



- (51) **International Patent Classification:**
C04B 28/14 (2006.01) *C04B 28/16* (2006.01)
- (21) **International Application Number:**
PCT/EP2014/062062
- (22) **International Filing Date:**
11 June 2014 (11.06.2014)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
13290143.0 12 June 2013 (12.06.2013) EP
- (71) **Applicant:** LA CHAPE LIQUIDE [FR/FR]; 500 Rue Marcel Demonque, Zone du pôle technologique Agroparc, F-84000 Avignon (FR).
- (72) **Inventor:** BOCQUET, Anne-Claire; 84 allée des Aubépines, F-84130 Le Pontet (FR).
- (74) **Agents:** AUGUST & DEBOUZY AVOCATS et al.; 6/8 Avenue de Messine, F-75008 Paris (FR).
- (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, IR, IS, JP, KE, KG, 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, SA, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

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



WO 2014/198742 A1

(54) **Title:** THERMALLY CONDUCTIVE SCREED

(57) **Abstract:** A composition suitable for use as floor screed is provided, which composition comprises hydraulic binder and expanded graphite, characterized in that the amount of expanded graphite is less than 12 %w, the %w being based upon the weight of said hydraulic binder.

THERMALLY CONDUCTIVE SCREED

Field of the invention

- 5 The present invention relates to compositions suitable for use as floor screed, the compositions being based on hydraulic binders.

Background of the invention

10 A floor screed is used in buildings to level and flatten the underlying concrete layer and in which pipes and cables can be housed. It should have a good thermal conductivity in case it houses ducts for floor heating. A self-leveling screed is a liquid mortar mainly formed from a hydraulic binder such as cement or calcium sulphate, aggregates and different additives; it is supplied on the job site by truck mixer or directly via a transmix distribution system.

15 Floor screeds based on cement and/or calcium sulphate binders are well known in the art.

Attempts have been made to improve the thermal conductivity of floor screeds by adding expanded graphite, as described in DE10049230. According to DE10049230, an amount of expanded graphite of 5%w to 35%w, based upon
20 the dry weight of the floor screed is added to change the thermal conductivity, the size of the expanded graphite particles being in the range of 0.001 to 1 mm.

Summary of the invention

25 It is an object of the present invention to provide compositions suitable for thermally conductive screeds based hydraulic binders, and thermally conductive floor screeds.

The invention further relates to floor screeds and floor heating systems obtained
30 by using compositions according to the invention.

The invention also relates to the use of compositions according to the invention for floor screeds and floor heating systems.

- 5 According to a first aspect of the present invention, a floor screed composition is provided, the composition comprising a hydraulic binder and expanded graphite, the amount of expanded graphite being less than 12 %w, the %w being based upon the weight of said hydraulic binder .
- 10 The weight percentage "X %w" of the expanded graphite means that X gram of expanded graphite is used per 100 gram of hydraulic binder .

By the term "hydraulic binder", reference is made to what is usually understood as hydraulic binders, i.e. compounds having the property to hydrate in the
15 presence of water and moisture to get a solid mechanical property. Hydraulic Binder in particular may comprise Portland cement in accordance with the standard EN 197-1 or aluminous cement. The hydraulic binder may also comprise calcium sulfate.

- 20 This calcium sulfate can be beta calcium sulfate and/or alpha calcium sulfate from natural or synthetic origin, or anhydrous calcium sulfate, e.g. anhydrite II or anhydrite III, obtained from sources of synthesis (for example fluoro anhydrite) or natural sources, e.g. by calcining natural or synthetic gypsum (e.g. from the desulfurization FGD gypsum). Examples of suitable calcining processes are
25 classic calcination process or process Rocal™. One may use mixtures of different sources of calcium sulphate. The screed the invention generally meets the requirements of the European standards EN 13454-1 (binder) and EN 13813 (mortar) for calcium sulphate for fluid screed mortars and binders

Calcium sulphate, usually as anhydride, may comprise at least 50% by weight of calcium sulphate, preferably at least 85% or even significantly 100%.

The screed may further comprise fillers of various kinds (calcareous, siliceous, Silica fume, fly ash can be used in addition to the calcium sulfate.

5

According to some embodiments, the hydraulic binder may be calcium sulphate. The used calcium sulphate preferably is anhydride.

The use of expanded graphite leads to higher values of thermal conductivity compared to unexpanded graphite.

10

If the amount of expanded graphite is above 12 weight % with respect to the weight of hydraulic binder, the cost of the formulation for use as a screed is too high, the further addition may not necessarily bring much additional increase of thermal conductivity, and there may be a potential reduction of mechanical

15

performance.

Despite the low dosage of expanded graphite in the composition according to the invention, a thermal conductivity increase is obtained and thermal conductivity values, as measured according to NF EN 993-15, of at least 1.8 W/m.K, even of 20 2 W/m.K or more, or 2.2 W/m.K or more, e.g. 2.5 W/m.K or more, or even 2.8 W/m.K or more may be obtained. The low amounts of expanded graphite in the composition according to the present invention offers further advantages such as low additional dust generation and the ease of incorporation said graphite without excessive floating in aqueous medium.

25

According to some embodiments, the composition may comprise expanded graphite in an amount of at least 0.01%w, the %w being based upon the weight of said hydraulic binder.

According to some embodiments, the composition may comprise expanded graphite in an amount of at least 0.4%w, the %w being based upon the weight of said hydraulic binder.

30

The floor screed composition according to the present invention comprises expanded graphite preferably in an amount of from 0.4 to 6 weight% with respect to the weight of hydraulic binder. Compositions comprising expanded graphite in an amount of from 0.4 to 4 weight% with respect to the weight of hydraulic binder are particularly preferred.

The expanded graphite may have a specific BET surface ranging from 5 to 50m²/g, e.g. about 25 m²/g

The expanded graphite may have a bulk density (scott density) ranging from 0.01 to 0.1 g/cm³, about 0.04 g/cm³, measured by ASTM n° E 153-59 T.

According to some embodiments, the expanded graphite may have a mean particle size D50, as measured by laser diffraction, ranging from 1 to 100µm.

The expanded graphite may have a mean particle size D50, as measured by laser diffraction, ranging from 20 to 60µm .

The floor screed composition usually comprises aggregate, e.g. sand, and may comprise other additives such as plasticizers, anti foaming agents, fluidizers, superplasticizers and dispersants, SiC, B₄C and/or Al₂O₃.

According to some embodiments, the expanded graphite may be present in an amount less than 2.5 %w, the %w being based upon the weight of said floor screed composition.

This weight percentage "X %w" of the expanded graphite means that X gram of expanded graphite is used per 100 gram of the floor screed composition in pourable form, i.e. ready to be used to provide the floor screed on the job site.

The floor screed composition according to the present invention comprises expanded graphite preferably in an amount less than 1.5 %w, the %w being based upon the weight of said floor screed composition. Floor screed comprising expanded graphite in an amount of from 0,001 to 2,5 weight%, such as in the
5 range of 0.001%w to 1.5%w with said %w being based upon the weight of said floor screed composition are particularly preferred.

According to some embodiments, the floor screed composition may further comprise an anti foaming agent.

10 According to some embodiments, the anti foaming agent may be selected from silicone-based antifoaming agents, fatty acids, esters, polypropylene glycols, and combinations thereof.

The amount of anti foaming agent is preferably between 0.01 and 2%w, and more preferred between 0.01 and 0.5%w, the %w based upon the weight of said
15 hydraulic binder.

According to some embodiments, the floor screed composition may further comprise fluidizing agents and/or dispersants and/or plasticizers and/ or superplasticizers.

20 The fluidizing agents and/or dispersants and/or plasticizers and/ or superplasticizers may be selected from sulfonated condensation products of formaldehyde and naphthalene, sulfonated condensation products of formaldehyde and melamine, comb-branched copolymers having a backbone of acrylic and metacrylic acid, esterified with polycabroxylates or polyoxyalkylenes,
25 such as polyoxyethylenes and combinations thereof.

The total amount of fluidizing agents and/or dispersants and/or plasticizers and/ or superplasticizers are is preferably between 0.01 and 2%w, and more preferred between 0.02 and 1%w, the %w based upon the weight of said
30 hydraulic binder.

When fluidizing agents and/or dispersants and/or plasticizers and/ or superplasticizers are used, and an antifoaming agent is used, the weight ratio anti foaming agent over fluidizing agents and/or dispersants and/or plasticizers and/ or superplasticizers is between 0.005 and 200, preferably between 0.05 and 20.

The floor screed composition is combined and mixed with water to form a suitable floor screed in wet state. After applying the wet floor screed, the screed cures and evaporates part of the water. The floor screed so obtained is in dry state . The weight ration of water/calcium sulphate is preferably between 0.27 and 0.70, and more preferred between 0.35 and 0.55 such as between 0.35 and 0.45 .

According to a second aspect of the present invention, a floor screed composition according to the first aspect of the invention is used for the manufacture of a floor screed.

According to some embodiments, the floor screed being provided may have a thermal conductivity measured according to NF EN 993-15 of at least 1,8 W/mK.

According to some embodiments, the floor screed composition may further comprise aggregates.

According to a third aspect of the invention, a method to provide a floor screed composition is provided, the method comprises

- providing a hydraulic binder
- providing expanded graphite such that the amount of expanded graphite is less than 12 %w, the %w being based upon the weight of the hydraulic binder

- adding the expanded graphite to the hydraulic binder to provide a floor screed composition .

5 According to some embodiments, the addition of hydraulic binder and the expanded graphite may be performed in the presence of water.

According to some embodiments, at least part of the expanded graphite may be added to the hydraulic binder packed in a water soluble container.

10 This container can e.g. be a water soluble bag, e.g. a polyvinyl alcohol based bag.

According to some embodiments, at least part of the expanded graphite may be provided together with the water.

15 According to some embodiments, at least part of the expanded graphite may be provided together with the hydraulic binder.

The independent and dependent claims set out particular and preferred features of the invention. Features from the dependent claims may be combined with
20 features of the independent or other dependent claims, and/or with features set out in the description above and/or hereinafter as appropriate.

The above and other characteristics, features and advantages of the present invention will become apparent from the following detailed description, which
25 illustrate, by way of example, the principles of the invention. This description is given for the sake of example only, without limiting the scope of the invention.

Description of illustrative embodiments

30 The present invention will be described with respect to particular embodiments.

It is to be noticed that the term "comprising", used in the claims, should not be interpreted as being restricted to the means listed thereafter; it does not exclude other elements or steps. It is thus to be interpreted as specifying the presence of the stated features, steps or components as referred to, but does not preclude
5 the presence or addition of one or more other features, steps or components, or groups thereof. Thus, the scope of the expression "a device comprising means A and B" should not be limited to devices consisting only of components A and B. It means that with respect to the present invention, the only relevant components of the device are A and B.

10 Throughout this specification, reference to "one embodiment" or "an embodiment" are made. Such references indicate that a particular feature, described in relation to the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases "in one embodiment" or "in an embodiment" in various places throughout this specification are not
15 necessarily all referring to the same embodiment, though they could. Furthermore, the particular features or characteristics may be combined in any suitable manner in one or more embodiments, as would be apparent to one of ordinary skill in the art.

20 EXAMPLES

The following products were used for the preparation of the compositions in the examples :

- Calcium sulphate (CaSO_4) being binder named CAp and obtainable from La
25 Chape liquide;
- Sand being 0/4 Perrin (Dmax 4mm)
- Expanded graphite (Exp. C): Timrex® C-Therm™ 012 commercialised by Timcal;
- Natural graphite (Nat. C) : Timrex® 50x100 commercialized by Timcal;
- Silicon carbide(SiC) as commercialized under the name F600 by LAMPLAN;
- 30 -Boron carbide (B_4C) as commercialized under the name F120 by LAMPLAN

-Aluminium oxide (Al_2O_3) : as commercialized under the name F1200 by LAMPLAN

5 Table 1 summarizes the compositions of the mortars which have been prepared and tested as follows :

1 : mortar preparation

10 The binder (CaSO_4) and the additive are weighted and mixed for 5min with a turbula mixer. The sand is weighted, and the volume of water is defined and weighted as well.

First, the water is introduced in the mixer. The binder premixed with the additive is added and mixed for 30s at 140rpm, after which the sand is added.

15 The mixing procedure is continued according to the norm EN 196-1

2 : test specimen

After mixing the mortar is poured into two 14x16x4cm moulds

Let it dry for 28 days (at 20°C /65%HR) before testing

20 The test results are also added in the table 1. The amount of the additives which have been tested as thermal conductivity enhancers (i.e. expanded graphite, natural unexpanded graphite, silicon carbide, boron carbide and aluminium oxide) are expressed in weight % with respect to the weight of the calcium sulphate. The thermal conductivity (λ) has been measured on test specimens of 14x16x4 cm according to standard NF EN 993-15.

25

The results in table 1 show that compositions comprising the expanded graphite at the same dosage level expressed in weight % with respect to the binder, give higher thermal conductivities.

Table 1

	CaSO ₄	Sand	Water	Exp. C	Nat. C	SiC	B ₄ C	Al ₂ O ₃	λ
unit	kg/m ³	kg/m ³	l/m ³	wt%	wt%	wt%	wt%	wt%	W/mK
1a	650	1240	300	3					2.7
1b	650	1240	300	6					3.3
2	650	1240	300						1.9
3a	650	1240	300		3				2.1
3b	650	1240	300		6				2.5
3c	650	1240	300		11.5				2.6
4a	650	1240	300			3			2.1
4b	650	1240	300			6			2.1
4c	650	1240	300			11.5			2.2
5a	650	1240	300				3		2.0
5b	650	1240	300				6		2.1
5c	650	1240	300				11.5		2.2
6a	650	1240	300					3	2.1
6b	650	1240	300					6	2.2
6c	650	1240	300					11.5	2.1

w% are based upon weight of CaSO₄

- It is to be understood that although preferred embodiments and/or materials have been discussed for providing embodiments according to the present invention, various modifications or changes may be made without departing from the scope and spirit of this invention.

CLAIMS

- 5 1.- Floor screed composition, said composition comprising a hydraulic binder and expanded graphite, characterized in that the amount of expanded graphite is less than 12 %w, the %w being based upon the weight of said hydraulic binder .
- 10 2.- Floor screed composition according to claim 1 wherein said hydraulic binder is calcium sulphate.
- 15 3.- Floor screed composition according to claim 1 or 2 comprising expanded graphite in an amount of at least 0.01%w, the %w being based upon the weight of said hydraulic binder.
- 4.- Floor screed composition according to any one of the claims 1 to 3 comprising expanded graphite in an amount of at least 0.4%w, the %w being based upon the weight of said hydraulic binder.
- 20 5. - Floor screed composition according to any of the preceding claims wherein the expanded graphite has a mean particle size D50, as measured by laser diffraction, ranging from 1 to 100 μ m.
- 25 6.- Floor screed composition according to any of the preceding claims, wherein the expanded graphite being present in an amount less than 2.5 %w , the %w being based upon the weight of said floor screed composition.

- 7.- Floor screed composition according to any one of the preceding claims, wherein the floor screed composition further comprises an anti foaming agent.
- 5 8.- Floor screed composition according to any one of the preceding claims, wherein the floor screed composition further comprises fluidizing agents and/or dispersants and/or plasticizers and/ or superplasticizers.
- 9.- The use of a floor screed composition according to any of the claims 1 to 8
10 for the manufacture of a floor screed.
- 10.- A method to provide a floor screed composition, said method comprises
- providing a hydraulic binder
 - providing expanded graphite such that the amount of expanded
15 graphite is less than 12 %w, the %w being based upon the weight of said hydraulic binder
 - adding said expanded graphite to said hydraulic binder to provide a floor screed composition .
- 20 11.- Floor screed composition according claim 10 wherein the floor screed composition further comprises aggregates.
- 12.- A method according to claim 10 or 11, wherein the addition of hydraulic
25 binder and the expanded graphite being performed in the presence of water.
- 13.- A method according to claim 12, wherein at least part of the expanded
30 graphite is added to the hydraulic binder packed in a water soluble container.

- 14.- A method according to claim 10 to 13, wherein at least part of the expanded graphite is provided together with the water.
 - 15.- A method according to claim 10 to 14, wherein at least part of the expanded graphite is provided together with the hydraulic binder.
- 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/062062

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B28/14 C04B28/16
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	WO 2011/095634 A1 (KNAUF GIPS KG [DE]; HUMMEL HANS-ULRICH [DE]; SCHELLER LOTHAR [DE]; STI) 11 August 2011 (2011-08-11) the whole document	1-8, 10-15
X	DE 10 2004 039107 A1 (ANNELIESE ZEMENTWERKE AG [DE]) 30 June 2005 (2005-06-30) paragraphs [0021] - [0034] claims 1,4	1,3-5,8, 10-12,15
X	DE 103 41 299 A1 (FAGERDALA DEUTSCHLAND GMBH [DE]) 31 March 2005 (2005-03-31) paragraphs [0001], [0015] claim 9	1,10,15
	----- -/--	

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 5 August 2014	Date of mailing of the international search report 13/08/2014
---	---

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 Gattinger, Irene
--	---

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/062062

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101 376 583 A (UNIV SOUTHEAST [CN]) 4 March 2009 (2009-03-04) abstract claim 1	1,10
X	----- DE 100 49 230 A1 (ANNELIESE ZEMENTWERKE AG [DE]; ZAE BAYERN [DE]) 18 April 2002 (2002-04-18) cited in the application the whole document	1-15
A	----- EP 2 476 658 A1 (CUGINI S P A [IT]) 18 July 2012 (2012-07-18) the whole document -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/EP2014/062062

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2011095634	A1	11-08-2011	AU 2011212357 A1 02-08-2012
			EA 201201119 A1 30-01-2013
			EP 2533976 A1 19-12-2012
			JP 2013518803 A 23-05-2013
			US 2012305162 A1 06-12-2012
			WO 2011095634 A1 11-08-2011

DE 102004039107	A1	30-06-2005	NONE

DE 10341299	A1	31-03-2005	NONE

CN 101376583	A	04-03-2009	NONE

DE 10049230	A1	18-04-2002	NONE

EP 2476658	A1	18-07-2012	NONE
