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(54) Title: A RIGID POLYURETHANE PRECAST PANEL

(57) Abstract: The present invention relates to a flame retardant polyurethane concrete precast panel and its preparation method, and use of the precast panel in the field of construction. The precast panel comprises two concrete surface layers and a polyurethane foam layer located between the two surface layers, wherein the polyurethane foam is made from a reaction system comprising an isocyanate and a polyol. The flame retardant polyurethane concrete precast panel according to the present invention has both good insulation performance and satisfactory flame retardant performance (a flame retardant grade of B1).

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A rigid polyurethane precast panel

Technical field

The present invention relates to a flame retardant polyurethane precast concrete panel and its preparation method, and use of the precast panel in the field of construction.

5 Background

It becomes an important requirement for building panels to have good insulation and flame retardant performance because of the further improvement of environmental protection and safety requirements. In this respect, XPS panels and EPS panels have relatively poor insulation performance, while PU panels are not able to achieve the desired flame retardant performance even though they have the best insulation effect. Polyurethane foams have been used in the industry for insulation wall panels. It has also been tried in the industry to produce heat-insulating flame retardant precast panels by use of polyurethane foam and concrete.

15 CN 103974988 A discloses a process for producing a rigid polyurethane-polyisocyanurate-foam by using a polyol having a high proportion of secondary hydroxyl end groups. This application also relates to the rigid polyurethane-polyisocyanurate-foam obtainable therefrom and its use for the production of composite elements with suitable cover layers, as well as the composite elements obtained therefrom.

20 CN 105756274 A discloses a polyurethane-based precast concrete insulation element comprising: a) a base layer prepared from concrete; and b) a core layer prepared from a rigid polyurethane foam, wherein the rigid polyurethane foam is prepared from a polyurethane composition comprising: A) an isocyanate component comprising one or more polyisocyanates; B) an isocyanate-reactive component comprising: B1) a first polyether polyol, selected from the group consisting of polyether polyols prepared by using an amine as a starter and having a functionality of 2 to 4 and a hydroxyl number of 200 to 1000 mg KOH/g; B2) a second polyether polyol, selected from the group consisting of castor oil, modified castor oil, castor oil-started polyether polyol and having a functionality of 2 to 3 and a hydroxyl number of 100 to 200 mg KOH/g. The invention also relates to a method of preparing a precast concrete insulation element of the above polyurethane.

30 CN 101235659 A discloses a lightweight and integrated insulation wall panel having a core layer of rigid polyurethane foam, characterized in that a core layer of rigid polyurethane

foam is poured in between two layers of lightweight concrete wall panels. The preparation method comprises the steps of: first installing the lightweight concrete wall panels prepared according to the conventional method to ensure a certain thickness of the core layer; then pouring the rigid polyurethane foam into the core layer; and finally performing curing and reasonable maintenance. The lightweight and integrated insulation wall panel having a core layer of rigid polyurethane foam prepared according to the method of this application has advantages of good vibration damping, good sound proof, good fire retardance, good heat insulation, good water proof, light weight, high specific strength, compact structure, firmness, and good adaptability to deformation of the main structure. The product of the invention has a life time of up to 30 years under normal conditions of climate and temperature.

In spite of the above disclosures, the industry is still in urgent need of a polyurethane precast concrete panel having both good flame retardant effect and good insulation performance.

Summary of the Invention

In one aspect of the present invention, there is provided a flame retardant polyurethane concrete precast panel comprising two concrete surface layers and a polyurethane foam layer located between the two surface layers, wherein the polyurethane foam is made from a reaction system comprising the following components:

an isocyanate component A;

a component B comprising:

B1) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 170 to 270, preferably 190 to 250, particularly preferably 200 to 240, and a viscosity of 60000 to 120000 mPa.s, preferably 70000 to 100000 mPa.s, particularly preferably 75000 to 95000 mPa.s, and having a content of 15 to 45 pbw, preferably 20 to 40 pbw, particularly preferably 25 to 35 pbw, based on the total weight of component B;

B2) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 210 to 290, preferably 230 to 270, particularly preferably 240 to 260, and a viscosity of 8000 to 22000 mPa.s, preferably 10000 to 20000 mPa.s, particularly preferably 12000 to 18000 mPa.s, and having a content of 10 to 40 pbw, preferably 10

to 30 pbw, particularly preferably 15 to 25 pbw, based on the total weight of component B;

B3) at least one foaming agent;

B4) at least one flame retardant; and

5 B5) at least one catalyst.

The isocyanate component A of the polyurethane precast panel according to the present invention is preferably poly-MDI.

Preferably, the reaction system has an isocyanate index of 250 to 300, more preferably 270 to 290.

10 Preferably, the flame retardant has a content of 15 to 27 pbw, preferably 18 to 24 pbw, based on the total weight of component B.

Preferably, the flame retardant comprises tris(2-chloropropyl) phosphate and triethyl phosphate in a weight ratio of 5/1 to 10/1, preferably 7/1 to 9/1.

15 Optionally, the foaming agent is monofluorodichloroethane in an amount of 18 to 28 pbw, preferably 21 to 25 pbw, based on the total weight of component B.

Preferably, the component B further comprises lactic acid in an amount of 0.1 to 1.5 pbw, preferably 0.5 to 1.3 pbw, and particularly preferably 0.7 to 1.2 pbw, based on the total weight of component B.

20 Preferably, the reaction system further comprises silicone oil in an amount of 1 to 4 pbw, preferably 1 to 3 pbw, based on the total weight of component B.

Preferably, the catalyst comprises a foaming catalyst, a gel catalyst and a trimerization catalyst in a total amount of 2.00 to 6.50 pbw, preferably 2.9 to 4.9 pbw, based on the total weight of component B.

25 Preferably, the reaction system further comprises water in an amount of 0.5 to 3 pbw, preferably 1 to 2 pbw, and particularly preferably 1 to 1.6 pbw, based on the total weight of component B.

Preferably, the precast panel has a thickness of 2 cm to 15 cm, preferably 3 cm to 10 cm, and particularly preferably 4 cm to 8 cm.

Preferably, the polyurethane foam has a thickness of 1 cm to 10 cm, preferably 2 cm to 8 cm, and particularly preferably 2 cm to 4 cm.

- 5 Preferably, the polyurethane foam has a density of 40 to 60 kg/m³, particularly preferably 40 to 55 kg/m³.

Preferably, the reaction system has a gelation time of >100 seconds, preferably >110 seconds, and particularly preferably >120 seconds.

- 10 Preferably, the reaction system according to the present invention has a climbing height of >70 cm, preferably >80 cm, and particularly preferably >90 cm during the gelation.

The polyurethane foam according to the present invention has a flame retardant grade of B1 (tested according to GB8624-2012).

- 15 Through a large number of experiments, it has been unexpectedly found that the polyurethane reaction system consisting of components including isocyanate, polyester polyol, foaming agent, catalyst and flame retardant according to the present invention has good fluidity and good filling, and the polyurethane concrete precast panel made thereof has satisfactory flame retardant performance (a grade of B1), in addition to stable quality and good insulation performance.

- 20 In another aspect of the present invention, there is provided a method for preparing a polyurethane concrete precast panel according to the present invention, which comprises the steps of preparing two surface layers of concrete and reacting a polyurethane reaction system comprising the following components to prepare an intermediate layer, thereby obtaining the polyurethane concrete precast panel:

an isocyanate component A;

- 25 a component B comprising:

B1) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 170 to 270, preferably 190 to 250, particularly preferably 200 to 240, and a viscosity of 60000 to 120000 mPa.s, preferably 70000 to 100000 mPa.s, particularly preferably

75000 to 95000 mPa.s, and having a content of 15 to 45 pbw, preferably 20 to 40 pbw, particularly preferably 25 to 35 pbw, based on the total weight of component B;

5 B2) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 210 to 290, preferably 230 to 270, particularly preferably 240 to 260, and a viscosity of 8000 to 22000 mPa.s, preferably 10000 to 20000 mPa.s, particularly preferably 12000 to 18000 mPa.s, and having a content of 10 to 40 pbw, preferably 10 to 30 pbw, particularly preferably 15 to 25 pbw, based on the total weight of component B;

B3) at least one foaming agent;

B4) at least one flame retardant; and

10 B5) at least one catalyst.

Preferably, the reaction system has an isocyanate index of 250 to 300, more preferably 270 to 290.

Preferably, the flame retardant has a content of 15 to 27 pbw, preferably 18 to 24 pbw, based on the total weight of component B.

15 Preferably, the flame retardant comprises tris(2-chloropropyl) phosphate and triethyl phosphate in a weight ratio of 5/1 to 10/1, preferably 7/1 to 9/1.

Preferably, the method comprises the steps of:

20 adding a concrete slurry to a first mold cavity, setting a template along the inner circumference of the cavity wall of the first mold cavity before curing of the concrete, and demolding after curing to obtain a first concrete panel;

adding a concrete slurry to a second mold cavity, and, before curing thereof, fastening the side of the first concrete panel with the template onto the concrete of the second mold cavity;

25 curing the concrete of the second mold cavity to form a second concrete panel, forming a hollow cavity between the first concrete panel and the second concrete panel, and then demolding;

pouring the polyurethane reaction system into the hollow cavity, and, after curing thereof, obtaining the precast concrete panel.

Preferably, the template has at least one injection hole.

Preferably, the template is selected from one or more of an EPS panel, an XPS panel, a polyurethane panel, and a wood panel.

5 Preferably, the reaction system has an isocyanate index of 250 to 300, more preferably 270 to 290.

Preferably, the flame retardant has a content of 15 to 27 pbw, preferably 18 to 24 pbw, based on the total weight of component B.

Preferably, the flame retardant comprises tris(2-chloropropyl) phosphate and triethyl phosphate in a weight ratio of 5/1 to 10/1, preferably 7/1 to 9/1.

10 In yet another aspect of the present invention, there is provided the use of a polyurethane concrete precast panel according to the present invention in the field of construction.

In yet another aspect of the present invention, there is provided a building comprising a polyurethane concrete precast panel according to the present invention.

Detailed Description

15 The following terms used in the present invention have the following definitions or explanations.

The term "pbw" refers to the mass fraction of each component of the polyurethane reaction system.

20 The term "functionality" refers to the value determined according to the industry formula: functionality = hydroxyl number * molecular weight / 56100, wherein the molecular weight is determined by GPC high performance liquid chromatography.

The term "isocyanate index" refers to the value calculated by the following formula:

isocyanate index (%) = (mole number of isocyanate groups (NCO groups) in the component A) / (mole number of hydroxyl groups (OH groups) in the component B) X 100%.

Components of the polyurethane foam reaction system

A) Polyisocyanates

Any organic polyisocyanates can be used to prepare the rigid polyurethane foams of the present invention, including aromatic, aliphatic and alicyclic polyisocyanates, and combinations thereof. The polyisocyanates can be represented by the general formula $R(NCO)_n$, wherein R represents an aliphatic hydrocarbon group having 2 to 18 carbon atoms, an aromatic hydrocarbon group having 6 to 15 carbon atoms, or an araliphatic hydrocarbon group having 8 to 15 carbon atoms, and $n = 2$ to 4.

Usable polyisocyanates include, but are not limited to, vinyl diisocyanate, tetramethylene 1,4-diisocyanate, hexane diisocyanate (HDI), dodecyl 1,2-diisocyanate, cyclobutane-1,3-diisocyanate, cyclohexane-1,3-diisocyanate, cyclohexane-1,4-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, hexahydrotoluene-2,4-diisocyanate, hexahydrophenyl-1,3-diisocyanate, hexahydrophenyl-1,4-diisocyanate, perhydrodiphenylmethane-2,4-diisocyanate, perhydrodiphenylmethane-4,4-diisocyanate, phenylene-1,3-diisocyanate, phenylene-1,4-diisocyanate, diphenylethylene-1,4-diisocyanate, 3,3-dimethyl-4,4-diphenyldiisocyanate, toluene-2,4-diisocyanate (TDI), toluene-2,6-diisocyanate (TDI), diphenylmethane-2,4'-diisocyanate (MDI), diphenylmethane-2,2'-diisocyanate (MDI), diphenylmethane-4,4'-diisocyanate (MDI), a mixture of diphenylmethane diisocyanates and/or their homologues having more rings, polyphenyl polymethylene polyisocyanate (poly-MDI), naphthylene-1,5-diisocyanate (NDI), their isomers, any mixtures of them and their isomers.

Usable polyisocyanates also include isocyanates modified by carbodiimide, allophanates, or isocyanates, preferably but not limited to, diphenylmethane diisocyanates, diphenylmethane diisocyanates modified by carbodiimide, their isomers, mixtures of them and their isomers.

The polyisocyanates, when used in the present invention, include isocyanate dimers, trimers, tetramers, or combinations thereof.

The organic polyisocyanates of the present invention have an NCO content of 20 to 33 wt%, preferably 25 to 32 wt%, and particularly preferably 30 to 32 wt%. The NCO content is measured according to GB/T 12009.4-2016.

The organic polyisocyanates can also be used in the form of polyisocyanate prepolymers. These polyisocyanate prepolymers can be obtained by reacting an excess of the aforementioned organic polyisocyanates with a compound having at least two isocyanate-reactive groups at a temperature of, for example, 30 to 100°C, preferably about 80°C. The polyisocyanate prepolymers of the present invention have an NCO content of 20 to 33 wt%, preferably 25 to 32 wt%. The NCO content is measured according to GB/T 12009.4-2016.

The polyurethane reaction system of the present invention has an isocyanate index of 250 to 300, preferably 270 to 290.

B) Polyols

The polyols of the present invention can be polyether polyols, polyester polyols, polycarbonate polyols, and/or mixtures thereof.

The polyether polyols can be prepared by known processes. Usually, ethylene oxide or propylene oxide is available for preparation by using ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, diethylene glycol, glycerol, trimethylolpropane, pentaerythritol, triethanolamine, toluenediamine, sorbitol, sucrose, or any combinations thereof as a starter.

In addition, the polyether polyols can also be prepared by reacting at least one alkylene oxide containing an alkylene of 2 to 4 carbon atoms with a compound containing 2 to 8, preferably but not limited to 3 to 8 active hydrogen atoms or another reactive compound in the presence of a catalyst.

Examples of the polyether polyols usable in the present invention are polyether polyols started with an aromatic amine, preferably propylene oxide-based polyether polyol started with diphenylmethanediamine. The polyether polyol started with diphenylmethanediamine and/or toluenediamine has a functionality of 3.6 to 4.4, a hydroxyl number of 290 to 4200 mg KOH/g, and a content of 10 to 35 pbw, preferably 15 to 25 pbw, and a viscosity of <30000 mPa·s at 25 °C (measured according to GB/T 12008.8-1992, the same below).

The polyether polyols usable in the present invention also include difunctional polyether polyols.

The polyester polyols are prepared by reacting a dicarboxylic acid or a dicarboxylic anhydride with a polyol. The dicarboxylic acid is preferably, but not limited to, an aliphatic carboxylic acid having 2 to 12 carbon atoms, for example: succinic acid, malonic acid,

glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, dodecyl carboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, terephthalic acid, and mixtures thereof. The dicarboxylic anhydride is preferably, but not limited to, phthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, and mixtures thereof. The polyol is
5 preferably, but not limited to, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, dipropylene glycol, 1,3-methylpropanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, neopentyl glycol, 1,10-decanediol, glycerol, trimethylolpropane, or mixtures thereof. The polyester polyols also include those made from lactones. The polyester polyols made from lactones are preferably, but not limited to, those
10 made from ϵ -caprolactone.

Processes for preparing polyester polyols well known in the art include a batch process which usually comprises two stages. In the first stage, a polyol such as ethylene glycol, propylene glycol, diethylene glycol, trimethylolpropane, pentaerythritol, 1,4-butanediol or the like, and a dicarboxylic acid such as phthalic acid, adipic acid, halogenated phthalic acid
15 or the like or an anhydride thereof (phthalic anhydride or the like) are subjected to esterification and polycondensation at 140 to 200 °C, and then most of the by-product water is removed by evaporation under atmospheric pressure at a top temperature of the fractionation column controlled to be 100 to 102 °C, and the remaining is kept at 200 to 230 °C for 1 to 2 h. At this time, the acid value is generally reduced to 20 to 30 mg KOH/g. In
20 the second stage, vacuum pumping is performed and the vacuum is gradually increased to remove traces of water and excess diol compound under reduced pressure so as to cause the reaction to proceed in the direction of forming a polyester polyol having a lower acid value. It may be referred to as "vacuum melt process". It is also possible to carry out water by continuously introducing an inert gas such as nitrogen, which is called "carrier gas melt
25 process". An azeotropic solvent such as toluene may be added to the reaction system, and the generated water can be slowly taken out by a water separator when the toluene is refluxed. This method is called "azeotropic distillation process".

The polyurethane reaction system according to the present invention comprises the following polyester polyols:

30 B1) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 170 to 270, preferably 190 to 250, particularly preferably 200 to 240, and a viscosity of 60000 to 120000 mPa.s, preferably 70000 to 100000 mPa.s, particularly preferably 75000 to 95000

mPa.s, and having a content of 15 to 45 pbw, preferably 20 to 40 pbw, particularly preferably 25 to 35 pbw, based on the total weight of component B;

5 B2) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 210 to 290, preferably 230 to 270, particularly preferably 240 to 260, and a viscosity of 8000 to 22000 mPa.s, preferably 10000 to 20000 mPa.s, particularly preferably 12000 to 18000 mPa.s, and having a content of 10 to 40 pbw, preferably 10 to 30 pbw, particularly preferably 15 to 25 pbw, based on the total weight of component B.

Foaming agents

10 The foaming agents usable in the present invention can be various physical foaming agents or chemical foaming agents.

Usable foaming agents include water, halogenated hydrocarbons, hydrocarbon compounds or the like. Usable halogenated hydrocarbons are preferably pentafluorobutane, pentafluoropropane, chlorotrifluoropropene, hexafluorobutene, HCFC-141b (monofluorodichloroethane), HFC-365mfc (pentafluorobutane), HFC-245fa (pentafluoropropane) or any mixtures thereof. Usable hydrocarbon compounds include 15 preferably butane, pentane, cyclopentane (CP), hexane, cyclohexane, heptane, and any mixtures thereof.

The foaming agent according to the present invention is preferably monofluorodichloroethane in an amount of 18 to 28 pbw, preferably 21 to 25 pbw, based on 20 the total weight of component B.

The polyurethane reaction system according to the present invention further optionally comprises water in an amount of 0.5 to 3 pbw, preferably 1 to 2 pbw, and particularly preferably 1 to 1.6 pbw, based on the total weight of component B.

Flame retardants

25 The flame retardants usable in the present invention include, but are not limited to, the following types: alkyl phosphates, such as triethyl phosphate, tributyl phosphate, tris(2-ethylhexyl) phosphate, tris(2-chloroethyl) phosphate, tris(2,3-dichloropropyl) phosphate, tris(2,3-dibromopropyl)phosphate, Pyrol99 or the like; aryl phosphates, such as cresyl-diphenyl phosphate, tricresyl phosphate, triphenyl phosphate, (2-ethylhexyl)-diphenyl 30 phosphate or the like; biscyclopentadienes, such as chlordane anhydride or the like;

halogenated aliphatic hydrocarbons, especially bromides such as dibromomethane, trichlorobromomethane, dichlorobromomethane, as well as aromatic bromides such as octabromodiphenyl oxide, pentabromoethyl benzene, tetrabromobisphenol A, and other halogenides. Furthermore, there are tris(dibromopropyl) phosphate, halogenated
5 cyclohexanes and derivatives thereof, decabromobiphenyl ether and derivatives thereof. The inorganic flame retardants include tellurium compounds, hydroxy aluminum, magnesium hydroxide, borates or the like.

Preferably, the flame retardant according to the present invention is selected from the group consisting of tris(2-chloropropyl) phosphate, triethyl phosphate, and mixtures thereof. In
10 particular, the weight ratio of tris(2-chloropropyl) phosphate to triethyl phosphate is preferably 5/1 to 10/1, more preferably 7/1 to 9/1.

Catalysts

The catalyst according to the present invention includes a foaming catalyst, a gel catalyst and a trimerization catalyst. Here, the foaming catalyst is selected from one of
15 pentamethyldiethylenetriamine, bis-dimethylaminoethylether, N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylbutylenediamine and tetramethylhexamethylenediamine or any mixtures thereof; the gelation catalyst is selected from one of dimethylcyclohexylamine and dimethylbenzylamine or any mixtures thereof; the
20 trimerization catalyst is selected from one of methylammonium salts, ethylammonium salts, octylammonium salts or hexahydrotriazines and organometallic bases or any mixtures thereof. The catalyst according to the present invention preferably has a content of 2.00 to 6.50 pbw, preferably 2.9 to 4.9 pbw, based on the total weight of component B.

The polyurethane foam reaction system according to the present invention further optionally comprises a surfactant, wherein the surfactant is preferably, but not limited to, an ethylene
25 oxide derivative of siloxane. The surfactant has a content of 1 to 4 pbw, preferably 1 to 3 pbw, based on the total weight of component B.

Polyurethane concrete precast panel

The polyurethane concrete panel according to the present invention comprises two surface layers and a polyurethane foam layer located between the two face layers, wherein the
30 polyurethane foam is made from a reaction system comprising the following components:

an isocyanate component A;

a component B comprising:

5 B1) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 170 to 270, preferably 190 to 250, particularly preferably 200 to 240, and a viscosity of 60000 to 120000 mPa.s, preferably 70000 to 100000 mPa.s, particularly preferably 75000 to 95000 mPa.s, and having a content of 15 to 45 pbw, preferably 20 to 40 pbw, particularly preferably 25 to 35 pbw, based on the total weight of component B;

10 B2) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 210 to 290, preferably 230 to 270, particularly preferably 240 to 260, and a viscosity of 8000 to 22000 mPa.s, preferably 10000 to 20000 mPa.s, particularly preferably 12000 to 18000 mPa.s, and having a content of 10 to 40 pbw, preferably 10 to 30 pbw, particularly preferably 15 to 25 pbw, based on the total weight of component B;

15 B3) at least one foaming agent;

B4) at least one flame retardant; and

B5) at least one catalyst.

Preferably, the precast panel has a thickness of 2 cm to 15 cm, preferably 3 cm to 10 cm, and particularly preferably 4 cm to 8 cm.

20 Preferably, the polyurethane foam has a thickness of 1 cm to 10 cm, preferably 2 cm to 8 cm, and particularly preferably 2 cm to 4 cm.

Preferably, the polyurethane foam has a density of 40 to 60 kg/m³, preferably 40 to 55 kg/m³.

Preferably, the reaction system has a gelation time of >100 seconds, preferably >110 seconds, and particularly preferably >120 seconds.

25 Preferably, the reaction system according to the invention has a climbing height of >70 cm, preferably >80 cm, and particularly preferably >90 cm during the gelation.

The polyurethane foam according to the present invention has a flame retardant grade of B1 (tested according to GB8624-2012).

Generally, it is required that the polyurethane system has good fluidity because of the large size and narrow flow path of a polyurethane concrete precast panel. However, well-known polyether polyols having good flame retardance normally have a large viscosity, particularly a large initial viscosity and thereby poor fluidity. Furthermore, the system with a high isocyanate index reacts too fast, resulting in too fast viscosity growth during the reaction and worse fluidity, which is not conducive to filling. Thus, it is impossible to obtain a uniform, qualitatively stable polyurethane foam and precast panel. Through repeated experiments, it has been surprisingly found that the reaction system comprising a high-viscosity polyester polyol and other components compatible therewith according to the present invention overcomes the technical problems of poor fluidity and poor filling of a system having a high viscosity and a high isocyanate index. Since the fluidity and filling of the system are well improved, the resulting polyurethane precast panel has a more stable quality, in addition to both good insulation performance and good flame retardance.

Method for preparing a polyurethane concrete precast panel

The method for preparing a polyurethane concrete panel according to the present invention comprises the steps of preparing two surface layers of concrete and reacting a polyurethane reaction system comprising the following components to prepare an intermediate layer, thereby obtaining the polyurethane concrete precast panel:

an isocyanate component A;

a component B comprising:

B1) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 170 to 270, preferably 190 to 250, particularly preferably 200 to 240, and a viscosity of 60000 to 120000 mPa.s, preferably 70000 to 100000 mPa.s, particularly preferably 75000 to 95000 mPa.s, and having a content of 15 to 45 pbw, preferably 20 to 40 pbw, particularly preferably 25 to 35 pbw, based on the total weight of component B;

B2) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 210 to 290, preferably 230 to 270, particularly preferably 240 to 260, and a viscosity of 8000 to 22000 mPa.s, preferably 10000 to 20000 mPa.s, particularly preferably

12000 to 18000 mPa.s, and having a content of 10 to 40 pbw, preferably 10 to 30 pbw, particularly preferably 15 to 25 pbw, based on the total weight of component B;

B3) at least one foaming agent;

B4) at least one flame retardant; and

5 B5) at least one catalyst.

Preferably, the reaction system has an isocyanate index of 250 to 300, more preferably 270 to 290.

Preferably, the flame retardant has a content of 15 to 27 pbw, preferably 18 to 24 pbw, based on the total weight of component B.

10 Preferably, the flame retardant comprises tris(2-chloropropyl) phosphate and triethyl phosphate in a weight ratio of 5/1 to 10/1, preferably 7/1 to 9/1.

Preferably, the method comprises the following steps:

15 adding a concrete slurry to a first mold cavity, setting a template along the inner circumference of the cavity wall of the first mold cavity before curing of the concrete, and demolding after curing to obtain a first concrete panel;

adding a concrete slurry to a second mold cavity, and, before curing thereof, fastening the side of the first concrete panel with the template onto the concrete of the second mold cavity;

20 curing the concrete of the second mold cavity to form a second concrete panel, forming a hollow cavity between the first concrete panel and the second concrete panel, and then demolding;

pouring the polyurethane reaction system into the hollow cavity, and, after curing thereof, obtaining the precast concrete panel.

Preferably, the template has at least one injection hole.

25 Preferably, the template is selected from one or more of an EPS panel, an XPS panel, a polyurethane panel, and a wood panel.

Use of a polyurethane concrete precast panel in a building

The present invention also provides the use of the aforementioned polyurethane concrete precast panel according to the present invention in the field of construction.

A building

5 The present invention also provides a building comprising the aforementioned polyurethane concrete precast panel according to the present invention.

Examples

The test methods of the examples are indicated as follows:

10 The term "filling density" refers to the weight of polyurethane per unit volume in the closed cavity of a mold. Its unit is kg/cm^3 or lb/ft^3 , and the specific reference is made to the test standard GB/T 6343.

15 The term "core density" refers to the density of the center of a foam tested in the case of overfilling in the mold used in the production of polyurethane concrete panels, namely the density of the molded foam core (the weight of polyurethane per unit volume after removal of the skin). Its unit is kg/cm^3 or lb/ft^3 , and the specific reference is made to the test standard GB/T 6343.

20 The term "heat conductivity" refers to the quantity of heat that passes in 1 second (1 s) through a material of an area of 1 m^2 and a thickness of 1 m when its opposite faces differ in temperature by 1 degree (K, $^{\circ}\text{C}$) under conditions of stable heat transfer. Its unit is $\text{W}/(\text{m}\cdot\text{K})$ or $\text{BTU}\cdot\text{in}/\text{hr}\cdot\text{ft}^2\cdot^{\circ}\text{F}$ (K here can be replaced by $^{\circ}\text{C}$), and the specific reference is made to the test standard GB 3399.

25 The term "compressive strength" refers to the maximum compressive stress experienced by a specimen in a compression test up to rupture (brittle material) or yield (non-brittle material). It characterizes the ability of a material to resist compressive loads without failure. In the test of rigid polyurethane foam, the compressive strength is generally measured at a pressure of 10% deformation. Its unit is kPa or psi, and the specific reference is made to the test standard GB 8813.

The term "gelation time" refers to the time from the start of the reaction between NCO and the active H-containing group to being gelatinous (the polyurethane reaction is divided into a foaming reaction and a gelation reaction; and the specific test is based on wire drawing of a stick).

- 5 The climbing height during gelation refers to the climbing height of a polyurethane mixture (in a liquid state at the beginning) in a climbing tube (internal instrument) having a diameter of 8 cm and a length of 2 m when its volume rapidly expands to increase its height along the climbing tube at an ambient temperature of 30 degrees (i.e. during gelation of the system).

- 10 The term "dimensional stability" refers to the ability of a material to maintain its external dimensions under the action of mechanical force, heat or other external conditions. The specific reference is made to the test standard GB 8811.

The term "compressive creep" refers to the test to determine the increase of the compressive deformation of a material with time under a specified load. The specific reference is made to the test standard GBT 20672-2006.

- 15 The term "water vapor permeability" refers to the quantity of water vapor that permeates in 1 hour (1 h) through a material of an area of 1 m² and a thickness of 1 m when its opposite faces differ in water vapor partial pressure of 1 Pa under conditions of stable permeation. Its unit is g/(m·h·Pa) or ng/(m·h·Pa), and the specific reference is made to the test standard QB/T 2411 -1998.

- 20 The term "water absorptivity" refers to the physical quantity of water absorption of an object under normal atmospheric pressure, expressed as a percentage. The specific reference is made to the test standard GBT 8810-2005.

The term "adhesive strength" refers to the bonding force on per unit area of bonding surface. The specific reference is made to the test standard GB 50404-2017, Appendix B.

- 25 The term "flame retardant grade" characterizes the ability of a polyurethane material to prevent the flame from burning and spreading. The specific reference is made to the test standard GB8624-2018.

Preparation of flame retardant polyurethane concrete precast panels according to the inventive and comparative examples:

Dependent on the product size, the pre-prepared mold cavity is adjusted and the position of the internal fixing parts is measured. The concrete of Model C30 is uniformly spread in the first mold cavity by using a concrete pouring machine, and the mold cavity is oscillated to make the concrete surface even, thereby obtaining a first concrete panel. Subsequently, the pre-prepared steel bar truss and a four-side-sealed 3cm-thick polyurethane panel/template with a density of 45 kg/m³ are inserted around the first concrete panel and pressed moderately until the polyurethane panel and the concrete panel are closely contacted. They are then transferred by a conveyor to a steaming kiln for maturing, and taken out after 20 minutes to obtain a first concrete panel. The concrete is poured into a second mold cavity, and said first concrete panel is flipped reversely to insert the steel bar truss above the mold cavity and template into the uncured second concrete panel until the template and the uncured concrete of the second concrete panel are closely contacted. They are then transferred by a conveyor to a steaming kiln for maturing, and taken out after 20 minutes. The first and second concrete panels are removed from the mold cavity, and the raw materials of components A and B (specific compositions and weight ratios as follows) of the polyurethane reaction system are poured into the hollow cavity formed between the first and second concrete panels through one or more injection holes reserved in advance on the template by using the Henneck HK 650 conventional high pressure pouring machine after the temperature is adjusted to 20-25 °C. After 24 hours of indoor standing without leaving the template, a polyurethane precast concrete panel is obtained. The resulting polyurethane precast concrete panel has a thickness of 6 cm, wherein the polyurethane foam has a thickness of 3 cm.

Indication of raw materials and equipments in Example 1:

Component A of polyurethane reaction system:

Desmodur44V20L: Poly-MDI with an NCO content of 31.5% and a viscosity of 160 mPa·s at 25 °C, from Covestro Polymers (China) Co., Ltd.;

Component B of polyurethane reaction system:

Baymer 28BB133: from Covestro Polymers (China) Co., Ltd.;

Polyester polyol 1: CLD830 having a hydroxyl number of 210 to 230, and a viscosity of 70000 to 120000 mPa.s (25°C), having a content of 30 pbw, from Shanghai Keketic Materials Technology Development Co., Ltd.;

Polyester polyol 2: CF6255 having a hydroxyl number of 240 to 260, and a viscosity of 13000 to 17000 mPa.s (25°C), having a content of 20 pbw, from Jiangsu Fusheng New Materials Co., Ltd.;

5 Flame retardant 1: Tris(2-chloropropyl) phosphate (TCPP) having a content of 19 pbw, from Dongguan Sanwei Chemical Co., Ltd.;

Flame retardant 2: Triethyl phosphate (TEP) having a content of 3 pbw, from Zhangjiagang Yarui Chemical Co., Ltd.;

Silicone oil: B8545 having a content of 2 pbw, from Evonik Specialty Chemicals (Shanghai) Co., Ltd.;

10 Catalyst 1: N,N-dimethylbenzylamine (BDMA) having a content of 0.925 pbw, from Dongguan Guangsiyuan Polyurethane Material Co., Ltd.;

Catalyst 2: 1,3,5-tris(dimethylaminopropyl)hexahydrotriazine having a content of 0.27 pbw, from Air Chemical (China) Co., Ltd.;

15 Catalyst 3: potassium isooctylate (K15) having a content of 2.61 pbw, from Changzhou Ruiao Additive Co., Ltd.;

Other additives: lactic acid (LA) having a content of 0.995 pbw, from Yancheng Fuyu Chemical Materials Co., Ltd.;

Foaming agent: monofluorodichloroethane (HCFC-141b) having a content of 19.89 pbw, from Guangzhou Zhongye Chemical Co., Ltd.;

20 Other foaming agent: water having a content of 1.31 pbw;

HK650 conventional high pressure pouring machine: from Hennecke Company;

Concrete: Model C30, a conventional product from the relevant market;

Inner mold: made of a non-combustible material, from the relevant market;

25 The weight ratio of component A to component B of polyurethane reaction system in Example 1 is 1.239, and the isocyanate index is 278.

Indication of raw materials and equipments in Comparative Example 1:

Component A of polyurethane reaction system:

Desmodur44V20L: Poly-MDI with an NCO content of 31.5% and a viscosity of 160 mPa·s at 25 °C, from Covestro Polymers (China) Co., Ltd.;

Component B of polyurethane reaction system:

5 Baymer 28BB131: from Covestro Polymers (China) Co., Ltd.;

Polyether polyol 1: NJ4502 having a hydroxyl number of 440 to 460, and a viscosity of 15000 to 20000 mPa.s (25°C), having a content of 53.78 pbw, from Nanjing Ningwu Chemical Co., Ltd.;

10 Polyether polyol 2: NJ210 having a hydroxyl number of 107 to 127, and a viscosity of 100 to 300 mPa.s (25°C), having a content of 4.29 pbw, from Nanjing Ningwu Chemical Co., Ltd.;

Polyether polyol 3: Ethylene glycol having a hydroxyl number of 1800 to 1820, and a viscosity of 20 to 30 mPa.s (16°C), having a content of 1.72 pbw, from Jinan Haili Chemical Co., Ltd.;

15 Polyester polyol 1: PS 3152 having a hydroxyl number of 305 to 325, and a viscosity of 2000 to 3000 mPa.s (25°C), having a content of 12.88 pbw, from Nanjing Jinling Stepan Chemical Co., Ltd.;

Polyester polyol 2: Ecoflame B-627 having a hydroxyl number of 305 to 325, and a viscosity of 70000 to 120000 mPa.s (25°C), having a content of 12.88 pbw, from Unibrom Co., Ltd.;

20 Flame retardant 1: Tris(2-chloropropyl) phosphate (TCPP) having a content 8.58 pbw, from Dongguan Sanwei Chemical Co., Ltd.;

Silicone oil 1: B8545 having a content of 0.86 pbw, from Evonik Specialty Chemicals (Shanghai) Co., Ltd.;

Silicone oil 2: DC193 having a content of 1.72 pbw, from Air Chemical (China) Co., Ltd.;

25 Catalyst 1: N,N-dimethylcyclohexylamine (PC8) having a content of 0.43 pbw, from Air Chemical (China) Co., Ltd.;

Catalyst 2: potassium acetate (KAC) having a content of 0.6 pbw, from Shanghai Haiqu Co., Ltd.;

Other foaming agent: water having a content of 2.27 pbw;

HK650 conventional high pressure pouring machine: from Hennecke Company;

Concrete: Model C30, a conventional product from the relevant market;

Inner mold: made of a non-combustible material, from the relevant market;

- 5 The weight ratio of component A to component B of polyurethane reaction system in Comparative Example 1 is 1.39, and the isocyanate index is 126.

Indication of raw materials and equipments in Comparative Example 2:

Component A of polyurethane reaction system:

- 10 Desmodur44V20L: Poly-MDI with an NCO content of 31.5% and a viscosity of 160 mPa·s at 25 °C, from Covestro Polymers (China) Co., Ltd.;

Component B of polyurethane reaction system:

PTC 8061-20: from Covestro Polymers (China) Co., Ltd.;

- 15 Polyether polyol 1: DC635C having a hydroxyl number of 485 to 505, and a viscosity of 2500 to 3500 mPa.s (25°C), having a content of 7.89 pbw, from Nanjing Ningwu Chemical Co., Ltd.;

Polyester polyol 1: RB79 having a hydroxyl number of 205 to 225, and a viscosity of 80000 to 120000 mPa.s (25°C), having a content of 27.62 pbw, from Yabao (China) Co., Ltd.;

Flame retardant 1: Tris(2-chloropropyl) phosphate (TCPP) having a content of 26.54 pbw, from Dongguan Sanwei Chemical Co., Ltd.;

- 20 Flame Retardant 2: B251 having a hydroxyl number of 320 to 340, and a viscosity of 30000 to 50000 mPa.s (25°C), having a content of 33.54 pbw, from Solvey China Co., Ltd.;

Catalyst 1: N,N-dimethylbenzylamine (BDMA) having a content of 0.62 pbw, from Dongguan Guangsiyuan Polyurethane Material Co., Ltd.;

- 25 Catalyst 2: 1,3,5-tris(dimethylaminopropyl)hexahydrotriazine having a content of 0.31 pbw, from Air Chemical (China) Co., Ltd.;

Silicone oil 1: B8545 having a content of 1.64 pbw, from Evonik Specialty Chemicals (Shanghai) Co., Ltd.;

Silicone oil 2: B8538 having a content of 1.64 pbw, from Evonik Specialty Chemicals (Shanghai) Co., Ltd.;

- 5 Other foaming agent: water having a content of 0.2 pbw;

Additive 1		Weight
1	Lactic acid (>85%), from Yancheng Fuyu Chemical Materials Co., Ltd.	200 g
2	Polyether polyol DC635C, from Nanjing Ningwu Chemical Co., Ltd.	100 g

Additive 2		Weight
1	Potassium isooctanoate (K15), from Changzhou Ruiao Additive Co., Ltd.	210 g
2	Triethyl phosphate (TEP), from Zhangjiagang Yarui Chemical Co., Ltd.	90 g

The following mixture was added continuously in Comparative Example 2:

Mixture	Weight ratio
Component B of polyurethane reaction system	100
Additive 1	0.77
Additive 2	3.78
Monofluorodichloroethane (HCFC-141b), from Guangzhou Zhongye Chemical Co., Ltd.	26.2
Component A of polyurethane reaction system	200

- 10 HK650 conventional high pressure pouring machine: from Hennecke Company;

Concrete: Model C30, a conventional product from the relevant market;

Inner mold: made of a non-combustible material, from the relevant market;

The polyurethane reaction system in Comparative Example 2 has an isocyanate index of 360.

Table 1: Performance test data of polyurethane foams of Example 1 (Ex 1) and Comparative Examples 1 and 2 (CE 1 and CE 2)

PU system		Ex 1	CE 1	CE 2
Filling density, kg/m ³		45.00	45.00	45.00
Mold temperature, °C		45-50	45-50	45-50
Demolding time, min		15	15	15
Core density, kg/m ³		40 average	40 average	40 average
Heat conductivity, mW/m*K, 10°C		19.53	19.60	19.56
Heat conductivity, mW/m*K, 10°C, 28 days		19.98	20.12	20.09
Compressive strength	⊥, kPa	140.0	150.0	153.0
	⊥, kPa	150.0	155.0	151.0
	//, kPa	180.0	178.0	183.0
Fluidity test by using a climbing tube	Gelation time (TG)	128	126	80
	Climbing height during gelation (HG)	93.1	93	63
Dimensional stability (high- and low-temperature dimensional change rate)	-30°C, 48 h, vol%	0.80	0.70	0.76
	+70°C, 48 h, vol%	1.30	1.38	1.33
Compressive creep	70°C, 40 kPa, 7 days (%)	3.80	3.90	3.82
Water vapor permeability	23°C/relative humidity gradient 0-50%	5.9	5.8	5.8
Water absorptivity	%	2.20	2.35	2.26
Bond strength	(MPa)	156/158/121	160/162/122	126/115/102
Flame retardant grade	GB8624-2012	B1	B2	B1

5 The experimental results show that Comparative Example 1 has the same filling density as Example 1, and the mold can also be filled. However, the polyurethane foam of Example 1 achieves a flame retardant grade of B1, while the foam of Comparative Example 1 achieves only a flame retardant grade of B2. It can be seen that the flame retardant performance of the polyurethane foam according to the present invention is greatly improved.

10 The polyurethane foam of Comparative Example 2 reaches a flame retardant grade of B1 and has the same filling density as Example 1, but the mold is not filled. It can be seen that the polyurethane foam reaction system according to the present invention can better fill the mold when compared with the prior art, and result in a polyurethane foam which has uniform foaming, good quality and excellent insulation and flame retardant performance.

Although the present invention has disclosed the above preferred examples, it is not intended to limit the present invention. Any person skilled in the art can make various changes and modifications without departing from the spirit and scope of the present invention. The scope of protection shall be based on the scope of the patent claims.

Claims:

1. A flame retardant polyurethane concrete precast panel comprising two concrete surface layers and a polyurethane foam layer located between the two surface layers, wherein the polyurethane foam is made from a reaction system comprising the following components:

5 an isocyanate component A;

a component B comprising:

10 B1) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 170 to 270, preferably 190 to 250, particularly preferably 200 to 240, and a viscosity of 60000 to 120000 mPa.s, preferably 70000 to 100000 mPa.s, particularly preferably 75000 to 95000 mPa.s, and having a content of 15 to 45 pbw, preferably 20 to 40 pbw, particularly preferably 25 to 35 pbw, based on the total weight of component B;

15 B2) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 210 to 290, preferably 230 to 270, particularly preferably 240 to 260, and a viscosity of 8000 to 22000 mPa.s, preferably 10000 to 20000 mPa.s, particularly preferably 12000 to 18000 mPa.s, and having a content of 10 to 40 pbw, preferably 10 to 30 pbw, particularly preferably 15 to 25 pbw, based on the total weight of component B;

B3) at least one foaming agent;

B4) at least one flame retardant; and

B5) at least one catalyst.

20 2. The precast panel according to claim 1, wherein the reaction system has an isocyanate index of 250 to 300, preferably 270 to 290.

3. The precast panel according to claim 1, wherein the flame retardant B4) has a content of 15 to 27 pbw, preferably 18 to 24 pbw, based on the total weight of component B.

25 4. The precast panel according to any one of claims 1 to 3, wherein the flame retardant comprises tris(2-chloropropyl) phosphate and triethyl phosphate in a weight ratio of 5/1 to 10/1, preferably 7/1 to 9/1.

5. The precast panel according to any one of claims 1 to 3, wherein the foaming agent is monofluorodichloroethane in an amount of 18 to 28 pbw, preferably 21 to 25 pbw, based on the total weight of component B.
- 5 6. The precast panel according to any one of claims 1 to 3, wherein the component B further comprises lactic acid in an amount of 0.1 to 1.5 pbw, preferably 0.5 to 1.3 pbw, particularly preferably 0.7 to 1.2 pbw, based on the total weight of component B.
7. The precast panel according to any one of claims 1 to 3, wherein the precast panel has a thickness of 2 cm to 15 cm, preferably 3 cm to 10 cm, and particularly preferably 4 cm to 8 cm.
- 10 8. The precast panel according to any one of claims 1 to 3, wherein the polyurethane foam has a thickness of 1 cm to 10 cm, preferably 2 cm to 8 cm, and particularly preferably 2 cm to 4 cm.
9. The precast panel according to any one of claims 1 to 3, wherein the polyurethane foam has a density of 40 to 60 kg/m³, particularly preferably 40 to 55 kg/m³.
- 15 10. The precast panel according to any one of claims 1 to 3, wherein the reaction system has a gelation time of >100 seconds, preferably >110 seconds, and particularly preferably >120 seconds.
11. The precast panel according to any one of claims 1 to 3, wherein the reaction system has a climbing height of >70 cm, preferably >80 cm, particularly preferably >90 cm during the gelation.
- 20 12. The precast panel according to any one of claims 1 to 3, wherein the polyurethane foam has a flame retardant grade of B1 (tested according to GB8624-2012).
13. A method for preparing a polyurethane concrete precast panel according to any one of claims 1 to 12, which comprises the steps of preparing two surface layers of concrete and reacting a polyurethane reaction system comprising the following components to prepare an intermediate layer, thereby obtaining the polyurethane concrete precast panel:
- 25 an isocyanate component A;
- a component B comprising:

5 B1) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 170 to 270, preferably 190 to 250, particularly preferably 200 to 240, and a viscosity of 60000 to 120000 mPa.s, preferably 70000 to 100000 mPa.s, particularly preferably 75 to 95 kmPa.s, and having a content of 15 to 45 pbw, preferably 20 to 40 pbw, particularly preferably 25 to 35 pbw, based on the total weight of component B;

10 B2) at least one polyester polyol having a functionality of 2 to 3, a hydroxyl number of 210 to 290, preferably 230 to 270, particularly preferably 240 to 260, and a viscosity of 8000 to 22000 mPa.s, preferably 10000 to 20000 mPa.s, particularly preferably 12000 to 18000 mPa.s, and having a content of 10 to 40 pbw, preferably 10 to 30 pbw, particularly preferably 15 to 25 pbw, based on the total weight of component B;

B3) at least one foaming agent;

B4) at least one flame retardant; and

B5) at least one catalyst.

15 14. The method according to claim 13, wherein the reaction system has an isocyanate index of 250 to 300, preferably 270 to 290.

15. Use of a polyurethane concrete precast panel according to any one of claims 1 to 12 in the field of construction.

20 16. A building comprising a polyurethane concrete precast panel according to any one of claims 1 to 12.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/079931

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G18/16 C08G18/40 C08G18/42 C08G18/76 C08L75/06 C09D175/06 B29C39/12 B32B27/40 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) C08G C08L C09D B32B B29C 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 <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>WO 2017/207536 A1 (BASF SE [DE]; CONSTRUCTION RESEARCH & TECH GMBH [DE]) 7 December 2017 (2017-12-07) page 2, lines 20-24; claims 1-19; figure 1 page 6, lines 23-27 page 8, lines 12-13, 26-27 page 9, line 21 page 11, lines 10-15 page 12, lines 9-10, 19-25, 24-37 -----</td> <td>1-16</td> </tr> <tr> <td>Y</td> <td>US 2016/347904 A1 (KALUSCHKE TOBIAS [DE] ET AL) 1 December 2016 (2016-12-01) paragraphs [0008], [0016], [0079], [0115], [0155], [0197]; claims 9-10 -----</td> <td>1-16</td> </tr> <tr> <td>A</td> <td>CN 101 235 659 A (GUANGXI INST OF BUILDING RES & [CN]) 6 August 2008 (2008-08-06) claims 1-2 -----</td> <td>1-16</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	WO 2017/207536 A1 (BASF SE [DE]; CONSTRUCTION RESEARCH & TECH GMBH [DE]) 7 December 2017 (2017-12-07) page 2, lines 20-24; claims 1-19; figure 1 page 6, lines 23-27 page 8, lines 12-13, 26-27 page 9, line 21 page 11, lines 10-15 page 12, lines 9-10, 19-25, 24-37 -----	1-16	Y	US 2016/347904 A1 (KALUSCHKE TOBIAS [DE] ET AL) 1 December 2016 (2016-12-01) paragraphs [0008], [0016], [0079], [0115], [0155], [0197]; claims 9-10 -----	1-16	A	CN 101 235 659 A (GUANGXI INST OF BUILDING RES & [CN]) 6 August 2008 (2008-08-06) claims 1-2 -----	1-16
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☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.														
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Date of the actual completion of the international search 22 January 2020		Date of mailing of the international search report 04/02/2020												
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 Scheuer, Sylvie												

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2019/079931

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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