



- (51) **International Patent Classification:**  
*C08G 18/38* (2006.01)    *C08K 3/34* (2006.01)  
*C08J 9/00* (2006.01)
- (21) **International Application Number:** PCT/PL2012/000032
- (22) **International Filing Date:** 15 May 2012 (15.05.2012)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:** P.394959    20 May 2011 (20.05.2011)    PL
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- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, 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, 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, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report (Art. 21(3))
  - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))



(54) **Title:** BINARY AGENT FOR THE MODIFICATION OF POLYURETHANE MATERIALS

(57) **Abstract:** The subject of the invention is a binary agent for the modification of polyurethane materials, characterised by that it comprises a liquid component containing potassium hydroxide of between 2 and 65 % by weight, potassium silicate of between 1.8 and 29.8 % by weight, water of between 5.5 % by weight and a solid component in the form of expanded perlite of between 0.1 and 45 % by weight.

## BINARY AGENT FOR THE MODIFICATION OF POLYURETHANE MATERIALS

The present invention relates to a binary agent for the modification of polyurethane materials, in particular as regards controlled forming of the porosity and structure of polyurethane materials, reducing fire threats and improving the physico-chemical properties of the final polyurethane material modified with such an agent.

Polyurethanes are polymers with a very wide range of applications in many branches of industry. Depending on the method of their production and the technological additives, they are used to produce clothing laminates, protective coatings, lacquer paints, glues as well as widely applied rigid or elastic foams. Polyurethanes are characterised by elasticity of closed and open pores and mechanical resistance to fire threats. The main two groups of polyurethanes are polyurethanes with the names: PUR and PIR which are mixtures of polyols with the appropriate cross-linking additives.

Polyisocyanurates (PIR) belong to the polyurethane group. The difference between typical polyurethane (PUR) and polyisocyanurate foams is that the proportion of isocyanates in the production of PIR is decisively higher than in PUR and, as a result, material with better mechanical and thermal insulation properties is obtained. However, the most important characteristics to distinguish between PIR and PUR materials is a much higher temperature resistance and reduced flammability. Typical polyurethanes undergo thermal decomposition at the temperature of 200°C, whilst in polyisocyanurates this temperature is 300°C.

Polyurethane foams are polyurethane materials with a very wide range of applications. The main classification of foams is their division into elastic and rigid ones. Elastic foams are applied for example in the textile industry, whilst rigid foams are used in the production of furniture, and in the automotive, aircraft and construction industries. As regards rigid foams, especially the ones used in construction as thermal insulation materials, one of their important

characteristics which has an effect on their mechanical properties is i. a. their porosity. The quality of the pores (open, closed), their number in a unit of volume, and the method of their manufacture, as well as technological additives have a major impact in the final product.

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The requirements for the composition and properties of polyurethane and polyisocyanurate materials especially in view of the impact of the additives on the natural environment get stricter together with the increase in the quantity and scope of application of materials of this type, hence, there is a need to  
10 replace existing technological additives such as expanding agents, plasticizers, fillers, etc. with substances which would provide the material with the required mechanical and insulation properties and which, at the same time, would be neutral to the natural environment during use, and also in their thermal decomposition.

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Korean patent application WO09011533A1 presents adiabatic material which comprises expanded perlite and polyurethane, and the method of obtaining them as well as construction materials containing adiabatic material. The material according to the invention contains expanded perlite particles with a  
20 definite diameter and expanded perlite with such an average particle diameter as to fill in the gaps between the perlite particles with the definite particle diameter, as well as a single-component water-expandable urethane binder. The adiabatic material according to the invention is light, has perfect adiabatic properties, is fire resistant and holds back the spreading of flames.

25 US patent application US RE37095 (E1) presents thermosetting foams, preferably polyisocyanurate or polyurethane ones, obtained through extrusion, which enables the application of a large filler quantity. The method of obtaining the material comprises the introduction of polyol, isocyanate and filler particles in an extruder and mixing them. A catalyser is added while the components are  
30 being integrated in the extruder. The catalyser may be added also in the last barrel of the extruder or in its head. The foam with the filler content of more than 12% is easy to obtain. The filler may be: aluminum trihydrate, perlite, carbon black, diatomite, ammonium phosphate, fly ashes, calcium silicate, calcium

carbonate. The method according to the invention is applied to obtain foam boards.

5 The subject of examination was therefore a binary agent for controlled forming of the porosity and structure of polyurethane materials which would make it possible to obtain PUR and PIR foams with the required physico-chemical properties and would thus enable controlled production of materials with the required pore parameters, such as quality (open, closed) and quantity and, simultaneously, the materials obtained would meet the environmental quality  
10 requirements, particularly where chemical compounds are released in high temperature.

The aim of the invention is to provide a binary agent for the modification of polyurethane materials, particularly as regards controlled forming of the porosity  
15 and structure of polyurethane materials which would make it possible to obtain polyurethane materials with very good thermal insulation properties, and especially high resistance to moisture penetration, with considerable thermal resistance and increased fire resistance.

20 The nature of the invention is therefore a binary agent for the modification of polyurethane materials, characterised in that it consists of a liquid component containing potassium hydrate of between 2 and 65 % by weight, potassium silicate of between 1.8 to 29.8 % by weight, water of 5.5 % by weight and a solid component in the form of expanded perlite of between 0.1 and 45 % by  
25 weight.

Preferably, according to the invention, the perlite grain size is between 0.3 and 12.0 mm.

30 During laboratory tests on the production of polyurethane materials using the well-known method, with the use of the binary agent according to the invention, and on the production of said materials for semi-technological and technological scale with the application of the binary agent according to the invention, it was unexpectedly found that it was unexpectedly found that the operation of

potassium silicate in water environment containing potassium hyrate, by regulating the porosity of the polyurethane mass, causes linear development of polymerization with parallel formation of microsphere nuclei containing inert gas.

- 5 A derivative of the transformations as described is also the unexpected additive building in of silicate polymers and sub-polymers (of potassium silicate) into the formed structure of the polyurethane polymer.

10 Controlled forming of the porosity and structure of polyurethane materials with the use of the binary agent as a modifier according to the invention is effected through reactions and conversions with isocyanates during exothermic transformations. It was unexpectedly found that the increase in electrical conductivity caused by the alkaline environment results in the homogenization of the components and an even distribution of the gaseous phase.

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The application of the solid component in the form of expanded perlite with the appropriate grain size of the binary agent according to the invention enables the adsorption and absorption of water released from this component with a delay, which is advantageous for the kinetics of the reaction and the ultimate structure  
20 of the polyurethane material.

The modifier according to the invention is presented in more detail in preferable examples of its production which, however, do not restrict its scope.

25 Example 1

The following are introduced in a vessel with a mixing arm:

potassium hydroxide of 2.5 kg

potassium silicate of 0.2 kg

water of 0.6 kg.

- 30 Then, the mixing arm is set to motion and, after approx. 5 minutes, ca. 3.3 kg of a liquid component of the binary agent according to the invention is obtained which is ready to be used together with perlite – the solid component – in the quantity of 0.8 kg and with the grain size of 0.5 mm.

Both components are prepared independently, stored in separate packaging and added at different stages of obtaining the modified polyurethanes.

### Example 2

5 A stationary example of obtaining PUR polyurethanes modified with the binary agent according to the invention.

A liquid component with the following composition is introduced in a vessel with a mixing arm:

potassium hydroxide of 2.5 kg

10 potassium silicate of 0.2 kg

water of 0.6 kg.

Then, the mixing arm is set to motion and, after approx. 5 minutes, a mixture is obtained which, in the quantity of 1.8 % by weight, is introduced in the polyol (PUR), and then, all material is mixed for 2 minutes and, while mixing  
15 continuously, the quantity of 2.1 % by weight of the solid component in the form of perlite with the grain size of 1.8 mm is introduced in the mixture, and then, all material is mixed for 1.5 minutes and the masterbatch is treated with isocyanate of 105% by weight.

20 The quantities of the liquid component, the solid component and of the isocyanate are calculated with relation to the quantity of the polyol.

All material is mixed for 10 seconds until expansion begins.

Reaction time: 3.5 min.

### 25 Example 3

A stationary example of obtaining PIR polyurethanes modified with the binary agent according to the invention.

A liquid component with the following composition is introduced in a vessel with a mixing arm:

30 potassium hydroxide of 2.5 kg

potassium silicate of 0.3 kg

water of 0.7 kg.

Then, the mixing arm is set to motion and, after approx. 5 minutes, a mixture is obtained which is introduced, in the quantity of 1.9 % by weight, in the polyol

(PIR), then all material is mixed for 2 minutes, and while mixing continuously, the quantity of 2.9 % by weight of perlite with the grain size of 0.5 mm is introduced in the mixture, and then, all material is mixed for 1.5 minutes and the masterbatch is treated with isocyanate in the quantity of 160% by weight.

- 5 The quantity of the liquid component, the solid component and of the isocyanate is calculated with relation to the quantity of the polyol.

All material is mixed for 9 seconds until expansion begins.

Reaction time: 3.0 min.

- 10 The introduction of the solid component in the form of perlite with the required grain size into the liquid component mixed with polyol enables more effective homogenisation of the polyol with the liquid component and does not have an effect on distorting the quantitative proportions between the different components of the agent according to the invention.

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Polyurethane materials modified with the binary agent according to the invention demonstrate advantageous geometrical distribution of pores. The application of the binary agent for the modification of polyurethane materials according to the invention enables regulation of the structure of the pores  
20 (open, closed) and a reduction of the material's density, and has an effect on the elasticity of the material, its resistance parameters, thermal resistance and vibroacoustic properties.

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What is claimed is:

- 5 1. Binary agent for the modification of polyurethane materials, wherein it comprises a liquid component containing potassium hydroxide of between 2 to 65 % by weight, potassium silicate of between 1.8 and 29.8 % by weight, water of between 5.5 % by weight and a solid component in the form of expanded perlite of between 0.1 and 45 % by weight.
- 10 2. Binary agent according to claim 1 wherein the perlite grain size is between 0.3 and 12.0 mm.

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**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/PL2012/000032

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C08G18/38 C08J9/00 C08K3/34  
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)  
C08L C08G C08K C08J

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

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A	US 2005/281999 A1 (HOFMANN RAY F [US] ET AL) 22 December 2005 (2005-12-22) examples 17-19, 19B, 21B, 21F, 21G, 21I claims 1, 3, 9-13	1, 2
A	US 6 403 688 B1 (LUONGO JOSEPH S [US]) 11 June 2002 (2002-06-11) examples 1-5 claims 1, 2	1, 2
A	GB 2 454 990 A (3GATES PATENT LTD [IE]) 27 May 2009 (2009-05-27) claims 1-5, 11, 19-22	1, 2
A	WO 94/00004 A1 (UNIV STRATHCLYDE) 6 January 1994 (1994-01-06) example 1	1, 2
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Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "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

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- "&" document member of the same patent family

Date of the actual completion of the international search <b>6 September 2012</b>	Date of mailing of the international search report <b>14/09/2012</b>
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer <b>Russell, Graham</b>
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## INTERNATIONAL SEARCH REPORT

International application No  
PCT/PL2012/000032

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 357 429 A (BLOUNT DAVID H) 2 November 1982 (1982-11-02) claims 1-3 -----	1,2
A	US 4 346 180 A (BLOUNT DAVID H) 24 August 1982 (1982-08-24) example 6 claims -----	1,2

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Information on patent family members

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