(19) World Intellectual Property Organization

International Bureau





PCT

(43) International Publication Date 9 April 2009 (09.04.2009)

(51) International Patent Classification: *C04B 26/02* (2006.01) *C04B 26/18* (2006.01)

(21) International Application Number:

PCT/IT2007/000696

(22) International Filing Date: 3 October 2007 (03.10.2007)

(25) Filing Language: Italian

(26) Publication Language: English

- (71) Applicant (for all designated States except US): STONE ITALIANA SPA [IT/IT]; Via del Perlar, 2, I-37135 Verona (IT).
- (72) Inventor; and
- (75) Inventor/Applicant (for US only): DALLA VALLE, Roberto [IT/IT]; Via Sen. Montresor, 11, I-37012 Bussolengo (IT).
- (74) Agent: SANDRI, Sandro; Europatent Euromark S.r.l., Via Locatelli, 20, I-37122 Verona (IT).

- (10) International Publication Number WO 2009/044417 A1
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, 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, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, 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, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report



(54) Title: AGGLOMERATED MATERIAL FOR FLOORINGS AND COVERINGS, AS WELL AS A METHOD FOR OBTAINING THE SAME

(57) Abstract: An agglomerated material used in the production of slabs, tiles and blocks for floorings and coverings. The material consists of a mixture comprising 50 to 70% white quartz, 20 to 30% glass powder, 0.5 to 2% microspheres and 8 to 10% resin and additives. The microspheres are made from glass and have a granulometry of approximately 0.15 to 025 mm.

WO 2009/044417 - 1 - PCT/IT2007/000696

"AGGLOMERATED MATERIAL FOR FLOORINGS AND COVERINGS, AS WELL AS A METHOD FOR OBTAINING THE SAME"

TECHNICAL FIELD

The present invention describes an agglomerated material for floorings and coverings comprising a mixture of unfinished stony material, microspheres and glass powder, colorants and mica, a binder preferably consisting of a resin and a filler preferably consisting of white quartz, where the unfinished stony material is mixed with these components in powder, granular or similar form.

The present invention also refers to a method for the industrial production of tiles, slabs and blocks made from the agglomerated material according to this invention.

10

15

25

30

The present invention primarily applies to the production of floorings and coverings for indoor and outdoor applications for use in the construction industry.

A further use of the agglomerated material would be a metallized embodiment for use in the production of kitchen worktops, tables and other items of furniture.

BACKGROUND ART

Agglomerated materials consisting of various mixtures of marble, granite, quartz, natural stone and silica sands agglomerated to obtain a synthetic material for use as floor and wall coverings have been known for some time.

Frequent attempts have been made to give the surface of this material a glossy sheen intended to create a pleasing appearance and an enhanced visual impact especially in applications in large open spaces.

These attempts, consisting mainly of adding colorants to the basic mixture, have not however produced a product with a lasting glossy finish or a glossy sheen which is distributed uniformly over the entire surface of the agglomerated material treated in this way.

It would be particularly advantageous to be able to produce a glossy stonebased agglomerated material with a uniform colour and granulometry whose proportions could also be precisely specified at the outset. It would also be WO 2009/044417 - 2 - PCT/IT2007/000696

advantageous if this material had isotropic reflecting properties, features which are not common in natural stone.

One of the known production methods consists of several stages starting with the crushing of the basic material comprising the agglomerate. The crushed material is mixed with a hot polymerizing resin to form a paste which is then moulded under vacuum using vibrocompression to produce slabs of the shape required. Finally, the resinous material in the slabs is hardened or hot polymerized.

5

10

15

20

25

30

After production with this method, the slabs of material are polished and then cut to size, chamfered, thicknessed and countersunk.

It should be noted that the percentage of resin used in this type of mix is of crucial importance and needs to be chosen with considerable care and precision.

If the amount of resin is too high, the slab will be too soft and will have a closed, honeycomb structure which will not allow any air trapped in the paste to escape during the subsequent vacuum-vibrocompression moulding stage.

If, on the other hand, the amount of resin used is insufficient, the resulting paste will be too dry, have a poor consistency and will not bond sufficiently during vibrocompression moulding.

One of the known methods for increasing the hardness and wear resistance of slabs of agglomerated material is to add a very fine silica powder or sand to the paste. In this case the silica does not impregnate the resin but acts a filler and at the same time enables a reduction in the quantity of resin necessary.

Another method known to specialists in the sector involves the production of agglomerated material in blocks. Once the resin has been polymerized and the agglomerated material hardened, the blocks are cut into slabs to form floor or wall tiles or made-to-measure components such as steps, bathroom surfaces, kitchen tops and window sills.

This type of agglomerated material has good mechanical characteristics which make it suitable for walling and flooring applications outdoors. However, it does have a drawback in that it has an opaque, non-reflecting surface and is not therefore suitable for enhancing the appearance of architectural features or creating a sense of space. Partially reflecting agglomerated material has the drawback that it does not maintain its gloss over a long enough period of time.

WO 2009/044417 - 3 - PCT/IT2007/000696

A further drawback is that slabs which are cut from a block require sanding and polishing, two operations which can sometimes make the machined surfaces opaque.

In order to increase surface gloss and sheen, it is general practice to include resins, additives, colorants, silica powders, silica sands and a special material called crystobalite in the raw materials used to make agglomerate pastes.

5

10

15

20

25

30

Crystobalite is a rare crystalline mineral occurring naturally as silica dioxide or silica. This mineral has a white-yellowish, glassy appearance and crystallizes in the tetragonal system; it does not have individual split crystallites but groups of spheroidal shape.

Crystobalite is found in igneous rock and traces have been found in lunar rocks and meteorites.

Silica sands, silica and crystobalite are recognised as improving the appearance of the final product but are all harmful to health, not to the final users of wall and floor coverings, but rather to those involved in the manufacturing processes and laying the material. All these materials are health hazards and the source of a serious disease called silicosis.

This disease is caused by prolonged exposure to crystalline silica dioxide which occurs naturally in quartz, chalcedony and opal. Those at risk are industrial workers exposed to airborne concentrations higher than 1%.

The highest risks occur in the manufacture and cutting of slabs and cladding tiles made from agglomerated materials containing silica, silica powders and crystobalite.

The hazard level depends on the percentage level of crystalline silica dioxide in the air inhaled and the length of exposure.

DISCLOSURE OF INVENTION

The purpose of the present invention is to eliminate or significantly reduce the disadvantages of the known method by providing an agglomerated material comprising a base made from stony material, a binding agent preferably consisting of a resin and a filler preferably consisting of glass powder, glass microspheres and white quartz powder. The agglomerated material is used to make slabs, tiles or

WO 2009/044417 - 4 - PCT/IT2007/000696

blocks which have surfaces reflecting light in multiple directions and a product which is generally whiter than traditional products.

This purpose is fulfilled by the agglomerated material described in the present invention and characterised in the main claims below.

The dependent claims describe a preferred embodiment of the invention.

The present invention also includes a method for manufacturing slabs and blocks of metallized agglomerated material according to the invention.

This method is described in claim 5.

5

10

15

20

25

The dependent claims to claim 5 describe a preferred embodiment of the manufacturing method according to the invention.

The agglomerated material described in the present invention consists of a mixture comprising 50 to 70% white quartz, 20 to 30% glass powder, 0.5 to 2% microspheres and 8 to 10% resin and additives.

In a preferred embodiment of the invention the microspheres are made from glass and have a granulometry of approximately 0.15 to 0.25 mm.

The agglomerated material according to the present invention, even though it contains no silica, silica powder or crystobalite, has excellent physical and mechanical characteristics. It has an exceptionally glossy sheen and is very white.

The slabs produced in this way are whiter than those produced with conventional methods.

The glossy slabs obtained with this process would be suitable for use in churches, museums and other imposing public buildings. They could also be used as table tops, kitchen worktops and floor and walling tiles.

Slabs of metallized agglomerated material made according to the present invention could be cut to size without losing their glossy sheen or whiteness. No further surface polishing would be needed. This material has an exceptional aesthetic appeal and at the same time is simpler and easier to prepare and install.

This metallized agglomerated material can withstand high breaking loads and is very resistant to scratching and corrosion particularly by acid.

A further purpose of this invention is to provide a production method for manufacturing slabs of metallized agglomerated material in preset sizes.

WO 2009/044417 - 5 - PCT/IT2007/000696

The production method employs automated machinery where one or more computers control the various steps in the method. The first step of the method consists of the crushing of the stony base material.

In the second step of the method the crushed stone is mixed with quartz, glass microspheres and glass powder in a special mixing machine. A suitable binder and a colorant are added to this mixture.

5

10

15

20

25

30

The binder could be any suitable resin and in a preferred embodiment would be a polymer resin.

In the third method step the product mixture is poured into the mould of a press where a pressing force is applied to the product. This combined with the activation of a vibrating device and a vacuum device forms the slab into a preset shape, usually square, of a predefined thickness and density.

After this step the slab is conveyed into an oven where it hardens, thanks to the action of the chemical additives, at a preset temperature and for a suitably selected period of time.

The slab leaves the oven and is conveyed to the work stations downstream for further treatment. Treatment could consist of polishing on one or both faces, cutting to size, chamfering, thicknessing and countersinking. After these operations the slab is conveyed to the waxing, drying and packing stations.

The method described above enables the continuous production of agglomerated material slabs precisely conforming to the lengths, widths and thicknesses specified and having a glossy sheen and a brilliant white colour.

In addition to the polymerizing catalysts and accelerants added to the mixture employed with this method, it would also be possible to add brass, aluminium, alloy or other metallic components to the basic paste mixture in order to produce special optical effects and other types of appearance.

A further advantage of agglomerated materials is that they have a high resistance to atmospheric and chemical corrosion and also to wear and scratching. The synthetic tiles and slabs manufactured from this material are therefore highly durable and their glossy sheen remains unchanged with the passing of time.

WO 2009/044417 - 6 - PCT/IT2007/000696

The next section describes a non-limiting example formulation of the agglomerated mixture according to the invention used to produce the slabs employing the method described above.

5

DESCRIPTION OF AN EXAMPLE EMBODIMENT

The example described below indicates the components of the agglomerated material according to the invention and their percentages by weight of the total weight of a material sample and where the formula is that for a single press:

COMPONENTS	% WEIGHT	KG
TOTAL COLOUR	3.00	15.0
UP 205/14 resin	9.3	46.4
Kalemaden quartz 0.1/0.3 mm	48.5	242
Kalemaden quartz 0.3/0.5 mm	15.6	78
Microspheres 0.15-0.25 mm	1.0	5
PIN 327, 30 micron	25.6	128
TOTAL:	103.00	499.4

The UP 205/14 resin consists of the following materials:

Catalytic additives	% of resin	Kg
CATALYST	2.21	1.027
MEMO SILANE	1.21	0.56
ACCELERANT	0.18	0.084

The embodiments of the invention described above are intended as examples only.

The invention is in no way limited to these embodiments and includes all the possible modifications and variants which enter within the terms of this invention and the claims below.

For example, the mixture used in one embodiment of the agglomerated material according to the present invention could contain inclusions of various types

WO 2009/044417 - 7 - PCT/IT2007/000696

such as fragments of metal and wood in addition to the polymerizing catalysts and accelerants.

The invention as described above refers to a preferred embodiment which is non-limiting. Clearly the invention includes the numerous possible variants which are technically equivalent.

WO 2009/044417 - 8 - PCT/IT2007/000696

CLAIMS

- 1. An agglomerated material used for the production of slabs, tiles or blocks for floorings and coverings, consisting of a mixture wherein the mixture consists of 50 to 70% white quartz, 20 to 30% glass powder, 0.5 to 2% microspheres and 8 to 10% resin and additives.
- 2. An agglomerated material used for the production of slabs according to the foregoing claim 1 wherein the microspheres are made from glass and have a granulometry of approximately 0.15 to 0.25 mm.

5

10

25

- 3. An agglomerated material according to the foregoing claims 1 and 2 wherein the resin is a polyester-based resin.
 - 4. An agglomerated material according to the foregoing claims from 1 to 3 wherein the quartz used has a white colour.
- 5. A method for the production of slabs made from the agglomerated material according to the foregoing claims wherein the method consists of a step where the crushed stony base material and inert fillers are mixed with a binder, a step where the material is pressed and vibrocompressed under vacuum, a step where the material is heated in an oven to a preset temperature for a preset time in order to catalyse the binder, and wherein the material comprises a mixture consisting of 50 to 70% white quartz, 20 to 30% glass powder, 0.5 to 2% microspheres and 8 to 10% resin and additives and wherein the purpose of the method is to produce slabs, tiles and blocks of a high quality and of a white colour.
 - 6. A method according to claim 5 wherein the slabs leaving the firing step are subject to polishing, cutting, chamfering, thicknessing and countersinking operations in various combinations or as single operations.
 - 7. A method according to claim 5 wherein the mixture comprises total colour 3.00% (15.00 kg.), UP 205/14 resin 9.3% (46.4 kg.), Kalamaden quartz with 0.1/0.3 mm granulometry 48.5% (242 kg.), Kalamaden quartz with 0.3/0.5 mm granulometry 15,6% (78 kg.), microspheres of 0.15-0.25 mm 1.0% (5 kg.), PIN 327 glass powder 30 micron 25.6% (128 kg.), for a total weight of 514.40 kg.
 - **8.** A method according to claim 5 wherein the UP 205/14 resin comprises the following materials:

WO 2009/044417 - 9 - PCT/IT2007/000696

- catalyst 2.21% (1.027 kg.), MEMO silane 1.21% (0.56 kg.) and accelerant 0.18% (0.084 kg.).
- 9. Flooring and covering tiles and slabs wherein these items are made from a bonded mixture comprising 50 to 70% white quartz, 20 to 30% glass powder,0.5 to 2% microspheres and 8 to 10% resin and additives.

INTERNATIONAL SEARCH REPORT

International application No PCT/IT2007/000696

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B26/02 C04B2 C04B26/18 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) CO4B 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 practical, search terms used) EPO-Internal C. DOCUMENTS CONSIDERED TO BE RELEVANT Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. US 2006/270758 A1 (ONG IVAN W [US] ET AL) 1-6.9Α 30 November 2006 (2006-11-30) the whole document WO 2005/111126 A (TONCELLI LUCA [IT]) 1-6.9A 24 November 2005 (2005-11-24) the whole document WO 2004/043873 A (UNIV SOUTHERN QUEENSLAND Α [AU]; VAN ERP GERARDUS MARIA [AU]) 27 May 2004 (2004-05-27) the whole document US 7 198 833 B1 (WEST ALBERT C [US]) Α 3 April 2007 (2007-04-03) the whole document Further documents are listed in the continuation of Box C. See patent family annex. Special categories of cited documents: 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 "A" document defining the general state of the art which is not considered to be of particular relevance earlier document but published on or after the international "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to "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) involve an inventive step when the document is taken alone 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 docu-"O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled in the art. document published prior to the international filing date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 13/08/2008 1 August 2008 Authorized officer Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016 Gattinger, Irene

INTERNATIONAL SEARCH REPORT

International application No PCT/IT2007/000696

(Continua	tion). DOCUMENTS CONSIDERED TO BE RELEVANT		<u> </u>
Category*	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
4	US 6 004 663 A (SWARTS DONALD EUGENE [US]) 21 December 1999 (1999-12-21) the whole document		
•			
			· .
		•	
		A +	
		•	
. •			
•		•	
		-	
	·		· ·
			·
			·

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 7,8

Present claims 7 and 8 relate to a product defined by components, which are characterized by terms that appear to be trade names:

Claim 7 and 8: UP 205/14 resin Claim 7: PIN 327 glass powder

Claim 8: MEMO silane

The use of these product names in the present context is considered to lead to a lack of clarity within the meaning of Art. 6 PCT. The lack of clarity is such as to render a meaningful complete search impossible.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

International application No. PCT/IT2007/000696

INTERNATIONAL SEARCH REPORT

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:
Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:
2. Claims Nos.: 7,8 because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).
Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)
This International Searching Authority found multiple inventions in this international application, as follows:
As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search reportcovers only those claims for which fees were paid, specifically claims Nos.:
<u> </u>
No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
Remark on Protest The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
No protest accompanied the payment of additional search fees.
·

INTERNATIONAL SEARCH REPORT

information on patent family members

International application No PCT/IT2007/000696

	atent document d in search report		Publication date	Patent family Publication member(s) date	
US	2006270758	A1	30-11-2006	NONE	
WO	2005111126	A	24-11-2005	CA 2564401 A1 24-11-20 EP 1761593 A1 14-03-20 KR 20070010181 A 22-01-20 US 2007257391 A1 08-11-20	107 107
WO	2004043873	A	27-05-2004	CA 2506077 A1 27-05-20 EP 1581461 A1 05-10-20 US 2006014878 A1 19-01-20	05
US	7198833	B1	03-04-2007	NONE	
us	6004663	Α	21-12-1999	AT 184237 T 15-09-19 AU 694652 B2 23-07-19 AU 5431896 A 16-10-19 CN 1179749 A 22-04-19 DE 69604164 D1 14-10-19 DE 69604164 T2 04-05-20 EP 0817721 A1 14-01-19 JP 3020611 B2 15-03-20 JP 10505031 T 19-05-19 TR 960900 A2 21-10-19 WO 9630204 A1 03-10-19	998 998 999 900 998 998