

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
18 May 2017 (18.05.2017)

(10) International Publication Number
WO 2017/080569 A1

(51) International Patent Classification:
E04C 2/04 (2006.01)

(21) International Application Number:
PCT/EP2015/002557

(22) International Filing Date:
18 December 2015 (18.12.2015)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10 2015 014 513.4
11 November 2015 (11.11.2015) DE

(71) Applicant: **KNAUF GIPS KG** [DE/DE]; Am Bahnhof 7,
97346 Iphofen (DE).

(72) Inventor: **BRÜCKNER, Sylvia**; Salvatorstrasse 15B,
97074 Würzburg (DE).

(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, 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, ST, 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))

(54) Title: BUILDING PRODUCTS WITH GRAPHENE OR GRAPHENE OXIDE

(57) Abstract: The invention relates to building products, in particular building boards, which comprise graphene and/or graphene oxide.



WO 2017/080569 A1

Building products with graphene or graphene oxide

The invention relates to building products, in particular building boards. In particular, the invention relates to building products and building boards which comprise a material with a hexagonal honeycomb structure, preferably in a monomolecular layer thickness.

Building products such as building boards, partition wall boards, floor screeds, plasters or fillers are known from the prior art. All these products have to have a certain strength with respect to mechanical and/or thermal loading. There are various possible ways of producing these properties in a specific product. The simplest way is for the base materials for the production of this product to be selected corresponding to the desired property. If, however, combinations of a plurality of properties are desired in a product, the appropriate choice of a base material is often not sufficient. Functional materials in the broadest sense are used in these cases.

Materials comprising two dimensional networks with a monomolecular layer thickness such as graphene or silicene are relatively new materials on the market of material sciences. They have outstanding mechanical, chemical and electrical properties, which are intended to be used within the scope of this invention.

Graphene is a material which forms the basic structure of graphite. Graphite comprises layers of graphene stacked upon one another in an ordered or random manner, said layers being held together in layer packs by means of relatively weak van der Waals forces. The mechanical properties of graphite are dominated by the layer pack bonding by means of van der Waals forces. The layers held together by the van der Waals

- 2 -

forces can be split up relatively easily into smaller layer packs by shearing. This property enables, for example, the use of graphite in pencil leads for writing.

In contrast with this, no van der Waals bonds are present in graphene, because it
5 consists of monomolecular layers and not layer packs, as is the case with graphite. In an ideally constituted graphene, there is a hexagonal basic structure, wherein six C atoms are each bonded together by non-localised covalent double bonds to form honeycomb structures. The bonding energy between two of these C atoms is among the most powerful known in nature and stands at approx. 5.9 eV. This explains the very
10 much greater mechanical stability of this material compared to graphite: It has been demonstrated that graphene has a greater tear resistance than steel.

Graphene oxide has good mechanical properties similar to those of graphene. The basic structure is similar to graphene, i.e. it involves monomolecular layers of
15 hexagonal-honeycomb structures, which however have a more pronounced corrugation compared to graphene. Graphene oxide is water-soluble and forms a colloidal dispersion with water, which is very well suited for the production of paper-like films and for use as a coating agent.

20 The terms "graphene" and "graphene oxide" are also understood to mean modifications/derivatives of functionalized compounds which are directly derived from these materials.

Within the scope of this invention, the terms graphene and graphene oxide denote not
25 only the pure substances, but also mixtures, in particular mixtures of graphene and/or graphene oxide with graphite. Graphene-containing or graphene oxide-containing mixtures are ones which contain more than 1 vol.-% graphene or graphene oxide, particularly preferably more than 3 vol.-% and especially preferably more than 10 vol.-% graphene or graphene oxide in the dry matter, verified by atomic force microscopy in
30 combination with Raman spectroscopy. This restriction of the lower limit serves

- 3 -

essentially to differentiate between graphene-containing dispersion products and exclusively graphite-containing dispersions.

Following literature, graphene here is denoted as graphene in its form with a monomolecular layer thickness, but also in layer stacks of less than 10 graphene layers upon one another (see Eigler, S. and Hirsch, A. (2014): Chemie an Graphen und Graphenoxid – eine Herausforderung für Synthesechemiker, Angew. Chem. 2014, Vol. 126, S. 2 – 23). Layer stacks of graphene with 11 and more graphene layers are understood to mean graphite.

The fundamental idea of the invention is based on the use of graphene and graphene oxide in building materials in general and building boards in particular. Building materials include in particular building boards, partition wall boards, floor screeds, plasters and fillers.

Particularly preferably, building materials are on a calcium sulphate-containing base, i.e. anhydrite-based, calcium sulphate-hemihydrate-based and gypsum-based building materials. Materials that have a calcium sulphate-containing base have a proportion of calcium sulphate of at least 10 wt.-%, preferably at least 50 wt-% and particularly preferably at least 80 wt.-% related to the dry binding material content of the mixture.

Alternatively, the invention can also be applied to cement-containing building products in general, wherein the calcium sulphate content of these products can lie below the aforementioned 10 wt.-% of the dry matter of the binding agent, or the product can even be essentially free from calcium sulphate. In this case, the binding agent can for example be a hydraulic cement, another inorganic binding agent such as for example water glass or an organic binding agent such as for example a natural or a synthetic resin.

- 4 -

Moreover, irrespective of their base material, building boards are covered by the invention if they contain a material with a hexagonal honeycomb structure and a monomolecular layer thickness. Building boards for drywall construction can comprise the most diverse materials, e.g. wood, gypsum, cement, microspheres (e.g. perlite, cenospheres of fly ash, ceramic microspheres) etc. as a base material. In particular, the tensile strength of graphene and graphene oxide can be used advantageously to improve the mechanical properties of the building boards, such as the sag resistance, breaking load and bending tensile strength.

Moreover, especially graphene with its two-dimensional hexagonal honeycomb structure and the monomolecular layer thickness has considerable potential for improving the fire resistance of building materials, in particular of building boards or plasters. The thermal conductivity of graphene is highly anisotropic: It is very high in the propagation direction of the two-dimensional lattice, but very low in directions perpendicular to the lattice propagation direction. This means that high temperatures on one side of a graphene layer are not conducted to its other side.

The invention thus relates to building products comprising graphene and/or graphene oxide. Furthermore, the invention relates to building boards comprising graphene and/or graphene oxide.

According to a particularly preferred embodiment of the invention, the building board comprises graphene and/or graphene oxide in the form of a layer. This layer can be present on at least one, preferably both surfaces of the building board. In this arrangement, it can for example serve as an external reinforcement against mechanical loads or also as a fire protection material (raising of the fire protection class).

In a further embodiment, the building board can be constituted by a plurality of (i.e. at least two) material layers. These material layers can be the same or different. In the case of lightweight plasterboards, production from different layers for weight reduction

- 5 -

with unchanged mechanical loading capacity, for example, is becoming increasingly prevalent. For this purpose, relatively stable and dense boundary layers are constituted, which surround a highly porous core layer in a sandwich-like manner. In order to reinforce and further develop this "lightweight construction", the reinforcement of the external side of the building boards is particularly suitable.

In a preferred development of the invention, however, it is also or additionally possible to dispose a layer of graphene and/or graphene oxide between two layers of the building board. This reinforcement strengthens the building board from the interior.

The graphene layer and/or graphene oxide layer can be applied over the full area or a partial area on the surface of the building board or between the material layers of the building board.

A further possibility consists in the use of individual strips of graphene or graphene oxide. The strips can be advantageously applied in the longitudinal and/or transverse direction of the building board, i.e. the two-dimensional board extension, so that they run for example in the direction of the maximum mechanical loading of the board. The strips can thus also be introduced in a lattice form onto and/or into the building board, wherein the desired strengthening of the mechanical loading capacity of the building board can be adjusted by means of the lattice spacings and/or the variability of the thickness and/or the area dimensions of the lattice.

Particularly preferably, graphene and/or graphene oxide is used in a paper-like form. Graphene oxide paper can be produced for example by colloidal solution of graphene oxide and subsequent deposition over the area and drying of the graphene oxide flakes. Graphene paper can now also be produced by arranging a plurality of graphene layers upon one another, immersing them in a bath of surfactant and then drying them. The films thus produced can be processed like paper, i.e. cut, folded and so forth.

- 6 -

According to a further embodiment of the invention, the graphene and/or graphene-oxide layer is present on a surface of the building board and is encased over the full or a partial area by a casing material, for example paperboard or (nonwoven) fabric.

- 5 In a further variant of this embodiment, the graphene or graphene-oxide layer is applied not on the surface of the building board, but on the casing material. The casing material can be joined, for example by adhesion, with the layer; the casing material can however also be coated or saturated by means of a dispersion for example. The coating can take place before the application of the casing on the building board, or the encased building
10 board can be subsequently provided with the coating or saturation.

The use of graphene- or graphene-oxide layers, over the full or a partial area, for example in the form of strips, advantageously assists the sag resistance, the flexural strength and the bending tensile strength of the building boards. The same also applies
15 of course to other building products.

A further possibility of using graphene and/or graphene oxide advantageously in building boards consists in using the graphene and/or graphene-oxide layer as reinforcement in the building material itself. Various variants are suggested for
20 implementing this embodiment: On the one hand, the reinforcement can be present in an orientated manner in the board in the form of strips in the direction of the greatest loading (in particular tensile loading). The lattice arrangement of graphene and/or graphene oxide strips described above is however also possible. A layer disposed in the building board that covers a partial or the full area is of course also possible.

25

- 7 -

Claims

- 5 1. Building products, in particular building boards, wherein the building products comprise graphene and/or graphene oxide.
- 10 2. Building products according to claim 1, wherein the building product is a building board.
3. The building board according to claim 2, wherein the building board comprises graphene and/or graphene oxide in the form of a layer.
- 15 4. The building board according to claim 3, wherein the layer is present on at least one surface of the building board.
5. The building board according to claim 3, wherein the building board comprises a plurality of identical and/or different material layers, and the layer is disposed
20 between two of these layers.
6. The building board according to claim 4 or 5, wherein the layer is applied over the full area or a partial area on this surface or between these two material layers.
- 25 7. The building board according to any one of claims 3 to 6, wherein the layer comprises individual strips.
8. The building board according to claim 7, wherein the strips extend in the
30 longitudinal and/or transverse direction of the building board.

- 8 -

9. The building board according to any one of claims 3 to 8, wherein the layer of graphene or graphene oxide is paper-like.
- 5 10. The building board according to any one of claims 3 or 4, wherein the at least one layer is overlapped over the full area or a partial area by a casing material.
11. The building board according to any one of claims 3 or 5 to 9, wherein the at least one layer is contained as a reinforcement in the building board material.
- 10 12. Use of graphene and/or graphene oxide, for the mechanical strengthening of building products or for raising the fire resistance class of building products, wherein the building products are in particular cement-containing, preferably gypsum-containing building products.
- 15 13. The use according to claim 12, wherein the graphene and/or the graphene oxide is used in membrane, film, paper, strip or shred form.
- 20 14. A method for producing building boards, wherein a building board and/or a casing material of the building board is coated at least in sections with a dispersion, wherein the dispersion comprises graphene and/or graphene oxide.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2015/002557

A. CLASSIFICATION OF SUBJECT MATTER
INV. E04C2/04
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)
E04C E04B

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	CN 103 362 273 A (TAIZHOU GORGEOUS PLASTIC CO LTD) 23 October 2013 (2013-10-23)	1-4,6,9, 11-14
Y	claims 1-4; figure 1 -----	5,7,8,10
X	CN 103 359 997 A (UNIV QINGDAO TECHNOLOGICAL) 23 October 2013 (2013-10-23) abstract; claim 2; figures 1-2 -----	1,12
X	CN 103 922 687 A (UNIV HENAN NORMAL) 16 July 2014 (2014-07-16) abstract; claims 1-3 -----	1,12
X	WO 2011/093765 A1 (MEDIA OCH IT SKOLAN I DJURSHOLM AKTIEBOLAG [EC]; SVENSSON ROLF [SE]) 4 August 2011 (2011-08-04)	1,12
Y	page 11, lines 16-23 ----- -/-	5,10



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

29 June 2016

Date of mailing of the international search report

13/07/2016

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

Vratsanou, Violandi

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/002557

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/329045 A1 (JONES MARK [GB]) 6 November 2014 (2014-11-06)	1,12
Y	paragraphs [0044] - [0045]; figure 1 -----	10
Y	US 8 580 132 B2 (LIN XIAO-YANG [CN] ET AL) 12 November 2013 (2013-11-12) column 7, line 65 - column 8, line 3; claim 1; figures 6, 7 -----	7,8
A	WO 2014/037882 A1 (TRUE 2 MATERIALS PTE LTD [SG]) 13 March 2014 (2014-03-13) abstract; claim 1 -----	1-14
A	WO 2011/095634 A1 (KNAUF GIPS KG [DE]; HUMMEL HANS-ULRICH [DE]; SCHELLER LOTHAR [DE]; STI) 11 August 2011 (2011-08-11) abstract; claim 1 -----	12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2015/002557

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 103362273	A	23-10-2013	NONE
CN 103359997	A	23-10-2013	NONE
CN 103922687	A	16-07-2014	NONE
WO 2011093765	A1	04-08-2011	EP 2529058 A1 05-12-2012 RU 2012136714 A 10-03-2014 SE 1000073 A1 30-07-2011 WO 2011093765 A1 04-08-2011
US 2014329045	A1	06-11-2014	AU 2012277587 A1 16-01-2014 EP 2723953 A1 30-04-2014 GB 2493492 A 13-02-2013 US 2014329045 A1 06-11-2014 WO 2013001286 A1 03-01-2013
US 8580132	B2	12-11-2013	CN 103359720 A 23-10-2013 TW 201341302 A 16-10-2013 US 2013264307 A1 10-10-2013
WO 2014037882	A1	13-03-2014	CA 2883527 A1 13-03-2014 CN 104797526 A 22-07-2015 EP 2892847 A1 15-07-2015 JP 2015526382 A 10-09-2015 KR 20150082197 A 15-07-2015 SG 11201501609P A 29-04-2015 US 2015210552 A1 30-07-2015 WO 2014037882 A1 13-03-2014
WO 2011095634	A1	11-08-2011	AU 2011212357 A1 02-08-2012 CN 104136216 A 05-11-2014 DK 2533976 T3 27-07-2015 EA 201201119 A1 30-01-2013 EP 2533976 A1 19-12-2012 JP 5758917 B2 05-08-2015 JP 2013518803 A 23-05-2013 SI 2533976 T1 31-08-2015 UA 102050 C2 27-05-2013 US 2012305162 A1 06-12-2012 WO 2011095634 A1 11-08-2011