

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

(19) World Intellectual Property  
Organization  
International Bureau



(10) International Publication Number  
**WO 2016/009257 A1**

(43) International Publication Date  
21 January 2016 (21.01.2016)

(51) International Patent Classification:

C04B 28/04 (2006.01) C04B 7/19 (2006.01)  
C04B 28/08 (2006.01) C04B 40/06 (2006.01)

(21) International Application Number:

PCT/IB2015/001017

(22) International Filing Date:

23 June 2015 (23.06.2015)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

A 567/2014 17 July 2014 (17.07.2014) AT  
A 10/2015 8 January 2015 (08.01.2015) AT

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(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))



WO 2016/009257 A1

(54) Title: DRY CEMENT MIXTURE

(57) Abstract: A dry cement mixture comprises Portland cement and an ultra- fine component consisting of at least one ultra-fine additive, said ultra-fine component being a hydraulic binder, wherein Portland cement is present in an amount of at least 70 wt% of the mixture and the ultra-fine component is present in an amount of at least 5 wt% of the mixture, wherein the ultra-fine component has a particle size distribution characterized by a particle diameter  $D_{10}$  of between 0,5 $\mu$ m and 2 $\mu$ m and a particle diameter  $D_{90}$  of between 2 $\mu$ m and 8 $\mu$ m.

Dry cement mixture

The invention refers to a dry cement mixture comprising Portland cement and an ultra-fine component consisting of at least one ultra-fine additive, said ultra-fine component being a hydraulic binder, as well as to a concrete composition comprising said cement mixture.

Concrete is a very widely used construction material with high strength and good durability. In addition to aggregates and water, it also contains Portland cement as a hydraulic binder, which produces strength-forming phases by solidifying and curing in contact with water. Concrete based on Portland cement clinker is thus one of the most important binders worldwide.

By adding various additives such as, e.g., granulated blast-furnace slag (gbfs), fly ash, natural pozzolans, calcined clays or ground limestone to Portland cement, Portland composite cements having different properties can be produced. At the same time, the specific emission of CO<sub>2</sub> will be reduced in the production of cement by substituting the cited additives for Portland cement, because during the production of Portland cement clinker about 0,9 tons of CO<sub>2</sub> per ton of Portland cement clinker will be emitted by the calcination of the raw materials and from the oxidation of the fuels in the rotary tubular kiln. The addition of additives to Portland cement has been an established practice for more than 100 years and is regulated in numerous cement and concrete standards.

The addition of ultra-fine additives, such as microcement or microsilica, to Portland cement is used to enhance the durability and the strength of the resulting concrete. The traditional way of formulating high durability and strength and very high

durability and strength concrete is based on using ordinary Portland cement with ultra-fine additions as a binder. The ultra-fine additions commonly used are often conditioned in bags and mixed into the Portland cement by hand at the respective concrete plant or at the construction site, which involves safety risks as well as quality uncertainties. The ultra-fine additions can also be stored in a dedicated silo on a concrete plant and introduced automatically, but this involves the need of very specific industrial equipment that represents additional investments.

Another disadvantage of using ultra-fine additives in a cement mixture is the elevated water demand, since the water demand rises with increasing fineness of the ultra-fine additives.

It is commonly assumed that the durability and the strength of the resulting concrete, such as the compressive strength, strongly depends on the proportion of the ultra-fine additions in the cement mixture, namely that the higher the content of ultra-fine additions is, the better the durability and strength of the concrete is. Producing ultra-fine additions is costly due to the elevated grinding effort. Therefore, the cost of the cement mixture rises with an increasing content of ultra-fine additions.

Therefore, it is an object of the present invention to provide a cement mixture that overcomes the above drawbacks. In particular, it is an object of the invention to provide a cement mixture that allows an easy and reliable manufacture of concrete at a stable quality level. It is a further object of the invention to reduce the water demand without impairing the workability of the concrete mass. Further, the resulting concrete shall

have excellent durability and strength at a reasonable production cost.

To solve these and other objects, the invention is characterized in that Portland cement is present in an amount of at least 70 wt%, preferably at least 80 wt% of the mixture and the ultra-fine component is present in an amount of at least 5 wt% of the mixture, wherein the ultra-fine component has a particle size distribution characterized by a particle diameter  $D_{10}$  of between 0,5 $\mu$ m and 2 $\mu$ m and a particle diameter  $D_{90}$  of between 2 $\mu$ m and 8 $\mu$ m.

Thus, the invention provides a premix binder based on a combination of a Portland cement with at least one ultra-fine additive. The ultra-fine particles added to the mix allow obtaining a binder showing high performances (durability and strength) that is therefore particularly adapted for the formulation of high and very high performance concretes. Mixing is performed on a cement plant with a dedicated device, which introduces the various components with high accuracy, and allows obtaining a very homogeneous mixture. The inventive cement mixture is preferably delivered to customers as a dry premix for concrete production, wherein the dry premix is packed in bags or other suitable containers.

The invention allows concrete manufacturers to produce high strength and high durability concrete using only one binder, instead of mixing ordinary cement with ultra-fine additions (such as silica fume) on site. Customer benefits are regularity of the quality of the concrete produced, ease-of-use (leading to cost savings), high performances of the concrete produced, and aesthetics (the premix binder color is lighter than most of traditional cement and ultra-fine additions used).

It has surprisingly been found that a relatively low content of the ultra-fine component together with a specific particle size distribution results in durability and compressive strength values that usually are only to be achieved with a substantially higher proportion of ultra-fine additives. In particular, the invention provides for an amount of Portland cement of at least 80 wt% of the mixture, which means that the mixture contains a maximum of 20 wt% of the ultra-fine component. According to the invention, the ultra-fine component is a hydraulic binder and has a particle size distribution characterized by a particle diameter  $D_{10}$  of between 0,5 $\mu$ m and 2 $\mu$ m and a particle diameter  $D_{90}$  of between 2 $\mu$ m and 8 $\mu$ m.

The ultra-fine component of the cement mixture may consist of one, two or more ultra-fine additives. According to a preferred embodiment of the invention, the at least one ultra-fine additive comprises slag, in particular ground blast furnace slag. More specifically, the at least one ultra-fine additive comprises slag, in particular ground blast furnace slag, preferably in an amount of > 70 wt%, in particular > 80 wt%.

According to a further preferred embodiment the ultra-fine component (consisting of one or more ultra-fine additives) has a content of slag, in particular ground blast furnace slag, of > 70 wt%, in particular > 80 wt%. Thus, the ultra-fine component consists mainly of slag particles.

The cement mixture may, in addition to the ultra-fine component, also contain further additives.

According to a preferred design of the cement mixture, Portland cement is present in an amount of at least 85 wt%, preferably

at least 90 wt% of the mixture and the ultra-fine component is present in an amount of at least 7 wt%, preferably at least 10 wt% of the mixture. Thus, the maximum content of the ultra-fine component is narrowed down to 15 wt%.

5

According to a further preferred embodiment, the weight ratio of Portland cement and ultra-fine component is between 85/15 and 95/5, in particular about 90/10.

10 As mentioned above, the ultra-fine component binder has a particle size distribution characterized by a particle diameter  $D_{10}$  of between  $0,5\mu\text{m}$  and  $2\mu\text{m}$ , whereas ultra-fine additives usually have a lower  $D_{10}$  value in order to achieve the required durability standards. In contrast thereto, it has surprisingly been  
15 found that the specific  $D_{10}$ -range as mentioned above also results in sufficient durability and strength of the concrete, while at the same time reducing water demand and costs.

According to a preferred embodiment, the ultra-fine component  
20 has a particle size distribution characterized by a particle diameter  $D_{10}$  of between  $0,7\mu\text{m}$  and  $1\mu\text{m}$ .

With regard to the  $D_{90}$  value, the ultra-fine component preferably has a particle size distribution characterized by a particle  
25 diameter  $D_{90}$  of between  $4\mu\text{m}$  and  $6\mu\text{m}$ . These preferred  $D_{90}$  values may be combined with the preferred  $D_{10}$  values as mentioned above.

Particularly good results have been achieved by using an ultra-  
30 fine component that has a particle size distribution characterized by a particle diameter  $D_{100}$  of  $10\mu\text{m} - 15\mu\text{m}$ , in particular  $12\mu\text{m}$ .

In the context of the present invention the particle size distribution is defined by indicating specific percentiles of the particle diameter. The  $D_{90}$ -percentile of the diameter indicates that 90% of the particles have a diameter that is smaller than the given value. For example, a value for  $D_{90}$  of  $4\mu\text{m}$  indicates that 90% of the particles have a diameter that is smaller than  $4\mu\text{m}$ . Analogously, the  $D_{10}$ -percentile of the diameter indicates that 10% of the particles have a diameter that is smaller than the given value.

In order to optimize the durability and strength of the resulting concrete, a specific particle size distribution of the Portland cement may also be adjusted. Preferably, the Portland cement has a particle size distribution characterized by a particle diameter  $D_{10}$  of between  $1\mu\text{m}$  and  $3\mu\text{m}$ , preferably between  $1,6\mu\text{m}$  and  $2\mu\text{m}$ , in particular  $1,8\mu\text{m}$ , and a particle diameter  $D_{90}$  of between  $30\mu\text{m}$  and  $60\mu\text{m}$ , preferably between  $35$  and  $45\mu\text{m}$ , in particular  $40\mu\text{m}$ .

The Portland cement preferably is a CEM I cement according to EN 197-1.

The invention also refers to a concrete composition comprising a cement mixture according to the invention, aggregates and water. Preferably, the water/cement ratio is chosen between  $0.3$  and  $0.6$ .

Finally, the invention also refers to a construction element comprising concrete produced using a concrete composition as described above.

In the following, the invention will be explained in more detail by reference to exemplary embodiments.

Example 1:

A dry cement mixture with the following components was produced.

- 5 - 90 wt% of Portland cement of the type CEM I 52,5 N
- 10 wt% of an ultra-fine blast furnace slag binder.

Portland cement having the following particle size distribution was used:  $D_{10} = 1,8\mu\text{m}$  and  $D_{90} = \text{ca. } 40\mu\text{m}$

- 10 Ultra-fine blast furnace slag binder having the following particle size distribution was used:  $D_{10} = \text{ca. } 0,8\mu\text{m}$  and  $D_{90} = \text{ca. } 5,5\mu\text{m}$

The resulting mixture had the following composition:

- 15 - Clinker: 86,06 wt%
- Blast furnace slag: 7,8 wt%
- Gypsum: 5,6 wt%
- Anhydrite: 0,3 wt%
- Dust: 0,2 wt%
- 20 - NaCl: 0,04 wt%

Example 2:

Concrete was produced from the dry cement mixture as described in example 1. The following components were mixed in a mixer:

- 25 - 410 kg of dry cement mixture as described in example 1
- 907 kg of aggregates with a nominal maximum coarse diameter of 12,5 mm
- 797 kg of sand with a nominal maximum coarse diameter of
- 30 4mm
- 90 kg of limestone filler
- Superplasticizer admixture in the amount of 1,2 wt% of the dry cement mixture

- 160 l of water

The wet concrete mass was poured into a form and cured to obtain a concrete block having the following mechanical strength values:

Compressive strength:

- 1 day: 39 MPa
- 7 days: 76 MPa
- 28 days: 89 MPa

Flexural strength:

- 28 days: 6 MPa

Young modulus:

- 28 days: 44 GPa

Example 3:

Concrete was produced from the dry cement mixture as described in example 1. The following components were mixed in a mixer:

- 450 kg of dry cement mixture as described in example 1
- 930 kg of aggregates with a nominal maximum coarse diameter of 12,5 mm
- 790 kg of sand with a nominal maximum coarse diameter of 4 mm
- 80 kg of limestone filler
- Superplasticizer admixture in the amount of 2,0 wt% of the dry cement mixture
- 148 l of water

The wet concrete mass was poured into a form and cured to obtain a concrete block having the following mechanical strength values:

Compressive strength:

- 1 day: 49 MPa
- 7 days: 81 MPa

- 28 days: 94 MPa

Flexural strength:

- 28 days: 6 MPa

Young modulus:

5 - 28 days: 43 GPa

Example 4:

A comparative study was carried out between concretes composed respectively of:

10 A/ C50/60 with ordinary Portland cement

B/ C50/60 with dry cement mixture with an optimized dosage

C/ C60/75 with ordinary Portland cement and silica fume addition

D/ C60/75 with dry cement mixture

15

The denominations "C50/60" and "C65/70" refer to the strength class according to Eurocode 2 (European Standard EN 1992). For example, C50/60 means that the concrete must have a compressive cylinder strength of 50 N/mm<sup>2</sup> and a cube compressive strength of  
20 60 N/mm<sup>2</sup>.

A/ C50/60 with ordinary Portland cement:

- 425 kg of ordinary Portland cement

25 - 315 kg of aggregates with a nominal maximum coarse diameter of 12 mm

- 670 kg of aggregates with a nominal maximum coarse diameter of 20 mm

- 730 kg of sand with a nominal maximum coarse diameter of 4 mm

30 - Superplasticizer admixture in the amount of 1,3 wt% of the dry cement mixture

- 175 l of water

The wet concrete mass was poured into a form and cured to obtain a concrete block having the following mechanical strength values:

Compressive strength:

- 5       - 1 day: 12 MPa
- 7 days: 47 MPa
- 28 days: 56 MPa
- 90 days: 57 MPa

10       Abrasion resistance coefficient (following the Compagnie Nationale du Rhône protocol):

$$C = 0,5$$

Shock resistance (following the Compagnie Nationale du Rhône protocol):

$$15 \quad \text{Volume caused by impacts} = 108 \text{ cm}^3$$

The concrete block showed the following characteristics in terms of durability:

- Internal porosity: 12,6%
- Gas permeability: 119 E-18 m<sup>2</sup>

20       Chloride diffusion coefficient (migration test in stationary electric field): 6,8 E-12 m<sup>2</sup>/s

B/ C50/60 with dry cement mixture with an optimized dosage

- 390 kg of dry cement mixture as described in example 1
- 25       - 315 kg of aggregates with a nominal maximum coarse diameter of 12 mm
- 670 kg of aggregates with a nominal maximum coarse diameter of 20 mm
- 765 kg of sand with a nominal maximum coarse diameter of 4
- 30       mm
- Superplasticizer admixture in the amount of 1,2 wt% of the dry cement mixture
- 180 l of water

The wet concrete mass was poured into a form and cured to obtain a concrete block having the following mechanical strength values:

Compressive strength:

- 5 - 1 day: 9 MPa
- 7 days: 44 MPa
- 28 days: 53 MPa
- 90 days: 57 MPa

10 Abrasion resistance coefficient (following the Compagnie Nationale du Rhône protocol):

$$C = 0,5$$

Shock resistance (following the Compagnie Nationale du Rhône protocol):

$$15 \text{ Volume caused by impacts} = 118 \text{ cm}^3$$

The concrete block showed the following characteristics in terms of durability:

- Internal porosity : 13%
- Gas permeability: 76 E-18 m<sup>2</sup>
- 20 - Chloride diffusion coefficient (migration test in stationary electric field): 8,0 E-12 m<sup>2</sup>/s

C/ C60/75 with ordinary Portland cement + silica fume addition:

- 415 kg of ordinary Portland cement
- 25 - 270 kg of aggregates with a nominal maximum coarse diameter of 12 mm
- 700 kg of aggregates with a nominal maximum coarse diameter of 20 mm
- 800 kg of sand with a nominal maximum coarse diameter of 4
- 30 mm
- 25 kg of silica fume addition
- Superplasticizer admixture in the amount of 1,8 wt% of the dry cement mixture

- 161 l of water

The wet concrete mass was poured into a form and cured to obtain a concrete block having the following mechanical strength values:

Compressive strength:

- 1 day: 22 MPa
- 7 days: 56 MPa
- 10 - 28 days: 70 MPa
- 90 days: 75 MPa

Abrasion resistance coefficient (following the Compagnie Nationale du Rhône protocol):

$$C = 0,3$$

15 Shock resistance (following the Compagnie Nationale du Rhône protocol):

$$\text{Volume caused by impacts} = 103 \text{ cm}^3$$

The concrete block showed the following characteristics in terms of durability:

- Internal porosity: 11,8%
- Gas permeability: 40 E-18 m<sup>2</sup>

Chloride diffusion coefficient (migration test in stationary electric field): 0,4 E-12 m<sup>2</sup>/s

25

D/ C60/75 with dry cement mixture:

- 440 kg of dry cement mixture as described in example 1
- 270 kg of aggregates with a nominal maximum coarse diameter of 12 mm
- 30 - 700 kg of aggregates with a nominal maximum coarse diameter of 20 mm
- 800 kg of sand with a nominal maximum coarse diameter of 4 mm

- Superplasticizer admixture in the amount of 1,8 wt% of the dry cement mixture
- 147 l of water

5 The wet concrete mass was poured into a form and cured to obtain a concrete block having the following mechanical strength values:

Compressive strength:

- 1 day: 15 MPa
- 10 - 7 days: 63 MPa
- 28 days: 74 MPa
- 90 days: 75 MPa

Abrasion resistance coefficient (following the Compagnie Nationale du Rhône protocol):

15  $C = 0,3$

Shock resistance (following the Compagnie Nationale du Rhône protocol):

$$\text{Volume caused by impacts} = 91 \text{ cm}^3$$

20 The concrete block showed the following characteristics in terms of durability:

- Internal porosity: 8,9%
  - Gas permeability:  $72 \text{ E-18 m}^2$
  - Chloride diffusion coefficient (migration test in stationary electric field):  $2,2 \text{ E-12 m}^2/\text{s}$
- 25

This study shows that the performance of the dry cement mixture of the invention enables to decrease the amount of binder in concrete without affecting its mechanical strength development and its durability. It also performs as well as mixtures composed of ordinary Portland cement and ultrafine high performance costly additions such as silica fume, from both a mechanical and a durability point of view. The dry cement mixture of

30

the invention allows the production of high performance concrete in an easy way, and at an optimized cost.

## Claims:

1. A dry cement mixture comprising Portland cement and an ultra-fine component consisting of at least one ultra-fine additive, said ultra-fine component being a hydraulic binder, characterized in that Portland cement is present in an amount of at least 70 wt% of the mixture and the ultra-fine component is present in an amount of at least 5 wt% of the mixture, wherein the ultra-fine component has a particle size distribution characterized by a particle diameter  $D_{10}$  of between 0,5 $\mu$ m and 2 $\mu$ m and a particle diameter  $D_{90}$  of between 2 $\mu$ m and 8 $\mu$ m.
2. Dry cement mixture according to claim 1, characterized in that Portland cement is present in an amount of at least 80 wt%, preferably at least 85 wt% of the mixture.
3. Dry cement mixture according to claim 1, characterized in that Portland cement is present in an amount of 70 - 79 wt% of the mixture.
4. Dry cement mixture according to claim 1, 2 or 3, characterized in that Portland cement is present in an amount of at least 85 wt%, preferably at least 90 wt% of the mixture and the ultra-fine component is present in an amount of at least 7 wt%, preferably at least 10 wt% of the mixture.
5. Dry cement mixture according to any one of claims 1 to 4, characterized in that the weight ration of Portland cement and the ultra-fine hydraulic component is between 85/15 and 95/5, in particular about 90/10.
6. Dry cement mixture according to any one of claims 1 to 5, characterized in that the ultra-fine component has a particle

size distribution characterized by a particle diameter  $D_{10}$  of between  $0,7\mu\text{m}$  and  $1\mu\text{m}$ .

7. Dry cement mixture according to any one of claims 1 to 6,  
5 characterized in that the ultra-fine component has a particle size distribution characterized by a particle diameter  $D_{90}$  of between  $4\mu\text{m}$  and  $6\mu\text{m}$ .

8. Dry cement mixture according to any one of claims 1 to 7,  
10 characterized in that the ultra-fine component has a particle size distribution characterized by a particle diameter  $D_{100}$  of  $10\mu\text{m} - 15\mu\text{m}$ , in particular  $12\mu\text{m}$ .

9. Dry cement mixture according to any one of claims 1 to 8,  
15 characterized in that the Portland cement has a particle size distribution characterized by a particle diameter  $D_{10}$  of between  $1\mu\text{m}$  and  $3\mu\text{m}$ , preferably between  $1,6\mu\text{m}$  and  $2\mu\text{m}$ , in particular  $1,8\mu\text{m}$ , and a particle diameter  $D_{90}$  of between  $30\mu\text{m}$  and  $60\mu\text{m}$ , preferably between  $35$  and  $45\mu\text{m}$ , in particular  $40\mu\text{m}$ .

20  
10. Dry cement mixture according to any one of claims 1 to 9, characterized in that the Portland cement is a CEM I cement according to EN 197-1.

25 11. Dry cement mixture according to any one of claims 1 to 10, characterized in that the at least one ultra-fine additive comprises slag, in particular ground blast furnace slag, in an amount of  $> 70 \text{ wt}\%$ , in particular  $> 80 \text{ wt}\%$ .

30 12. Dry cement mixture according to claim 11, characterized in that the ultra-fine component has a content of slag, in particular ground blast furnace slag, of  $> 70 \text{ wt}\%$ , in particular  $> 80 \text{ wt}\%$ .

13. A concrete composition comprising a cement mixture according to any one of claims 1 to 12, aggregates and water.

14. A construction element comprising concrete produced using  
5 a concrete composition according to claim 13.

**INTERNATIONAL SEARCH REPORT**

International application No PCT/IB2015/001017
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**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C04B28/04 C04B28/08 C04B7/19 C04B40/06  
 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 691 17 512 T2 (UNIV CALIFORNIA [US]) 11 July 1996 (1996-07-11) sample U; page 1, paragraph 1; claims 1-14; figures 1-4; example 7; tables 1-8 page 2, paragraph 2 - page 19, paragraph 3 -----	1-14
X	WO 2011/130482 A2 (ROMAN CEMENT LLC [US]; GUYNN JOHN M [US]; HANSEN ANDREW S [US]) 20 October 2011 (2011-10-20) sample 9 in table 2; page 1, line 33 - page 33, line 14; claims 1-41; figures 1A-7H; examples 1-20; tables 1,2 -----	1-14

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	"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
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search  22 September 2015	Date of mailing of the international search report  01/10/2015
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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  Büscher, Olaf
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/IB2015/001017
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