winchester Hampshire SO23 8SR (GB).
- (81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,

BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

- (84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

**Declarations under Rule 4.17:**

— *of inventorship* (Rule 4.17(iv))

**Published:**

— *with international search report* (Art. 21(3))

(54) **Title:** A METHOD OF FORMING A GYPSUM BASED PRODUCT

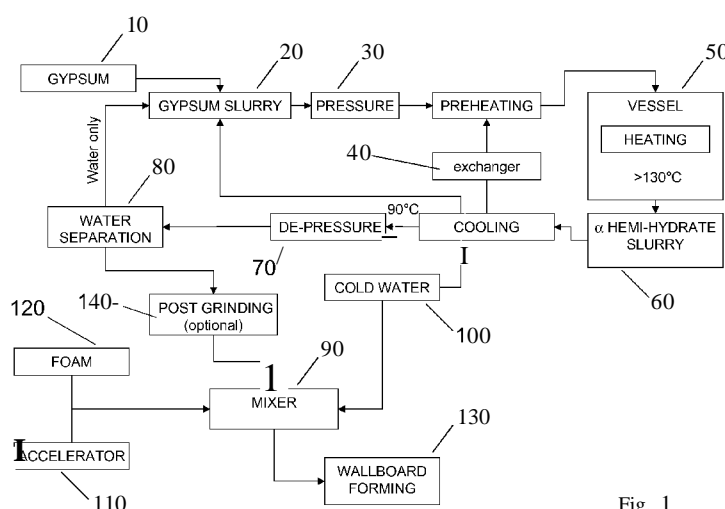


Fig. 1

(57) **Abstract:** A method of forming a gypsum based product is disclosed. The method comprises the steps of: calcining a mixture of water and gypsum under conditions of raised temperature and pressure within a vessel to produce an alpha-hemihydrate slurry therein; passing the alpha-hemihydrate slurry from the vessel to a mixer for mixing with additional water to produce a settable slurry, which is arranged to set to form the gypsum based product.

### **A Method Of Forming A Gypsum Based Product**

The present invention relates to a method of forming a gypsum based product.

5 Gypsum occurs naturally as a raw material in the form of calcium sulphate dihydrate. Gypsum containing products, such as plasterboard, are prepared by forming a mixture of calcined or dehydrated gypsum, namely calcium sulphate hemihydrate, with water, to form a settable slurry which is then cast into a pre-determined shape. The hemihydrate reacts with the water and becomes re-hydrated to the dihydrate crystal, which is then  
10 cured or dried to the solid state.

The hemihydrate form of gypsum is known to depend on the calcination process, and is categorised into two basic forms, the alpha-hemihydrate and the beta-hemihydrate. The beta-hemihydrate is typically formed by heating gypsum under atmospheric conditions,  
15 to drive off any moisture and chemically combined water to form dried crystals, which may then be ground to a fine powder. The beta-hemihydrate has long been the favoured hemihydrate in the production of gypsum wall boards or plasterboards, owing to the rapid re-hydration of the ground crystal in forming the slurry. However, the gypsum product derived from the beta-hemihydrate is typically soft and the beta-hydrate requires  
20 large volumes of water to produce the required slurry fluidity.

The alpha-hemihydrate is formed by heating gypsum under pressure to similarly remove the water associated therewith. The gypsum product derived from the alpha-hemihydrate however, is found to be harder and comprises a higher strength and density compared  
25 with beta-hemihydrate derived gypsum.

It is necessary to use substantial amounts of water in gypsum slurries in order to ensure proper flowability of the slurry. Unfortunately, most of this water must eventually be driven off by heating, which is expensive due to the high cost of the fuels used in the  
30 heating process. The heating step is also time-consuming. It is known that alpha-hemihydrate has a substantially lower water demand than beta-hemihydrate, meaning that if alpha-hemihydrate could be used in making wallboard, it would substantially reduce the water demand and hence the expense and time required to produce the wallboard. This is a further advantage associated with alpha-hemihydrate.

However, alpha-hemihydrate is not generally used commercially in the production of gypsum wallboard primarily due to its slower hydration rate compared to beta-hemihydrate, which would therefore require a slower passage of boards along the  
5 production line.

WO2007/084346 discloses a method for the production of alpha-type gypsum. A gypsum slurry is delivered into an autoclave, where it is heated typically to a temperature of about 280°F (about 137°C) under a pressure of 3-4 Bar and converted to alpha  
10 hemihydrate. The slurry exits the autoclave via a pressure let down valve and is delivered to a flash tank, where it is cooled and excess steam is collected.

US2008/0069762 discloses a process for making a blend of alpha- and beta-stucco. The process includes a slurry calcination step in which gypsum slurry is held in a reactor at a temperature of e.g. 149°C and a pressure of e.g. 3.4 to 4.8 Bar. The partially  
15 calcined gypsum product discharges from the reactor as a slurry comprising calcium sulphate dihydrate and alpha calcium sulphate hemihydrate and feeds an accumulator tank, which acts as a holding tank and permits release of the steam as the slurry's pressure drops to atmospheric pressure. The slurry then discharges from the  
20 accumulator tank and feeds a de-watering unit which removes water to produce a dewatered solids-containing product and a removed water stream. The dewatered product has a 2-6wt% free water moisture content. The dewatered product is fed to a board stucco kettle calciner at conditions to convert the majority or all of the gypsum in the dewatered product to beta calcium sulphate hemihydrate.

25

In accordance with the present invention as seen from a first aspect, there is provided a method of forming a gypsum based product, the method comprising the steps of:

calcining a mixture of water and gypsum under conditions of raised temperature and pressure within a vessel to produce an alpha-hemihydrate slurry therein;

30 passing the alpha-hemihydrate slurry from the vessel to a mixer for mixing with additional water to produce a settable slurry, which is arranged to set to form the gypsum based product.

Advantageously, the method eliminates the requirement for drying of the hemihydrate, which is associated with the conventional formation of the settable slurry, and therefore reduces the energy demands of the method. Moreover, the reduced water amounts associated with achieving the desired fluidity of alpha-hemihydrate settable slurry compared with beta-hemihydrate, provides a further energy saving since less water must be removed during the drying of the gypsum product.

Preferably, the calcination step comprises substantially filling the vessel with water and gypsum so that the vessel is substantially devoid of free space, such that the water produced during the calcination of gypsum is prevented from evaporating.

Preferably, the raised temperature comprises a temperature within the range between 110°C and 170°C, preferably between 120°C and 150°C, more preferably between 130°C and 140°C.

Typically, the pressure is adjusted in accordance with the operating temperature, such that the operating pressure corresponds to the vapour pressure of steam at the operating temperature. Preferably, the raised pressure comprises a pressure within the range 2-8 Bars, more preferably 3-5 Bars.

The method preferably further comprises the step of cooling the alpha-hemihydrate slurry after the calcination step. Typically, the step of cooling the alpha-hemihydrate slurry takes place while the alpha-hemihydrate slurry is still held at the raised pressure of about 2 to 8 Bars. Typically, the step of cooling the alpha-hemihydrate slurry is carried out using a heat exchanger. Preferably, the alpha-hemihydrate is cooled to a temperature less than 100°C, such as 90°C.

Preferably, after the step of cooling the alpha-hemihydrate slurry, the slurry is de-pressured to a pressure of 1 Bar (i.e. atmospheric pressure).

Typically, the method further comprises the step of substantially separating the water from the alpha-hemihydrate slurry after the step of reducing the pressure acting on the alpha-hemihydrate slurry. This may be done e.g. using a belt filter or a centrifugal separator, i.e. hydroclone. Preferably, in this case, the separated water is circulated for

mixture with a fresh quantity of gypsum, for introducing into the vessel to start a further calcination process. In this case, the heat energy contained within the separated water reduces the requirement for heating of the vessel to achieve the raised temperature of e.g. 110°C to 180°C.

5

In the case that water is separated from the alpha-hemihydrate slurry, the free water content of the remaining slurry is typically 1-30wt%, preferably 5-30wt%, more preferably 8-30wt%.

10 Preferably, the method further comprises the step of grinding the alpha-hemihydrate slurry to reduce the size of particulates therein. It is thought that grinding of the alpha-hemihydrate slurry results in a greater reactivity of the alpha-hemihydrate particles, so as to increase the hydration rate of the alpha-hemihydrate particles during the step of forming a settable slurry. The step of grinding the alpha-hemihydrate slurry may be  
15 carried out using wet grinding techniques. In this case, the grinding may be carried out at a temperature of 50°C or more, preferably 70°C or more, more preferably 80°C or more.

Methods for controlling the size of the alpha-hemihydrate particles during the calcination  
20 stage are known in the art and may be used as an alternative or in addition to the grinding step.

Preferably, during the step of passing the alpha-hemihydrate slurry from the calcination vessel to the mixer, the temperature of the alpha-hemihydrate slurry is maintained at  
25 70°C or more. By maintaining the temperature of the alpha-hemihydrate slurry at this level, it is thought that hydration of the alpha-hemihydrate particles to form a settable gypsum product may be avoided until entry of the alpha-hemihydrate slurry into the mixer. Preferably, the temperature of the alpha-hemihydrate slurry is maintained at over 80°C, more preferably over 85°C.

30

In addition, it is desirable that the step of passing the alpha-hemihydrate slurry from the calcination vessel to the mixer should not take too long, so as to further avoid hydration of the alpha-hemihydrate particles until entry of the particles into the mixer. Typically the time taken for the alpha-hemihydrate slurry to pass from the calcination vessel to the

mixer is less than 120 minutes, preferably less than 60 minutes, more preferably less than 30 minutes.

5 It is thought that the addition of cold water (e.g. about 20°C-30°C) in the mixer, for mixing with the alpha-hemihydrate slurry will rapidly decrease the temperature of the alpha-hemihydrate slurry, so as to promote the hydration of the alpha-hemihydrate particles to form a settable gypsum product.

10 The method further comprises the addition of one or more further additives to the hemihydrate slurry within the mixer, such as accelerators and foaming agents.

Preferably, the gypsum based product comprises a gypsum board.

15 In accordance with the present invention as seen from a second aspect, there is provided a method of forming a gypsum based product, the method comprising the steps of:

calcining a mixture of water and gypsum under conditions of raised temperature and pressure within a vessel to produce an alpha-hemihydrate slurry therein;

20 passing the alpha-hemihydrate slurry from the vessel to a mixer for mixing with additional water to produce a settable slurry, which is arranged to set to form the gypsum based product, wherein the alpha-hemihydrate slurry is passed from the vessel to the mixer without undergoing a drying stage.

25 Preferred features of the method of the second aspect may comprise one or more of the preferred features of the method of the first aspect.

30 An embodiment of the present invention will now be described by way of example only and with reference to the accompanying drawing which provides a schematic illustration of the steps associated with the method according to an embodiment of the present invention.

Referring to the drawing, the method according to an embodiment of the present invention comprises the initial step of forming a mixture 20 of water and gypsum 10 in a ratio of approximately 1 part gypsum to 1.5 parts water, pressurising the mixture in a

pressuriser 30 and pre-heating it by means of a heat exchanger 40 (e.g. a water/water heat exchanger). The mixture is then introduced into a calcination vessel 50, e.g. by means of a pump or in a long water column. The mixture is subsequently heated to a temperature in the range 130°C-140°C and the vessel 50 is pressurised to a pressure in the range 3-5 Bars. The vessel 50 is substantially filled with the mixture to remove any free space therein, such that the water within the vessel 50 and principally the water derived from the calcining of the gypsum, is prevented from evaporating and thus escaping from the vessel 50.

Following the calcination stage the resulting mixture of water and alpha-hemihydrate slurry 60 is cooled to a temperature of approximately 90°C using the heat exchanger 40, de-pressurised in a de-pressuriser 70 and passed to a separation unit 80, wherein the hemihydrate slurry is substantially separated from the water. The water is circulated from the separation unit 80 back to the vessel 50 to preheat subsequent water and gypsum before entering the vessel 50 and thus reduce the energy demands associated with the heating of the mixture. The alpha-hemihydrate slurry comprising approximately 6% water is passed from the separation unit 80 to a mixer 90, for subsequent post processing of the slurry which includes the addition of water 100 and optional additives, such as accelerators 110 (for reducing the setting time) and foaming agents 120 to produce a settable slurry. It is also envisaged however, that the post processing may further comprise the grinding of the hemihydrate slurry (e.g. in a screw grinder 140) to reduce the size of particulates disposed therein before the alpha-hemihydrate slurry is introduced into the mixer 90. In this respect, the hemihydrate slurry is passed to the mixer 90 to achieve the required fluidity and setting characteristics, without undergoing any drying stage, thereby reducing the energy demand in producing the gypsum product. Moreover, the resulting settable slurry comprising 30-40% water which is then passed to a production line 130 for subsequent preparation of a gypsum product such as a plasterboard, will require less curing owing to reduced amounts of water which are required to attain the desired fluidity of the alpha-hemihydrate settable slurry, compared with the amount of water required to attain the desired fluidity of a beta-hemihydrate settable slurry. Since alpha-hemihydrate typically has a slower hydration rate than beta-hemihydrate, the setting times for alpha-hemihydrate slurry are typically longer than for beta-hemihydrate slurry. Thus, in the manufacture of gypsum boards, it is generally

desirable when using alpha-hemihydrate slurry, to have a longer forming belt to provide sufficient time for setting of the slurry.



**Claims**

1. A method of forming a gypsum based product, the method comprising the steps of:

5        calcining a mixture of water and gypsum under conditions of raised temperature and pressure within a vessel to produce an alpha-hemihydrate slurry therein;

         passing the alpha-hemihydrate slurry from the vessel to a mixer for mixing with additional water to produce a settable slurry, which is arranged to set to form the gypsum based product.

10

2. A method according to claim 1 further comprising the step of reducing the water content of the alpha-hemihydrate slurry to provide a separate water stream from the alpha-hemihydrate slurry.

15        3. A method according to claim 1 or claim 2, wherein the calcination step comprises substantially filling the vessel with water and gypsum so that the vessel is substantially devoid of free space, such that the water produced during the calcination of gypsum is prevented from evaporating.

20        4. A method according to any one of the preceding claims, wherein the raised temperature comprises a temperature within the range 110°C to 170°C.

5. A method according to any one of the preceding claims, wherein the raised pressure comprises a pressure within the range 2 to 8 Bars.

25

6. A method according to any one of the preceding claims, further comprising the step of cooling the alpha-hemihydrate slurry after the step of calcining the mixture of water and gypsum.

30        7. A method according to claim 6, wherein the alpha-hemihydrate slurry is cooled to a temperature less than 100°C.

8. A method according to claim 6 or claim 7, comprising the further step, after the step of cooling the alpha-hemihydrate slurry, of de-pressurising the slurry.

9. A method according to claim 8 further comprising circulating the separated water stream to preheat further gypsum before entering the vessel.

5

10. A method according to claim 8 or claim 9, wherein after the step of reducing the water content of the alpha-hemihydrate slurry, the water content of the alpha-hemihydrate slurry lies within a range of 1-10wt%.

10 11. A method according to any preceding claim, further comprises the step of grinding the alpha-hemihydrate slurry to reduce the size of particulates therein.

12. A method according to any one of the preceding claims, wherein the step of passing the alpha-hemihydrate slurry from the vessel to the mixer comprises the step of  
15 maintaining the temperature of the alpha-hemihydrate slurry at over 70°C.

13. A method according to any one of the preceding claims, wherein the time taken for the alpha-hemihydrate slurry to pass from the vessel to the mixer is less than 120 minutes.

20

14. A method according to any preceding claim further comprising adding water to the hemihydrate slurry.

15. A method according to claim 14, further comprising the addition of one or more  
25 additives to the hemihydrate slurry within the mixer, such as an accelerator and/or a foaming agent.

16. A method according to any preceding claim, wherein the gypsum based product comprises a gypsum board.

30

17. A method of forming a gypsum based product, the method comprising the steps of:

calcining a mixture of water and gypsum under conditions of raised temperature and pressure within a vessel to produce an alpha-hemihydrate slurry therein;

passing the alpha-hemihydrate slurry from the vessel to a mixer for mixing with additional water to produce a settable slurry, which is arranged to set to form the gypsum based product, wherein the alpha-hemihydrate slurry is passed from the vessel to the mixer without undergoing a drying stage.

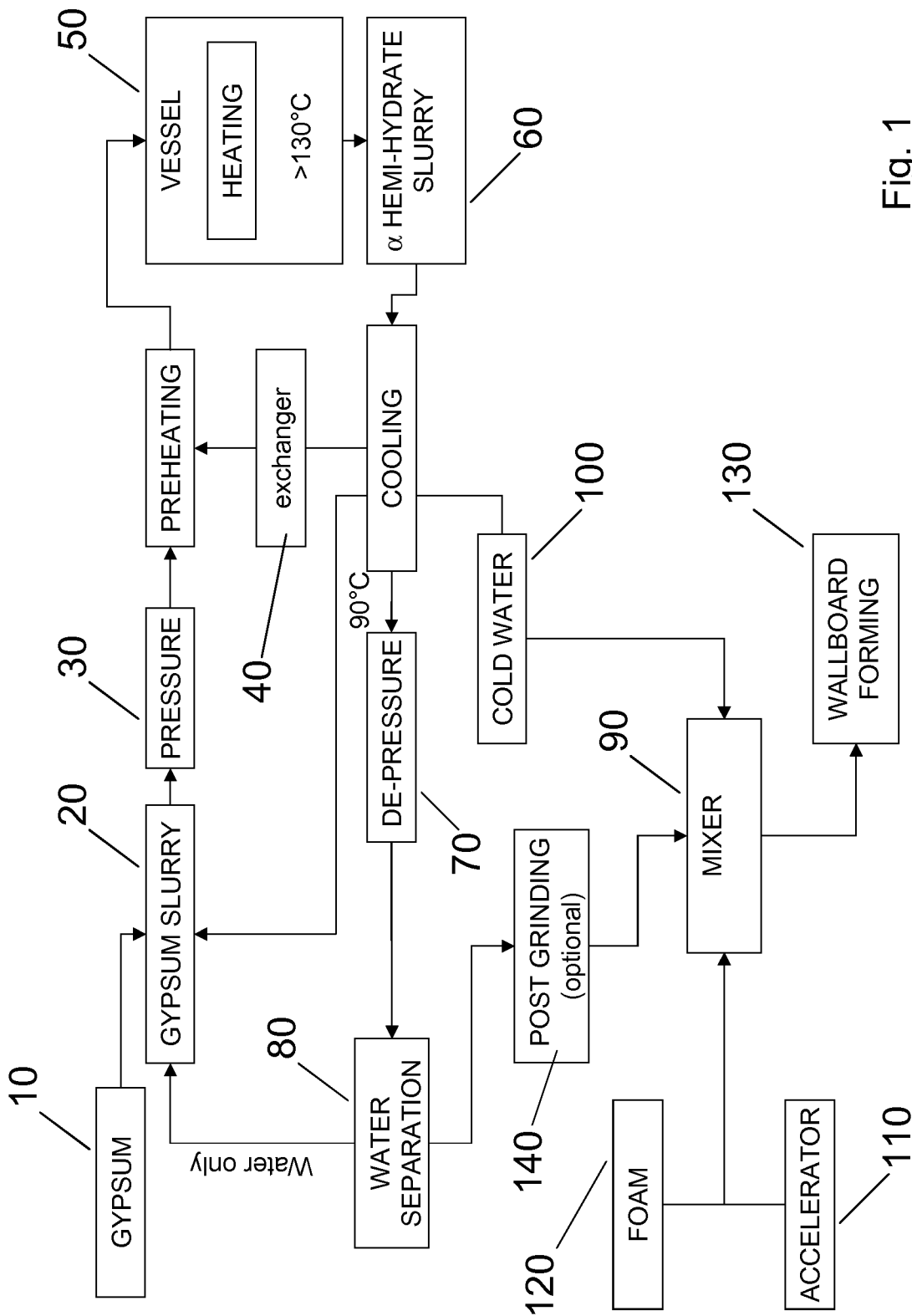


Fig. 1

# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2012/075353

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C04B11/032 C04B28/14  
ADD.

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

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

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 39 27 927 Al (RWK RHEIN WESTFAEL KALKWERKE [DE] ) 28 February 1991 (1991-02-28)	1-4,6-17
Y	col umn 1, line 2 col umn 1, line 30 - col umn 2, line 68 -----	5
Y	GB 2 213 810 A (RWK RHEIN WESTFAEL KALKWERKE [DE] ) 23 August 1989 (1989-08-23) page 1, paragraph 2 -----	5
A	EP 0 572 781 Al (HEIDELBERGER ZEMENT AG [DE] ) 8 December 1993 (1993-12-08) the whol e document -----	1-17



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

12 March 2013

Date of mailing of the international search report

26/03/2013

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040,  
Fax: (+31-70) 340-3016

Authorized officer

Roesky, Rai ner

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2012/075353

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3927927	AI	28-02- 1991	NONE
-----			
GB 2213810	A	23-08- 1989	BE 1003776 A3 09-06-1992
			DE 3800794 AI 27-07-1989
			GB 2213810 A 23-08-1989
			LU 87424 AI 14-06-1989
			NL 8803175 A 01-08-1989
-----			
EP 0572781	AI	08-12- 1993	AT 142609 T 15-09-1996
			DE 4217978 AI 02-12-1993
			DE 59303717 DI 17-10-1996
			DK 0572781 T3 10-03-1997
			EP 0572781 AI 08-12-1993
			ES 2094955 T3 01-02-1997
			GR 3021989 T3 31-03-1997
-----			