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

(19) World Intellectual Property Organization

International Bureau





(10) International Publication Number WO 2018/015938 A1

(43) International Publication Date 25 January 2018 (25.01.2018)

(51) International Patent Classification: *E06B 3/263* (2006.01) *C08G 18/09* (2006.01) *E06B 5/16* (2006.01)

(21) International Application Number:

PCT/IB2017/054463

(22) International Filing Date:

24 July 2017 (24.07.2017)

(25) Filing Language: Italian

(26) Publication Language: English

(30) Priority Data:

 102016000076956
 22 July 2016 (22.07.2016)
 IT

 102016000077120
 22 July 2016 (22.07.2016)
 IT

 102017000020023
 22 February 2017 (22.02.2017)
 IT

 102017000020006
 22 February 2017 (22.02.2017)
 IT

 102017000020013
 22 February 2017 (22.02.2017)
 IT

- (71) Applicant: DOORS & MORE S.R.L. [IT/IT]; Via 1° Maggio, 10, 38089 Storo (TN) (IT).
- (72) Inventors: MODESTI, Michele; Via Corsica, 19, 35127 Padova (PD) (IT). BENUSSI, Giampaolo; Corso Giacomo Matteotti, 15, 25122 Brescia (BS) (IT). POLETTI, Susanna; Via Trento, 84, 38089 Storo (TN) (IT). SAI, Gianfranco; Via S. Giovanni Nepomuceno, 26, 38089 Storo (TN) (IT).
- (74) Agent: AUTUORI, Angelo et al.; C/O Eureka IP Consulting, Via Monte Cengio, 32, 36100 Vicenza (IT).
- (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,

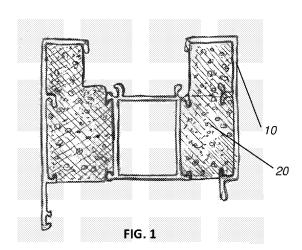
CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, 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:

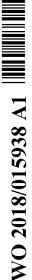
— with international search report (Art. 21(3))

(54) Title: HIGH FIRE-RESISTANT POLYISOCYANURATE, AND USE THEREOF TO MANUFACTURE FIRE DOOR OR WINDOW FRAMES AND/OR PROFILES THEREFOR



(57) Abstract: The invention regards a composition for preparing a polyisocyanurate consisting of: a) aromatic polyisocyanates; b) compounds having groups reactive towards isocyanates; c) possible additives.





HIGH FIRE-RESISTANT POLYISOCYANURATE, AND USE THEREOF TO MANUFACTURE FIRE DOOR OR WINDOW FRAMES AND/OR PROFILES THEREFOR

DESCRIPTION

Field of application

The present invention applies to the polymeric material technical industry, and it regards a high flame-resistant polyisocyanurate polymer, as well as the method for obtaining such polymers and the use thereof to manufacture fire doors/windows and/or profiles therefor.

Definitions

<u>Isocyanate index</u>: is the stoichiometric ratio between isocyanate groups which are reactive towards isocyanate, multiplied by 100. All groups present in the reaction mixture which are reactive towards the isocyanate group, but not the isocyanate group itself, are considered groups which are reactive towards isocyanate. Examples of groups which are reactive towards –NCO are OH-, SH-, NH-, CH- acid.

Aromatic isocyanate (or polyisocyanate): is a polyfunctional isocyanate containing at least one aromatic ring. Examples are 2,2' diphenylmethane diisocyanate, 2,4 diphenylmethane diisocyanate, 4,4' diphenylmethane diisocyanate, 2,4 toluene diisocyanate, 2,6 toluene diisocyanate, naphthalene diisocyanate.

<u>Isocyanate functionality</u>: is the average number of isocyanate groups per polyisocyanate mole.

Polyol functionality: is the average number of OH groups per polyol mole.

<u>Polyol hydroxyl number</u>: indicates the amount of OH groups in the polyol per weight unit thereof. It is usually established by titration through methods known to a man skilled in the art and it is expressed as mg of KOH per gram of polyol.

<u>Aromatic polyester polyol</u>: is a polyol prepared by condensing polyfunctional alcohols having 2 to 12 carbon atoms with polyfunctional aromatic carboxylic acids having 6 to 12 carbon atoms, such as for example phthalic acid, isophthalic acid, terephthalic acid or phthalic anhydride and naphthalene dicarboxylic acid isomers or anhydrides thereof.

<u>Deaerating agent</u>: is a compound suitable to be interposed in the surface of air bubbles in a mass undergoing reaction considerably reducing surface tension and facilitating the collapse of the air bubbles. For example, the deaerating agent could be polysiloxane in non-aqueous solution.

Chain extender agent: is a low molecular weight, di- or polyfunctional alcohol or amine

which contributes to increase of molecular weight and/or cross-linking and confers the polymer a more rigid structure. For example, typical chain extenders are 1,4-butanediol, ethylene glycol, 1,6-hexanediol, glycerine.

PCT/IB2017/054463

<u>Percentage by weight (% by weight)</u>: is the percentage of a component of interest in a mixture of interest by weight, the percentage by weight being compared to the total weight of the components in said mixture of interest.

<u>Composition</u>: mixture of reagents required to obtain the polyisocyanurate according to the invention.

<u>Door/window frame (or frames)</u>: is used to indicate the door/window frame, the closing element or shutter frame and the elements of the structure of a continuous glass window.

<u>Fire door/window</u>: closing element, for example a shutter, door, window or continuous glass window compartmentalisation wall of the fire damper, flame damper, smoke damper type or the like. These fire doors/windows must pass a certification and/or approval test before being placed in the market.

The reference certification and/or approval test for fire doors/windows in form of doors and/or windows is EN UNI 1634-1:2014 standard (Fire resistance and smoke control tests for door and shutter assemblies, openable windows and elements of building hardware - Part 1: Fire resistance test for door and shutter assemblies and openable windows) with temperature-time curve described in the EN UNI 1363-1 (Fire resistance tests - Part 1: General requirements) and EN UNI 1362-2:2001 (Fire resistance tests - Alternative and additional procedures) standards.

The reference certification and/or approval test for fire doors/windows in form of continuous glass window compartmentalisation wall (even with large surface, for example the façade of a building), which comprises a frame with structural and infill functions for example made of glass, is the EN UNI 1364-1:2015 standard (Fire resistance for non-loadbearing elements) with the temperature-time curve described in the EN UNI 1363-1 and EN UNI 1363-2:2001 standards.

In both cases, the certification and approval test does not regard a single component but rather the entire door/window as a whole.

<u>Density</u>: apparent density measured in compliance with the EN ISO 845:2006 standard (Determination of apparent density).

Compact polyisocyanurate: is used to indicate a substantially porosity-free solid

polyisocyanurate with density higher than 800 Kg/m³, preferably higher than 1000 Kg/m³ and in particular higher than 1100 Kg/m³.

State of the Art

Polyurethanes (abbreviated as PUR) are polymers obtained through condensation reaction between compounds containing R_1 with at least two isocyanate-reactive groups (-NCO) and R_2 compounds with at least two groups reactive towards the isocyanate for example the hydroxyl group (OH) and/or the amine group (NH₂). The isocyanate index, an index obtained by multiplying the isocyanate groups / groups reactive towards the isocyanate ratio by 100, is the most important parameter when defining a PUR. For example, a PUR obtained through reaction between an isocyanate group and a group reactive towards an isocyanate in a 1:1 stoichiometric ratio corresponds to a 100 isocyanate index.

A polyurethane with a 100 isocyanate index substantially consists of linear or branched chains $-[R_1$ -urethane group R_2 -urethane group- R_1]-. A polymer with index higher than 100 contains compounds of mutually reacting isocyanate groups forming trimers for instance. Given that the aforementioned trimers can be considered as cyanuric acid derivatives, the polymer is referred to as polyisocyanurate, abbreviated as PIR, or PUR/PIR system.

PUR is usually prepared in expanded form with density ranging between 30 kg/m³ and 800 kg/m³ by adding expanding agents which, developing a gas during polymerisation, cause the formation of an assembly of cavities, usually closed, in the viscous mass undergoing reaction, these cavities being incorporated and fixed in the hardened polymer. Expanding agents may be physical, i.e. low-boiling liquids which evaporate due to the considerable reaction heat, or chemical, for example water, which reacts with the –NCO group with final formation of CO₂.

Per se, PUR is not resistant to fire and it burns with considerable emission of dense and opaque smoke.

Appropriate additives and/or reagents, polyols generally, are added in a per se known manner prior to condensation reaction so as to increase fire resistance. They can act by diluting the polymer in that non-combustible (mineral fillers, alumina), creating water which absorbs heat and reduces degradation reactions (hydrated aluminium oxides), creating gases that do not sustain the flame (nitrogenated and/or chlorinated compounds), swelling (expansible graphite) or creating carbonaceous layers, commonly referred to by the English expression *char* (phosphorus compounds, phosphoric acid salts and/or esters, phosphinates) in the industry. Having a cross-

linked structure, PIR polymers reveal greater easiness towards aromatisation and the ensuing formation of carbonaceous compounds. Highly cross-linked PIR - with isocyanate index higher than 100, up to 1500 - is used in cases where fire resistance is required.

EP0464204 describes a polyisocyanurate with 150 isocyanate index expanded with freon and containing expanding graphite as flame retardant.

EP1288239 describes a process for preparing expanded PIR/PUR systems having a density of about 40 kg/m³ by means of a trimerisation catalyst and substituted carboxylic acids.

EP1770118 addresses a low-density polyisocyanurate, foamed by reaction between isocyanate and water, the latter present between 3% and 8% by weight of polyol. The polyol component is a polyester polyol mixture with an average hydroxyl number between 140 and 220 mg KOH/g.

All the aforementioned PUR/PIR or PIR polymers are expanded, substantially heat or acoustic insulators. After exposure to fire, the carbonaceous residue of a PIR expanded according to the prior art, is very friable even though the initial expanded PIR was rigid with good mechanical properties.

This is unacceptable when PIR is required to have sufficient mechanical resistance after exposure to the flame, for example after a fire breaks out.

EP1967535B1 describes a rigid and compact polyisocyanurate system, with good flame resistance, obtained from the condensation of an aromatic isocyanate with functionality lower than 2.5, with a polyether polyol having 95% of the OH groups on secondary carbon in presence of a tertiary amine and potassium formate as trimerisation catalyst. Chain extenders, fillers and flame-retardant additives are also present.

For some applications, for example for obtaining profiles for fire doors/windows frames, the carbonaceous residue is required not only to have a very high flame resistance but also a high mechanical resistance even after the fire. In the fire operating conditions, polymers are required to carbonise up to obtaining a compact carbonaceous structure provided with mechanical resistance with limited formation of smoke, in particular without forming dense and opaque smoke that makes it difficult to identify emergency escape routes or the surrounding environment. The absence of dense and opaque smoke is required by the current fire safety standards.

Currently known PUR/PIR systems do not meet the aforementioned standards fully. Even

though they pass the common fire reaction tests and do not sustain the flame, these prior art materials generate a considerable amount of opaque totally dark smoke in case of fire. Furthermore, though forming *char*, this carbonaceous residue does not maintain sufficient mechanical resistance and crumbles easily and rapidly even upon the slightest stress.

For some applications, for example in building structures or in complex products such as for example fire retardant or fire damper doors/windows, besides being required to pass appropriate tests provided for by the law, the entire element is particularly required to remain intact and not collapse. This implies that the polymer carbonisation product has sufficient mechanical properties, i.e. resistance to compression and bending. Thus, the structure remains intact even though parts thereof, for example exposed parts and thus for aesthetic purposes only, collapse or melt. For example, doors/windows with glass windows of the prior art having profiles containing PUR/PIR systems as the bearing structure do not pass the approval tests.

Fire doors/windows or the like generally consist of a framework, also referred to as "subframe", generally embedded in the support wall of the opening to be closed, a door/window frame connected to the subframe, for example by means of screws and a closing element connected to the door/window frame.

The closing element may consist of one or more openable doors and/or fixed elements. In both cases, they may comprise a door frame both for aesthetic and structural purposes and infill portions, such as glass.

In another embodiment, the door/window may form a continuous glass window compartmentalisation wall, even with large surface, for example a façade of a building, and it comprises a frame for structural and infill purposes, for example made of glass.

Obviously, such per se known glasses meet the appropriate high temperature and fire resistance quality requirements.

In case of a glass window fire door applied to a masonry wall, the subframe is embedded in the wall, the door/window frame is the door frame, the frame of the closing element is the shutter frame and the infill is constituted by a multilayer glass slab.

The door and shutter frames are built by the doors/windows specialist using straight semifinished products generally sold measuring six metres long and referred to as profiles, usually consisting of one or more straight elements referred to as profiles.

In any case, the profiles comprise one or more metal sections provided with one or more

hollow box-shaped bodies which enable a predetermined degree of heat insulation. The connection between the parts of the box-shaped bodies is often made of heat insulating material with the aim of increasing overall heat insulation. Furthermore, the interior of the box-shaped bodies is also filled with heat insulating material so as to enhance the insulating effect even further.

When manufacturing the frames, the profiles are cut to size, welded to each other to form the frames and subsequently painted with the paint being dried in a furnace at about 200° C. The insulating material must be inert, not react and not degrade at this temperature.

<u>Presentation of the invention</u>

An object of the present invention is to provide a polyisocyanurate, whether compact or expanded, with high flame resistance and capable of carbonising forming a resistant and self-sustaining residual carbonaceous structure without collapsing or crumbling upon exposure to the flame at the test conditions or in case of fire.

The polyisocyanurate according to the present invention will have extremely high fire resistance performance. For example, it will enable obtaining a fire door/window capable of passing the test in compliance with the UNI EN 1634-1 and/or UNI-EN 1364-1 standards.

As a matter of fact, under test conditions in compliance with the aforementioned standards and once subjected to the relative temperature-time curve, such material carbonises to a carbonaceous structure with mechanical properties sufficient to counter heat dilatations and sustain the entire structure.

The polyisocyanurate may be prepared starting from a composition, i.e. from a mixture of reagents including, respectively consisting of:

- a) aromatic polyisocyanates, preferably having average functionalities higher than or equal to 2.5;
- b) compounds having groups reactive towards isocyanates, preferably polyester polyols, more preferably aromatic polyester polyols, in which all OH groups are substantially primary groups;
- c) possibly at least one additive.

The polyisocyanurate may be prepared by mixing all the aforementioned components or, preferably, by mixing a first component A and a second component B.

Suitably, the first component A may be a polyol component which may comprise,

respectively consists of, one or more compounds having groups reactive towards the isocyanate as described above, possible one or more catalysts, possible additives such as surfactants and/or flame-retardant compounds, possible mineral fillers.

The second component B may comprise, respectively may consist of, isocyanate and/or oligomers and/or trimers obtained by reacting the isocyanate with itself, as described above.

Thus, the polyisocyanurate according to the invention may be obtained by mixing the two components A and B so that the isocyanate index is comprised between 200 and 400, preferably between 300 and 350.

Preferably, the isocyanates may be aromatic isocyanates having a functionality comprised between 2.7 and 2.9.

Examples of such isocyanates are 2,2- 2,4 and 4,4-diisocyanate, the mixtures of monomeric diphenylmethane with diphenylmethane diisocyanate homologs (polymeric MDI), or its oligomers, or 2,4- 2,6-toluene diisocyanate (TDI) or their mixtures, tetramethylene diisocyanate or its oligomers, hexamethylene diisocyanate (HDI) or its oligomers, naphthalene diisocyanate (NDI) or their mixtures. In any case, the average functionality of such polyisocyanates may be higher than 2.5.

Preferably, a mixture of 4,4'-diphenylmethane diisocyanate with isomers and homologs with higher functionality may be used so as to have a mixture functionality comprised between 2.7 and 2.9 and with NCO content preferably comprised between 25% and 35% by weight, more preferably between 30.5% and 32,5% by weight. The amount of isocyanate is comprised between 50% and 70%, preferably between 58% and 63% by weight compared to the total weight of all components used for preparing the formulation.

The compounds having groups reactive towards the isocyanate, referred to as "polyols", may all preferably be compounds containing at least two groups reactive towards isocyanate such as OH, SH, NH and CH-acid.

Such polyols may be prepared according to known methods.

Preferably, the polyester polyols may have a hydroxyl number comprised between 250 and 400 mg KOH/g, preferably between 300 and 350 mg KOH/g, and with functionality ranging between 2 and 3, preferably substantially equal to 2.

The polyester polyols may be prepared by condensing polyfunctional alcohols with polyfunctional carboxylic acids having 2 to 12 carbon atoms, such as phthalic acid, isophthalic acid,

terephthalic acid and naphthalene dicarboxylic acid isomers or their anhydrides.

The catalysts for facilitating the trimerisation of the isocyanate are known. Preferably, organometallic compounds may be used, preferably alkali metal salts of 1 to 10-carbon atom long-chain acids, preferably potassium organic salts such as for example potassium formate, potassium acetate, potassium octoate or their mixtures.

The catalysts may be used separately or mixed in a concentration ranging between 0.1% and 0.5% by weight, preferably between 0.3% and 0.4% by weight compared to the total weight of all components used to prepare the polyisocyanurate.

Further potential "traditional" catalysts are catalysis systems comprising tertiary amines. According to the invention, such amines do not confer additional advantages to cross-linking and thus the catalysis system could be amine-free, in particular tertiary amines so as to reduce the complexity of the catalysis system as well as the environmental impact thereof.

Suitably, the aforementioned composition could be free of chain extender agents.

Flame retardants, per se known to a man skilled in the art, could also be added to the reagents. Phosphoric acid esters such as triethyl phosphate, dimethyl propyl phosphate, phosphinates, for example ethyl ethane phosphinate, phosphonates such as diethyl ethane phosphonate, triethyl ethane phosphonate, dimethyl propyl pohosphonate, diphenyl-propyl phosphonate, or inorganic such as hypophosphites, red sulphur, preparations comprising red sulphur, expansible graphite, expanded graphite, hydrated aluminium oxide, antimony trioxide, ammonium polyphosphate, cyanuric acid derivatives such as melamine or their mixtures can be added for instance.

Suitably, flame retardants could preferably be added in an amount of 1% to 10% by weight, preferably between 3% and 5% by weight, compared to the total weight of all components used to prepare the formulation.

Conventional reinforcement organic and inorganic fillers and/or loads known to a man skilled in the art could be used optionally. Examples of inorganic fillers are mineral silicates, such as silica, phyllosilicates, glass balls, talc, kaolinite, wollastonite, aluminium oxides, titanium oxides and iron oxides, gypsum, baryte and inorganic pigments, variable length fibrous minerals such as glass, cellulose, polyamide, polyacrylonitrile, polyurethane, polyester and carbon fibres.

Inorganic and organic fillers can be used separately or in mixtures in amounts ranging between 0.1% and 30% by weight compared to the total weight of all components used to prepare

the polyisocyanurate compared to the total weight of all components used to prepare the composition.

Depending on the density of the polyisocyanurate, some additives can be used or omitted.

For example, it is preferable to avoid the use of water and expanding graphite to prepare substantially porosity-free compact polyisocyanurate with density higher than 800 Kg/m³, preferably higher than 1000 Kg/m³ and in particular higher than 1100 Kg/m³. Expanding graphite causes breaking upon expanding due to the temperature.

As a matter of fact, as known, the isocyanate group reacts with water forming CO_2 and this reaction is commonly used to obtain an expanded product. Even the humidity absorbed from the air by the reagents, polyol in particular, is per se sufficient to introduce a porosity that suffices to obtain a relatively low density into the formed polymer. The humidity present or absorbed by the aforementioned reagent system may be removed therefrom by adding additives for the adsorption of the same (dehydrating agent).

Zeolites suitably exchanged and dispersed in oil, castor oil for instance, can be used as adsorbents. An amount of isocyanate comprised between 1% and 3%, preferably between 2% and 2.5% by weight compared to the total weight of all components used for preparing the formulation, with 50% castor oil, is suitably added.

The average dimension of the zeolite particles may be lower than 200 μ m, preferably lower than 100 μ m with pore dimension preferably between 2 and 5 angstroms. The total water content will be lower than 0.5% by weight, preferably lower than 0.3% by weight compared to the total weight of all components used to prepare the formulation.

A deaerating agent in amounts between 0.01% and 1% by weight, preferably between 0.2 and 0.5% by weight, compared to the total weight of all components used to prepare the formulation, may be added so as to obtain the desired final density.

The deaerating agent may be a polyoxyalkene-polysiloxane-based copolymer.

Thus, a substantially porosity-free compact polyisocyanurate with density higher than 800 Kg/m³, preferably higher than 1000 Kg/m³ and even more preferably higher than 1100 Kg/m³, may be prepared starting from a composition, i.e. a mixture of reagents, that may include, that respectively consists of:

a) aromatic polyisocyanates, preferably having average functionalities higher than or equal to 2.5;

- b) compounds having groups reactive towards isocyanates, preferably polyester polyols, more preferably aromatic polyester polyols, in which all OH groups are substantially primary groups;
- c) at least one dehydrating agent, preferably a zeolite, for example the aforementioned one;
- d) at least one deaerating agent, for example the aforementioned one;
- e) possibly at least one further additive, for example at least one filler and/or at least one flame retardant agent and/or a surfactant.

Such composition may be free of tertiary amine and/or expanding graphite and/or chain extender agent.

The characteristics of the polyols and/or the isocyanate index of the composition may be the one mentioned above.

The aforementioned compact polyisocyanurate under the test conditions in compliance with the UNI EN 1634-1 or UNI EN 1364-1 standards, carbonises to a very compact and hard carbonaceous structure with mechanical properties sufficient to counter heat dilatations and sustain the entire structure.

The doors/windows obtained according to the invention may have a profile made up of the aforementioned compact polyisocyanurate, or the aforementioned compact polyisocyanurate may lie inside a "traditional" box-shaped structure so as to act as an insulator and contribute to the mechanical structure of the door/window.

In other words, the aforementioned compact polyisocyanurate characteristics enable to obtain a profile for doors/windows whose bearing structure is partly or exclusively made up of the compact polyisocyanurate. Finishing covers, for example made of plastic material, wood or light metal material, aluminium for example, may be applied on the profile thus obtained.

In this case, the compact polyisocyanurate acts both as a heat insulator and a mechanical structure for the door/window, the latter exclusively consisting of the compact polyisocyanurate.

To this end, the reagents from which the compact polyisocyanurate (composition) is obtained may be poured and/or injected into moulds and cured therein for a predetermined period of time.

On the other hand, the profile may include a box-shaped structure, made of any material, into which the reagents, from which the compact polyisocyanurate is obtained, may be poured

and/or injected and cured.

In this case, the compact polyisocyanurate acts as a heat insulator and cooperates with the box-shaped structure to confer the mechanical structure to the door/window.

In a polyisocyanurate having density higher than 400 Kg/m³ the expanding graphite would tend to break the finished product and thus it is preferable that it not be used. Another reason to avoid use thereof lies in the fact that it tends to sustain the flame when exposed thereto, hence preventing it from extinguishing.

Furthermore, a small amount of water may be used as expanding agent in a polyisocyanurate having a high density comprised between 400 kg/m³ and 800 kg/m³. Such expanding agent may consist of less than 1 phr of water per 100 phr of polyol, preferably less than 0.5 phr of water per 100 phr of polyol.

Preferably, the only expanding agent to be used may be water at the amounts indicated above.

Thus, a polyisocyanurate having high density comprised between 400 kg/m³ and 800 kg/m³, may be prepared starting from a composition, i.e. a mixture of reagents, which may include, which may respectively consist of:

- a) aromatic polyisocyanates, preferably having average functionalities higher than or equal to 2.5;
- b) compounds having groups reactive towards isocyanates, preferably polyester polyols, more preferably aromatic polyester polyols, in which all OH groups are substantially primary groups;
- c) at least one expanding agent consisting of less than 1 phr of water per 100 phr of polyol, preferably less than 0.5 phr of water per 100 phr of polyol;
- d) possibly at least one further additive, for example at least one filler and/or at least one flame retardant agent and/or a surfactant.

Such composition may be free of tertiary amine and/or expanding graphite and/or chain extender agent. Such composition may also be free of dehydrating agent and/or deaerating agent.

The characteristics of the polyols and/or the isocyanate index of the composition may be the one mentioned above.

The aforementioned high density polyisocyanurate under the test conditions in compliance with the UNI EN 1634-1 or UNI EN 1364-1 standards, carbonises to a hard carbonaceous structure

with mechanical properties high enough to counter heat dilatations and maintain the shape thereof without collapsing or crumbling.

The doors/windows obtained according to the invention may have a profile consisting of the aforementioned polyisocyanurate, or the aforementioned polyisocyanurate may lie inside a box-shaped structure so as to act as an insulator and contribute to the mechanical structure of the door/window. In particular, in case of blind doors which consist of a single box-shaped structure, the insulator remains intact without shattering into pieces, it does not accumulate at the lower part of the box-shaped element and it insulates the upper part of the door/window too.

In other words, the aforementioned polyisocyanurate characteristics enable to obtain a profile for doors/windows whose bearing structure is partly made up of the polyisocyanurate.

To this end, the reagents from which the high density polyisocyanurate (composition) is obtained may be poured and/or injected into special moulds and cured therein for a predetermined period of time.

On the other hand, the profile and/or blind door/window, may include a box-shaped structure, made of any material, into which the reagents, from which the polyisocyanurate is obtained, may be poured and/or injected and cured.

In this case, the polyisocyanurate acts as a heat insulator and cooperates with the box-shaped structure to confer the mechanical structure to the door/window.

A low density polyisocyanurate of the expanded type with density measured in compliance with the EN ISO 845:2006 standard comprised between 20 kg/m³ and 400 kg/m³, preferably comprised between 100 kg/m³ and 400 kg/m³ may be prepared starting from a composition, i.e. from a mixture of reagents, which may include, which may respectively consist of:

- a) aromatic polyisocyanates, preferably having average functionalities higher than or equal to 2.5;
- b) compounds having groups reactive towards isocyanates, preferably polyester polyols, more preferably aromatic polyester polyols, in which all OH groups are substantially primary groups;
- c) at least one expanding agent consisting of water;
- d) at least one flame retardant agent including expanding graphite;
- e) possibly at least one further additive, for example at least one filler and/or at least another flame retardant agent and/or a surfactant.

Such composition may be free of tertiary amine and/or chain extender agent. Such composition may also be free of dehydrating agent and/or deaerating agent.

Preferably, the only expanding agent to be used may be water.

The characteristics of the polyols and/or the isocyanate index of the composition may be the one mentioned above.

The aforementioned expanded polyisocyanurate may be obtained exclusively using water as the chemical expander: as a matter of fact, the isocyanate group reacts with water forming CO₂ and this reaction can be used to obtain an expanded product.

According to an aspect of the invention, the expansion, and thus the porosity and density of the resulting polyisocyanurate, may be controlled by introducing an appropriate amount of water.

The use of additional flame retardant, expanding graphite, is preferable in case of porous polyisocyanurate.

Expanding graphite is an intercalary compound into which, between the graphene layers, there is introduced counterion sulphate anion of a carbon layer positively charged by the anodic oxidation with which it is prepared. Above the oxidation temperature, about 200 °C, the intercalary groups decompose forming large amounts of gas which move the graphite layers away and insulate the polymer surface from the comburent.

As shown in example 7, after carbonisation according to the invention, polyisocyanurate maintains a residual mechanical resistance.

The polyisocyanurate according to the invention, whether of the compact, high density or expanded type, may be obtained by mixing the components A and B or all the components described above at amounts such to obtain an isocyanate index between 300 and 350 at a temperature comprised between 10 °C and 80° C, preferably between 30° C and 40° C.

The reaction is exothermic. Mixing may occur in line at high or low pressure or using RIM techniques, per se known. For example, in order to manufacture a coving, component B and component A may be conveyed through pumps to a high pressure in-line continuous mixer, preferably a 100 to 300 bars mixer, and introduced into the mould, premixed and pressurised.

This method enables filling large moulds, even moulds with complex flow paths. The polyol and the isocyanate are at a temperature between 30° C and 120° C, preferably between 50° C and 100° C. The mould temperature is comprised between 70° C and 130 °C, preferably between 85° C

and 110 °C. The reaction mixture which can be obtained according to the invention reveals a viscosity of about 800 mPas upon mixing at room temperature and a viscosity of about 600 mPas at 40° C. These viscosity values enable high fluidity.

Suitably, the aforementioned compositions may comprise a liquid phase and a solid phase, in which the latter is less than 5% by weight with respect to the total weight of the composition.

The invention may be clearer in light of the following examples, which shall be deemed provided for exemplifying and non-limiting purposes with respect to the invention.

Examples

Test method

The tests in compliance with the EN UNI 1634-1:2014 standard as regards doors and windows and in compliance with the EN UNI 1364-1:2015 standard as regards compartmentalisation, both to be carried out applying the temperature-time curve in compliance with the UNI 1363 standard part 1 and 2, require the introduction of the complete and finished door/window or continuous glass window, into a masonry wall measuring 4 x 4 metres representing the front surface of the test furnace. This test requires a large structure, several days of preparation time and it is very expensive. In addition, it can be exclusively used for certification by official bodies.

A method which revealed, as regards the polymer, data substantially identical to the data obtained from the standardised tests was formulated with the aim of testing the polyisocyanurate according to the invention. The tests below were carried out according to the following procedure.

An amount of polyisocyanate component B calculated so as to obtain the desired isocyanate index was added into a recipient containing a known amount of polyol component A under agitation. The obtained mixture is injected into a mould hardening therein.

After 5 minutes, the mould is opened and after a 24-hour ageing at room temperature, a cubic polymer specimen measuring 4 cm x 4 cm x 4 cm is taken from the resulting sample. The apparent density is measured in compliance with the EN ISO 845:2006 standard. The aforementioned specimen is placed on a heating plate with a 10 g/cm² load on the upper face and subjected to heating in air according to the temperature-time curve in compliance with EN ISO 1363. The temperature is detected by thermocouples arranged on the surface of the plate, on the upper face of the specimen and inside the specimen. The test is carried out qualitatively: presence

of flames, emission of smoke, dripping of the polymer due to the melting thereof, deformation due to the weight thereof and the applied load were observed. To pass the test, the specimen must carbonise without deforming, it must not drip and there should be no flames and/or smoke, dense smoke in particular.

<u>Preparing compact polyisocyanurates</u>

<u>Sample 1 - Very high density polyisocyanurate</u>

Polyol component A is prepared in a recipient in which aromatic polyester polyol (Isoexter, Coim, Italia) had been previously placed and to which - at room temperature, without cooling or heating, under agitation – a polyether modified polysiloxane copolymer surfactant (Tegostab, EVONIK), a potassium octoate in monoethylene glycol (Kosmos, EVONIK) as trimerisation catalyst, a phosphoric acid ester (triethyl phosphate) as flame retardant agent, zeolites 3A dispersed at 50% by weight in castor oil as dehydrating agent, a polysiloxane in glycols (BYK-067A, Altana) as deaerating agent were added in succession. After preparation, component A can be preserved for about six months at room temperature in a closed recipient so to prevent the absorption of atmospheric humidity.

Isocyanate component B is a polymeric mixture based on 4,4' diphenylmethane diisocyanate (MDI)with homologs and isomers, said polymeric mixture having a functionality of about 2.9 and with an overall NCO content in component B comprised between 30.5% and 32.5% by weight (Desmodur, Covestro). Component B can be preserved for about six months at room temperature in a closed recipient so to prevent the reaction of the isocyanate group with atmospheric numidity.

An amount of component B calculated so as to obtain an isocyanate index equivalent to 300 was added into a recipient containing a known amount of component A under agitation. The resulting mixture is injected into the mould hardening therein.

Table 1a shows the sample composition and the test thereof.

After carbonisation, the specimen revealed a glassy structure with a 980 kPa compression resistance measured in compliance with ISO 844.

<u>Samples 2 -6 - High density polyisocyanurate</u>

Polyol component A is prepared in a recipient in which aromatic polyester polyol (Isoexter,

Coim, Italia) had been previously placed and to which - at room temperature, without cooling or heating, under agitation — a polyether modified polysiloxane surfactant copolymer (Tegostab, EVONIK), a potassium octoate in monoethylene glycol (Kosmos, EVONIK) as trimerisation catalyst, a phosphoric acid ester (triethyl phosphate) as flame retardant agent, water, were added in succession. After preparation, component A can be preserved for about six months at room temperature in a closed recipient.

Isocyanate component B is prepared like in example 1.

An amount of component B calculated so as to obtain an isocyanate index equivalent to 300 was added into a recipient containing a known amount of component A under agitation. The resulting mixture is injected into the mould hardening therein.

The test is carried out as described in the test method.

Table 1a shows the sample compositions and the test thereof.

<u>Preparing expanded polyisocyanurates</u>

Samples 7 and 8 - Low density polyisocyanurate

Polyol component A is prepared like in example 2 with addition of expanding graphite with acid activation in flakes as an additional flame retardant agent, and water as a chemical expanding agent. After preparation, component A can be preserved for about six months at room temperature in a closed recipient.

Isocyanate component B is prepared like in example 2.

An amount of component B calculated so as to obtain the desired isocyanate index was added into a recipient containing a known amount of component A under agitation.

The test is carried out as described in the test method.

Table 1b shows the sample compositions and the test thereof.

After carbonisation, the sample 7 specimen revealed a porous glassy structure with a 133 kPa compression resistance measured in compliance with ISO 844.

Comparison examples

Samples 9 and 10 - Expanding graphite-free low density polyisocyanurates are unsuitable

The samples were prepared like in example 8 without adding expanding graphite.

The test is carried out as described in the test method.

Table 1b shows the sample compositions and the test thereof.

The samples, entirely identical to example 8, failed the test due to the absence of expanding graphite. The samples show that expanding graphite is required at low density.

Samples 11 - 16 - Non-aromatic polyol is unsuitable

Using an aliphatic polyester polyol with functionality comprised between 2 and 2.5, a 160 mg KOH/g hydroxyl number; (ISOEXTER), obtained from condensation of glycols or 2 to 12 carbon atom glycol mixtures, such as for example ethylene glycol, diethylene glycol, butanediol glycol, trimethylolpropane glycol, glycerine with 4 to 12 carbon atom aliphatic carboxylic acids such as for example adipic acid, succinic acid, glutaric acid, azelaic acid, sebacic acid, decanoic acid, samples 11 and 12 were prepared using the method described above.

The test is carried out as described in the test method.

Table 1b shows the sample compositions and the test thereof.

Using an aliphatic/aromatic polyester polyol with functionality comprised between 2.0 and 2.5, (ISOEXTER) with 240 mg KOH/g hydroxyl number; obtained from condensation of glycols or 2 to 10 carbon atom glycol mixtures, such as for example ethylene glycol, diethylene glycol, butanediol glycol, trimethylolpropane glycol, glycerine with 4 to 12 carbon atom aliphatic carboxylic acids such as for example adipic acid, succinic acid, glutaric acid, azelaic acid, sebacic acid, decanoic acid, dodecanoic acid and with carboxylic acids with at least one aromatic ring such as for example terephthalic acid or ortho-phthalic anhydride, samples 13 and 14 were prepared using the method described above.

The test is carried out as described in the test method.

Table 1c shows the sample compositions and the test thereof.

Samples 15 and 16 were prepared using the materials like in examples 13 and 14 without dehydrating or deaerating agents and with addition of a water chemical expanding agent and expanding graphite. Furthermore, the isocyanate index is lower in example 15.

The test is carried out as described in the test method.

Table 1c shows the sample compositions and the test thereof.

Samples 17 - 21 - Polyether polyol is unsuitable

Sample 17

Using an amine-based polyether polyol with functionality comprised between 2 and 4, preferably comprised between 2.5 and 3.0, a hydroxyl number comprised between 100 and 400 mg KOH/g, obtained from toluenediamine using ethylene and propylene oxide, sample 17 was prepared using the method described above. Other components like in table 1.

The test is carried out as described in the test method.

Table 1c shows the sample compositions and the test thereof

Samples 18 and 19

Samples 18 and 19, to which an ammonium phyllosilicate and polyphosphate were added as inorganic mineral filler, were prepared using the method described regarding example 17. Other components like in the table.

The test is carried out as described in the test method.

Tables 1c and 1d show the sample compositions and the test thereof.

Samples 20 and 21

Using a polyether polyol with average functionality comprised between 2 and 4, preferably comprised between 2.5 and 3.0, a 160 mgKOH/g hydroxyl number; with prevalent base of ethylene/propylene oxide or 2 to 4-carbon atom compounds, with molecular weight comprised between 700 and 1400 Da, samples 20 and 21 were prepared using the method described above. Other components like in the table.

The test is carried out as described in the test method.

Table 1d shows the sample compositions and the test thereof

Samples 22- 25 - Tertiary amines are not necessary

Samples 22 and 23

Using an aliphatic polyester polyol with functionality comprised between 2 and 2.5, a 160 mg KOH/g hydroxyl number; (ISOEXTER), obtained from condensation of glycols or 2 to 12 carbon atom glycol mixtures, such as for example ethylene glycol, diethylene glycol, butanediol glycol, trimethylolpropane glycol, glycerine with 4 to 12 carbon atom aliphatic carboxylic acids such as for example adipic acid, succinic acid, glutaric acid, azelaic acid, sebacic acid, decanoic acid, with a first N-ethyl morpholine catalyst or N,N dimethyl cyclohexylamine catalyst, a second potassium acetate

catalyst in diethylene glycol and a third carboxylated quaternary ammonium N-hydroxy-alkyl catalyst in ethylene glycol, samples 22 and 23 were prepared using the method described above. Further characteristics are indicated in table 1d, the results in table 2.

The test is carried out as described in the test method.

Table 1d shows the sample compositions and the test thereof

Samples 24 and 25

Using an aromatic polyester polyol with functionality comprised between 2 and 2.5, a 250 mg KOH/g hydroxyl number; (ISOEXTER), with a first N-ethyl morpholine catalyst, a second potassium acetate catalyst in diethylene glycol and a third carboxylated quaternary ammonium N-hydroxy-alkyl catalyst in ethylene glycol, samples 24 and 25 were prepared using the method described above. Further components and/or characteristics are indicated in tables 1d and 1e.

<u>Samples 26 and 27 - High density polyisocyanurates with expanding graphite break</u>

Polyol component A is prepared like in example 2 with addition of expanding graphite with acid activation in flakes as an additional flame retardant agent, and water as a chemical expanding agent. After preparation, component A can be preserved for about six months at room temperature in a closed recipient.

Isocyanate component B is prepared like in example 2.

An amount of component B calculated so as to obtain the desired isocyanate index was added into a recipient containing a known amount of component A under agitation.

The test is carried out as described in the test method.

Table 1e shows the sample compositions and the test thereof.

The present expanding graphite caused the breaking of the specimen during the test, the aforementioned breaking not being observed in samples 6 and 3 whose sole difference as compared to samples 26 and 27 lies in the absence of expanding graphite.

Table 1a

Parts compared to 100 of polyol, values expressed as phr (parts per hundred resin)

	Samp 1	Samp 2	Samp 3	Samp 4	Samp 5	Samp 6
Polyol	100	100	100	100	100	100
Polyol functionality	2.0	2.5	2.5	2.5	2.5	2.5

WO 2018/015938 PCT/IB2017/054463

Hydroxyl number	250	250	250	250	250	250
Potassium octoate	1.0	1.0	1.0	1.0	1.0	1.0
N-ethyl morpholine						
Potassium acetate						
Carboxylated quaternary						
ammonium N-hydroxy-alkyl						
Water	-	0.20	0.25	0.30	0.35	0.42
Surfactant	4	4	4	4	4	4
Mineral fillers						
Polyphosphates						
Triethyl phosphate	11	11	11	11	11	11
Expanding graphite						
Dehydrating agent	8					
Deaerating agent	1					
Polyisocyanate	180	180	180	180	180	180
Isocyanate functionality	2.9	2.9	2.9	2.9	2.85	2.85
NCO % by weight in	31	31	31	31	31.5	31.5
isocyanate	31	31			31.3	31.3
Density (ISO845:2006)	1050	800	700	600	500	400
kg/m ³	2000					
Dense smoke	No	No	No	No	No	No
Light smoke	No	No	No	No	Yes	Yes
Open flame	No	No	No	No	No	No
Dripping	No	No	No	No	No	No
Deformation	No	No	No	No	No	No
Breaking	No	No	No	No	No	No
Acceptable	Yes	Yes	Yes	Yes	Yes	Yes

Table 1b

Parts compared to 100 of polyol, values expressed as phr (parts per hundred resin)

Samp 7	Samp 8	Samp 9	Samp 10	Samp 11	Samp 12

Polyol	100	100	100	100	100	100
Polyol functionality	2	2.5	2	2.5	2.5	2.5
Hydroxyl number	250	250	250	250	160	160
Potassium octoate	1.0	1.0	1.0	1.0	1.0	1.0
N-ethyl morpholine						
Potassium acetate						
Carboxylated quaternary						
ammonium N-hydroxy-alkyl						
Water	1.7	5.6	3.1	5.3		
Surfactant	3	2.5	2.5	4	2.5	3
Mineral fillers						
Polyphosphates						
Triethyl phosphate	10	12	11	12	10	
Expanding graphite	10	10				
Dehydrating agent						6
Deaerating agent						
Polyisocyanate	143	180	180	180	116	155
Isocyanate functionality	2.85	2.9	2.85	2.85	2.7	2.7
NCO % by weight in	31.5	31.5	31.5	31.5	31	31
isocyanate	31.3	31.3	31.3	31.3		31
Density (ISO845:2006)	100	30	50	30	850	900
kg/m ³	100	30				
Dense smoke	No	No	No	No	Yes	Yes
Light smoke	No	No	Yes	Yes	Yes	Yes
Open flame	No	No	Yes	Yes	Yes	Yes
Dripping	No	No	No	No	Yes	Yes
Deformation	No	No	No	Yes	Yes	Yes
Breaking	No	No	No	No	No	No
Acceptable	Yes	Yes	No	No	No	No

Table 1c

Parts compared to 100 of polyol, values expressed as phr (parts per hundred resin)

	Samp 13	Samp 14	Samp 15	Samp 16	Samp 17	Samp 18
Polyol	100	100	100	100	100	100
Polyol functionality			2	2		
Hydroxyl number	240	240	240	240		
Potassium octoate	1.0	1.0	1.0	1.0	1.0	1.0
N-ethyl morpholine						
Potassium acetate						
Carboxylated quaternary						
ammonium N-hydroxy-alkyl						
Water			1.7	4.8		
Surfactant	3		3	2.5	2.5	2.5
Mineral fillers						30
Polyphosphates						30
Triethyl phosphate	10	10	10	10	11	11
Expanding graphite			10	10		
Dehydrating agent	7	8			6.5	6.5
Deaerating agent	0.3	0.3				
Polyisocyanate	143	171	143	180	128	154
Isocyanate functionality	2.85	2.85	2.85	2.85	2.85	2.85
NCO % by weight in	31.5	31.5	31.5	31.5	31.5	31.5
isocyanate	31.3	31.3	31.3	31.3	31.3	31.5
Density (ISO845:2006)	950	940	100	35	850	900
kg/m ³	330	340	100	33	030	300
Dense smoke	Yes	Yes	Yes	Yes	Yes	Yes
Light smoke	Yes	Yes	Yes	Yes	Yes	Yes
Open flame	No	No	Yes	Yes	Yes	No
Dripping	Yes	Yes	Yes	Yes	Yes	No
Deformation	Yes	Yes	Yes	Yes	Yes	Yes
Breaking	No	No	Yes	Yes	No	Yes

<u>Table 1d</u>
Parts compared to 100 of polyol, values expressed as phr (parts per hundred resin)

	Samp 19	Samp 20	Samp 21	Samp 22	Samp 23	Samp 24
Polyol	100	100	100	100	100	100
Polyol functionality				2.5	2.5	2.5
Hydroxyl number		160	160	160	160	250
Potassium octoate	1.0	1.0	1.0			
N-ethyl morpholine				0.3	0.3	0.3
Potassium acetate				2.0	2.5	2.0
Carboxylated quaternary ammonium N-hydroxy-alkyl				0.7	0.7	0.7
Water						1.1
Surfactant	3	3	4	2.5	3	2.5
Mineral fillers	40		60			
Polyphosphates	40		40			
Triethyl phosphate	11	10	10	10		10
Expanding graphite						5
Dehydrating agent	6.5	5	5		6	
Deaerating agent		0.4	0.4			
Polyisocyanate	179	115	153	116	155	180
Isocyanate functionality	2.85	2.85	2.85	2.7	2.7	2.7
NCO % by weight in isocyanate	31.5	31.5	31.5	31	31	31
Density (ISO845:2006) kg/m ³	850	930	850	850	900	50
Dense smoke	Yes	Yes	No	Yes	Yes	No
Light smoke		Yes	Yes	Yes	Yes	No
Open flame	No	Yes	No	Yes	Yes	No
Dripping	No	Yes	No	Yes	Yes	No

Deformation	Yes	Yes	Yes	Yes	Yes	No
Breaking	Yes	No	Yes	No	No	No
Acceptable	No	No	No	No	No	Yes

<u>Table 1e</u>
Parts compared to 100 of polyol, values expressed as phr (parts per hundred resin)

	Samp 25	Samp 26	Samp 27		
Polyol	100	100	100		
Polyol functionality	2.5	2	2.5		
Hydroxyl number	250	250	250		
Potassium octoate		1.0	1.0		
N-ethyl morpholine	0.3				
Potassium acetate	2.5				
Carboxylated quaternary	0.7				
ammonium N-hydroxy-alkyl	0.7				
Water	1.7	0.4	0.25		
Surfactant	3	4	4		
Mineral fillers					
Polyphosphates					
Triethyl phosphate	11	11	11		
Expanding graphite	10	10	5		
Dehydrating agent					
Deaerating agent					
Polyisocyanate	180	180	180		
Isocyanate functionality	2.7	2.9	2.9		
NCO % by weight in	31	31	31.5		
isocyanate					
Density (ISO845:2006)	150	400	700		
kg/m ³					
Dense smoke	No	No	No		
Light smoke	No	No	No		

Open flame	No	No	No		
Dripping	No	No	No		
Deformation	No	No	No		
Breaking	No	Yes	Yes		
Acceptable	Yes	No	No		

Embodiments of profiles for fire doors/windows

Various profiles for fire doors/windows were manufactured using the compositions like in examples 1 to 6, 8, 24 and 25, illustrated in FIGS. 1 - 9. In such figures, the frame of the profile is indicated with **10**, while the compact polyurethane is indicated with **20**.

The figures regard:

- FIG. 1: profile for fire damper doors/windows with lateral structures made of any material, hollow central bearing structure in which steel hardware can be housed, joining the parts made of polyisocyanurate according to example 1 above;
- FIG. 2: profile for fire damper doors/windows with lateral structures made of any material, central insulating structure for joining and sustaining in case of fire made of compact polyisocyanurate according to example 1 above with cavity for the passage of hardware;
- FIG. 3: profile for fire damper doors/windows with lateral structures and central bearing structure made of steel, connection between the parts made of compact polyisocyanurate according to example 1 above with heat-damping function;
- FIGS. 4a and 4b: profile for fire damper doors/windows with lateral structures and central bearing structure made of any material, central bearing structure made of compact polyisocyanurate according to example 1 above with heat-insulation function;
- FIGS. 5a and 5b: profile for fire damper doors/windows with lateral structures made of any material and central part made of polyisocyanurate according to example 3 above, with a U-shaped structure; the hardware which can for example be covered with an easily removable snap-fixed sheet is arranged in the cavity. This enables performing compulsory maintenance operations on the hardware of the fire damper door/window without removing the door/window from the hinges, by simply removing the cover sheet;
- FIG. 6: profile for fire damper doors/windows with lateral structures made of any material, central bearing structure obtained from pultrusion (thick dashes), connection of the structures

made of polyisocyanurate according to example 1 above (thin dashes). The compact polyisocyanurate is prepared *in situ* by injecting into the cavity formed by the other pre-assembled elements and an external mould. Central hole for the passage of the hardware;

- FIG. 7: profile for fire damper doors/windows obtained by adapting a traditional non-fire damper structure. Lateral bearing structure mutually joined using continuous heat-damping profiles (usually made of polyamide), turned into fire-damper by simply filling it by injecting the polyisocyanurate according to example 3 above (*in situ*) using the structure as a formwork.
 - FIG. 8: Perspective view of a steel blind fire door P.
- FIG. 9: Vertical section of the door of FIG. 8. Internal insulation made of polyisocyanurate according to example 8 above, prepared *in situ* by injecting the components into the cavity formed by the pre-assembled box-shaped element of the door used as a formwork. The door includes an infill element **V** made of stratified glass.

CLAIMS

- 1. A composition for preparing a polyisocyanurate, the composition consisting of:
 - a) aromatic polyisocyanates;
 - b) compounds having groups reactive towards isocyanates;
 - c) possibly at least one additive.

5

10

15

20

25

30

- 2. Composition according to claim 1, wherein the aromatic polyisocyanates have functionalities higher than or equal to 2.5, and preferably of 2.7 to 2.9.
- 3. Composition according to claim 1 or 2, wherein the compounds having groups reactive towards isocyanates include, respectively consist of, polyols having substantially all primary hydroxyl groups.
- 4. Composition according to the preceding claim, wherein the polyols are polyester polyols, preferably aromatic polyester polyols.
- 5. Composition according to claim 3 or 4, wherein the polyols have functionalities higher than or equal to 2, preferably substantially equal to 2.
- 6. Composition according to claim 3, 4 or 5, wherein the polyols have a hydroxyl number of 150 mgKOH / g to 350 mgKOH / g.
- 7. Composition according to any one of the preceding claims, having an isocyanate index of 200 to 400, preferably of 300 to 350.
- 8. Composition according to any one of the preceding claims, wherein said at least one additive is selected from the group consisting of: at least one filler, at least one dehydrating agent, at least one deaerating agent, at least one catalyst, at least one flame retardant agent, at least one surfactant agent, at least one expanding agent.
- 9. Composition according to any one of the preceding claims, wherein the composition is free of chain extender agents.
- 10. Composition according to any one of the preceding claims, wherein the composition is free of tertiary amine.
- 11. Composition according to any one of the preceding claims, comprising a liquid phase and a solid phase, wherein the latter is less than 5% by weight with respect to the total weight of the composition.
- 12. Composition according to any one of the preceding claims, wherein said at least one additive includes at least one trimerisation catalyst, the latter preferably consisting of at

least one fatty acid alkali salt.

5

10

15

20

25

30

- 13. Composition according to any one of the preceding claims, wherein said at least one additive includes at least one surfactant agent, preferably consisting of a polyether modified polysiloxane copolymer.
- 14. Composition according to any one of the preceding claims, wherein the polyisocyanurate has a density higher than 400 kg/m³ measured in compliance with the EN ISO 845:2006 standard.
- 15. Composition according to the preceding claim, wherein the polyisocyanurate is of the substantially porosity-free compact type with a density higher than 800 kg/m³ measured in compliance with the EN ISO 845:2006 standard, preferably higher than 1000 kg/m³, and more preferably higher than 1100 kg/m³.
- 16. Composition according to the preceding claim, wherein the composition is substantially free of water and/or air.
- 17. Composition according to claim 15 or 16, wherein said at least one additive includes:
 - d) at least one dehydrating agent;
 - e) at least one deaerating agent.
- 18. Composition according to the preceding claim, wherein the at least one deaerating agent is a polyoxyalkyl- polysiloxane in non-aqueous solution.
- 19. Composition according to claim 17 or 18, wherein the at least one dehydrating agent is a zeolite in castor oil.
- 20. Composition according to claim 14, wherein the polyisocyanurate has a density measured in compliance with the EN ISO 845:2006 standard comprised between 400 kg/m³ and 800 kg/m³, said at least one additive including at least one expanding agent consisting of less than 1 phr of water per 100 phr of polyol, preferably less than 0.5 phr of water per 100 phr of polyol.
- 21. Composition according to any one of claims 16 to 20, wherein the composition is free of expanding graphite.
- 22. Composition according to any one of claims 1 to 13, wherein the polyisocyanurate is of the expanded type with a density measured in compliance with the EN ISO 845:2006 standard comprised between 20 kg/m 3 and 400 kg/m 3 , preferably comprised

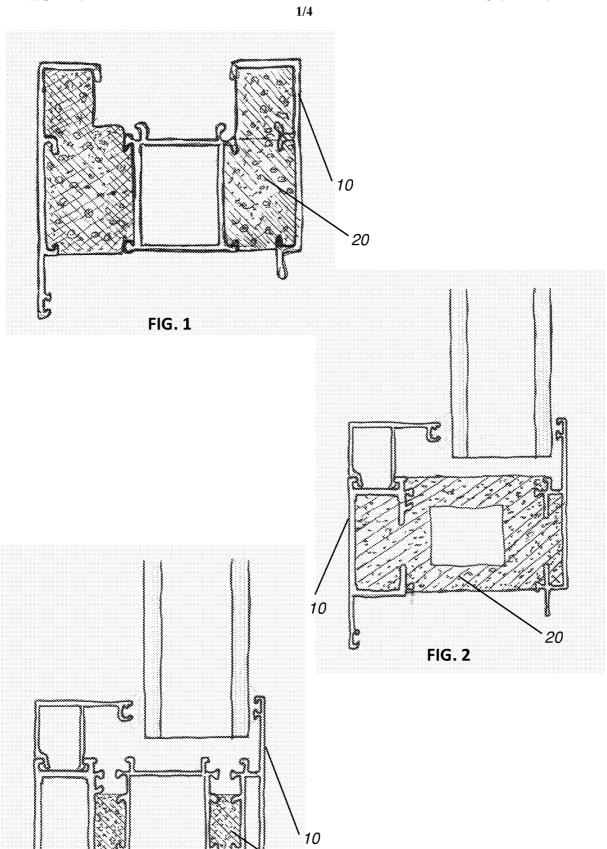
 \sim

between 100 kg/m³ and 400 kg/m³.

10

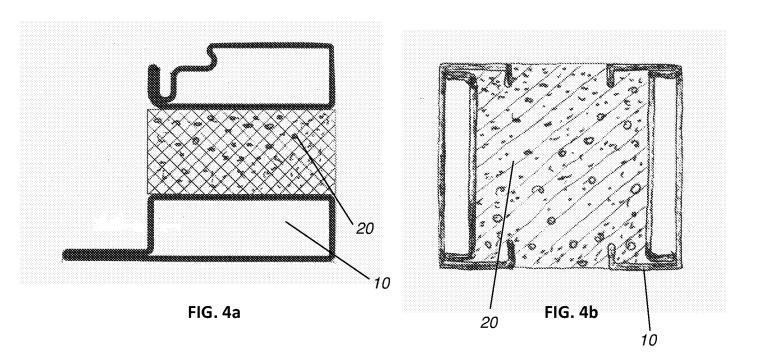
15

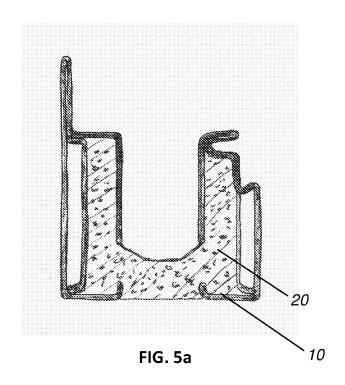
- 23. Composition according to the preceding claim, wherein said at least one additive includes at least one flame retardant agent consisting of expanding graphite, preferably in flakes.
- 5 24. Composition according to the preceding claim, wherein said expanding graphite is a mixture of flakes of at least two different dimensions.
 - 25. Composition according to claim 22, 23 or 24, wherein said at least one additive includes water.
 - 26. A method for preparing a polyisocyanurate comprising the steps of mixing and handling components a), b) and possibly c) as defined in any of the preceding claims.
 - 27. A polyisocyanurate that can be obtained by means of a method according to the preceding claim.
 - 28. Polyisocyanurate according to the preceding claim, wherein the polyisocyanurate is of the type with density higher than 800 kg/m 3 measured according to the EN ISO 845:2006 standard, preferably with density higher than 1000 kg/m 3 , more preferably with density higher than 1100 kg/m 3 .
 - 29. The use of a polyisocyanurate according to claim 27 or 28 for manufacturing profiles for fire doors/windows and/or for manufacturing fire doors/windows.
- 30. A profile for fire damper, flame damper, smoke damper fire doors/windows or the like, comprising or consisting of a polyisocyanurate according to claim 27 or 28.

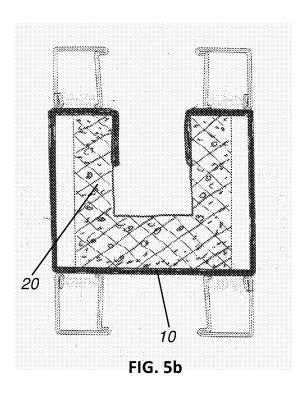


20

FIG. 3







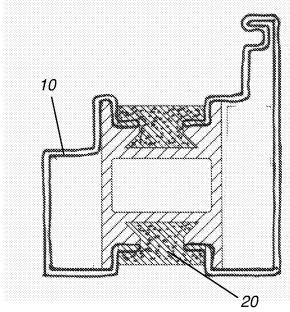
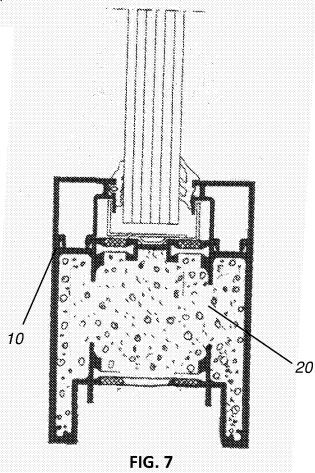


FIG. 6



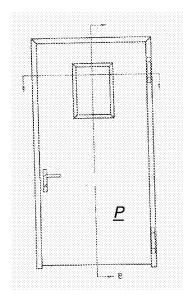


FIG. 8

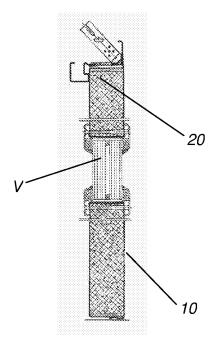


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No PCT/IB2017/054463

A. CLASSIFICATION OF SUBJECT MATTER INV. E06B3/263 E06B5/16

C08G18/09

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 E06B

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

С. DOCUMI	DOCUMENTS CONSIDERED TO BE RELEVANT						
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.					
Х	US 2015/028247 A1 (PETERS EDWARD NORMAN [US]) 29 January 2015 (2015-01-29) paragraph [0023]; examples 7-9; table 4	1-30					
Х	WO 2014/055318 A1 (BAYER MATERIALSCIENCE LLC [US]; COMBS GEORGE G [US]; PIGOTT SUSAN C [U) 10 April 2014 (2014-04-10) page 15, line 30 - page 16, line 2 examples 1-3; table 1	1-30					
X	US 4 317 791 A (LUEDKE HEIMO ET AL) 2 March 1982 (1982-03-02) column 3, line 7 column 4, lines 28-29 example 1	1-30					

Further documents are listed in the continuation of Box C.	X See patent family annex.
"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	Date of mailing of the international search report
1 November 2017	09/11/2017
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 Gallego, Adoración

1

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2017/054463

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT				
ategory*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.		
(US 3 644 168 A (BONK HENRY W ET AL) 22 February 1972 (1972-02-22) examples 1-7 column 5, lines 32-33,40-41; figures 1-3 column 6, lines 1-4,34-40; claim 1	1-30		
X	WO 2013/174844 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 28 November 2013 (2013-11-28) page 4, lines 1-29 page 6, lines 5-27 page 20, lines 11-35 examples 1-4; tables 1,2	1-30		
(US 6 245 826 B1 (WILSON JOE C [US] ET AL) 12 June 2001 (2001-06-12) column 1, lines 8-17; claim 1 column 14, lines 45-48 column 15, lines 13-27 column 19, lines 24-35; table 1 column 20, lines 14-17	1-30		
X	US 2015/051301 A1 (SCHLEIERMACHER STEPHAN [DE] ET AL) 19 February 2015 (2015-02-19) paragraphs [0021] - [0022], [0029] - [0032], [0036], [0049], [0055] - [0056], [0088], [0111], [0114]; examples 3,5,7,9,11	1-30		

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/IB2017/054463

Patent document cited in search report	Publication date	Patent family Publication member(s) date
US 2015028247 A	1 29-01-2015	CN 105377988 A 02-03-20 EP 3036288 A1 29-06-20 JP 6158431 B2 05-07-20 JP 2016529332 A 23-09-20 KR 20160028461 A 11-03-20 US 2015028247 A1 29-01-20 US 2016145405 A1 26-05-20 WO 2015012989 A1 29-01-20
WO 2014055318 A	1 10-04-2014	CA 2886641 A1 10-04-20 CN 104854156 A 19-08-20 EP 2904024 A1 12-08-20 US 2014094530 A1 03-04-20 US 2017058092 A1 02-03-20 WO 2014055318 A1 10-04-20
US 4317791 A	02-03-1982	AT 357766 B 25-07-19 BE 856616 A1 09-01-19 DE 2631167 A1 19-01-19 FR 2357586 A1 03-02-19 JP S538699 A 26-01-19 JP S598204 B2 23-02-19 NL 7707654 A 12-01-19 US 4317791 A 02-03-19
US 3644168 A	22-02-1972	NONE
WO 2013174844 A	1 28-11-2013	CN 104334599 A 04-02-20 EP 2855549 A1 08-04-20 JP 2015520260 A 16-07-20 RU 2014152834 A 20-07-20 US 2015118476 A1 30-04-20 US 2016303778 A1 20-10-20 WO 2013174844 A1 28-11-20
US 6245826 B	1 12-06-2001	US 6245826 B1 12-06-20
US 2015051301 A	1 19-02-2015	CN 104093759 A 08-10-20 EP 2812370 A1 17-12-20 JP 2015510535 A 09-04-20 KR 20140127856 A 04-11-20 RU 2014136188 A 27-03-20 US 2015051301 A1 19-02-20 WO 2013117541 A1 15-08-20