After heated to the temperature between 98 °C and 100 °C. Subsequently a saccharose is added, as well as additional melamine.
FIREPROOF ADDITIVE TO POLYURETHANES, FIREPROOF POLYURETHANE, METHOD OF PRODUCTION OF FIREPROOF ADDITIVE

Field of technology

The invention concerns the additive which increases the fire resistance of the polymer materials, mainly polyurethanes and foam polyurethanes, which are used, for example, in construction materials, means of transport and so on. The additive is not toxic and it has robust fireproof effect.

Prior state of the art

In industrial applications, polyurethanes represent a wide group of polymer materials with various features; they are basis for the paints and coating materials, for flexible foams, for fibers, but also for hard elastomers. Polyurethanes are produced by reactions between isocyanates and polyalcohols. Urethane group —\text{N}—\text{C}—\text{O}—\text{C}— is common for polyurethanes. During the main reaction there can be side reactions, for example, the releasing of the CO2 during the production of the foam polyurethane. This one is often used in the function of the construction of the thermal insulator. The common feature of the unrefined polyurethanes in the common forms is their low resistance to fire. The consumption of the polyurethanes increases by 5% per annum. From the overall volume, approx. 32% is consumed for the insulation of the buildings, 20% for the furniture and mattresses, 14% in car and aviation industry and 10% as coatings. Given the structure of the consumption of the polyurethanes, their fire resistance is highly desired.

Until recently, the fireproof additives, or flame retardants, on the basis of bromine (for example pentabromodiphenyl ether) have been used. Given the high toxicity, these additives are on the decline. The usage of boric acid (\text{HBO}_3, \text{CAS No} 10043-35-3), for example, has been widespread up to the mass fraction of 20%. Boric acid is an inorganic acid, which according to long-term tests can be toxic in high concentrations. Boric acid in itself or in the combination with the magnesium sulphate ensures only imperfect resulting fireproof effect.

According to invention JPS58222146, a use of pentaerythritol and ammonium polyphosphate in order to increase the fire resistance of polyurethane is known. Such combination has relatively weak effect. The solution according to RU2040531 (C1) uses expandable graphite, which in itself is expensive in necessary concentration and
not very effective, and which in high concentration undesirably affects other features of the polyurethane. Similar deficiencies accompany the solution according to DE4234374, DE1 0047024 with the use of melamine.

Other intumescent additives increasing the fire resistance are known. Such additives produce a surface foaming during the burning, whereby this foaming serves as a heat insulation. Usually the intumescent additives are composed of the source of the carbon for the foaming, the acid-producing compound and the compound which produces gases by its decomposition. In case of the polyurethane foam the walls of the individual cells are thin; they contain few materials in the contact layer and therefore the production of intumescence is difficult to realize.

Such solutions are known which use various dangerous substances as retardants, for example according to CN1 02924868 (A), or which use substances which degrade the initial physical and mechanical features of the original material.

A use of ammonium polyphosphate and melamine in the preparations for the improving of the fire resistance is known. Use of such substances in the individual fireproof applications is well-researched. The substances are in the applications used as indissoluble powders. For their use - as well as use with the other substances in polyurethanes - it is desirable to produce multiple additions between them without by-product. The resulting polymer should only contain the substances without any dangerous effects according to all known results and studies. The ingredients entering the process of polymerization should be commercially available with the respective appropriate environmental categorization in the REACH classification.

**Essence of the invention**

The deficiencies in the prior state of the art are significantly remedied by the fireproof additive to polyurethanes for slowing and/or preventing burning according to this invention, which essence lies in the fact that it contains a mixture of saccharose and co-polymer of pentaerythritol, ammonium polyphosphate and melamine in an aqueous solution.

In an additive according to this invention, the organic compound of saccharose (C12H22O11) has fireproof characteristics, but what is also important is an effect of the saccharose on the improvement of the mechanical strength of the polyurethane foam. This allows for other components of the fireproof additive to produce a microintumescent effect on the burned layer of the foam without the mechanical
collapse of the foam. Saccharose is also well soluble in the aqueous solution; it can be used in crystalline form of a classical food sugar or in form of a liquid glucose and fructose. The side-effect of the use of saccharose as an ingredient to polyurethane is an inhibition of the growth of the microorganisms, whereby this effect is achieved by the substance with no health hazard.

Copolymer of pentaerythritol, ammonium polyphosphate and melamine is created in such a way that pentaerythritol is poured into the water with temperature ranging from 15 °C to 25 °C; during continuous mixing the solution is heated up to the temperature of 52 °C to 68 °C; then during intensive mixing we pour ammonium polyphosphate to the solution and the solution is gradually heated to the temperature above 92 °C. After surpassing this temperature the melamine and the solution is heated to the temperature 98 °C to 100 °C.

The ingredients added to the solution can have following ratios (not counting the water):

- ammonium polyphosphate from 5% to 70% of the mass,
- pentaerythritol from 5% to 70% of the mass,
- melamine from 5% to 70% of the mass.

Water creating the environment before polymerization of the ingredients forms - at the beginning of the process - 30% to 90% of the overall solution. After reaching the temperature 98 °C to 100 °C the solution cools.

Saccharose will be added to the aqueous solution with the pre-produced copolymer, preferably before the cooling of the aqueous solution. Saccharose is added in the share of 5% to 70% of the overall mass of all ingredients without water. It is preferable if the saccharose is added after the addition of the ingredient to the polyurethane basis in the liquid form in the mass share ranging from 2% to 19% of the overall mass of the polyurethane mixture before foaming.

The resulting solution can be used in the liquid state or it is adapted by drying to the point where water forms 2,5% to 8% with the subsequent adjusting of the granulometry (or particles size) to the desired shape.

Ammonium polyphosphate \([\text{NH}_4 \text{PO}_4]_n\) is used as a food ingredient, an emulsifier (E545). It is also known to be a flame retardant for polyolefins and polyurethanes.

Pentaerythritol, 2,2-Bis(hydroxymethyl)1,3-propanediol, \(\text{C}_5\text{H}_{12}\text{O}_4\), CAS 115-77-5, is white crystalline powder, tetravalent monotopic alcohol. It is used for the
production of alkyd resins, emulsifiers, explosives, coatings, synthetic lubricating oils. It is considered to be an ecologic alternative to polychlorinated biphenyls (PCB).

Melamine, 2,4,6-triamino-1,3,5-triazine, C_6H_6N_6, CAS 108-78-1, is used mainly during production of plastics and nitrogen fertilizers. Melamine does not dissolve in the water, basically, and in its molecular structure it contains approx. 66% of nitrogen, which is released during burning and which thereby damps the fire. In small amount melamine is not toxic. Melamine is described as harmful in connection with its undesired presence in the food, but the toxic dose in the food is comparable with the table salt; such dose must surpass 3 g to 1 kg of the live weight of an individual. From this point of view the use of melamine according to this invention is basically harmless, because receiving such dose from the treated polyurethane can be ruled out. Even during continuous contact of the treated polyurethane with skin the harmful dose will not be transferred. Melamine prevents the burning process also by releasing CO2 and nitrogen gases during heat. This lowers the amount of oxygen in the boundary layer of the polyurethane to 13%, which stops the process of burning.

In the solution with three substances - ammonium polyphosphate, pentaerythritol, and melamine - a polymerization takes place, which results in the fireproof polymer with especially strong fireproof effect. In such combination the substances potentiate each other and cores of microintumescence are created in the mass of the polymer. With additive according to this invention a phenomenon has been perceived where little cores are created in the mass of the polymer and there is local inner intumescence surrounding them; the intumescence is relative in its size to the small dimensions of the cores, thereby the inventors have named this phenomenon "microintumescence". The fireproof additive prevents the process of burning by releasing CO2 and nitrogen gases around the cores in the mass. Saccharose cooperates with the copolymer; during the contact with the flames it creates a shell, whereby CO2 can be released, too. The shell creates a mechanically resistant structure necessary for the stabilization of the material during burning.

Combination of the abovementioned three active substances in the resulting polymer in the mixture with the saccharose achieves not only strong fire resistance, but thanks to microintumescence the polyurethane has good, almost unchanged mechanical characteristics in the core of the foam even after being exposed to fire.

All required raw materials as well as resulting product are categorized in the REACH evidence as substances without any harmful effects on the man. That means
that a method (or process) of polymerization and combination of safe substances have been found which lead to increased fire resistance at low costs and low energy demands on the process. The invention achieves high fireproof effects and does not use toxic substances.

The fireproof effects of the additive are heightened if such melamine is added to the aqueous solution which does not create copolymer with the other components, but it does increase the amount of nitrogen available for release during burning. The additional melamine can present a mass share of 10% to 60% from the overall mass of the polyurethane mixture before foaming.

The deficiencies in the prior state of the art are significantly remedied by the polyurethane or the mixture for the production of the polyurethane with the basis of the triol and/or polyl according to this invention, which essence lies in the fact that it includes saccharose and copolymer of pentaerythritol, ammonium polyphosphate and melamine. Triol in form of various hydroxyl derivates of hydrocarbons with three hydroxyl groups can form 40% to 80% of the mass of the polyurethane mixture. The mass share of the polyl as alcohol with two or multiple hydroxyl groups can form 6% to 45% of the mass of the polyurethane mixture.

Polyurethane mixture can include triethyl phosphate (TEP, C₆H₁₅O₄P₁) in amount of 1% to 35% of the mass, and stabilizers and a catalyzer on the basis of amines in the amount up to 3% of the mass.

If we want to increase the effects of the additive or decrease the amount of additive for a unit of a treated polyurethane we can in preferable arrangement supply the fireproof additive by a fine amorphous silicon dioxide powder S1O2 with a fraction below 5 μm, preferably below 1 μm. Such fraction of an amorphous powder silicon dioxide has high specific surface, usually 12 000 to 35 000 m²/kg. Such fraction of the ultra-fine silica fume is used for the refinement of the concrete, where it is called microsilica. However, in case of application of the microsilica to the concrete mixtures it is not improvement of the fire resistance which is achieved, but increase of the adhesiveness of the cement to the aggregate; microsilica functions as a core of the starting point of the hydration of the cement.

Microsilica is a mineral substance which originally appeared as a waste in certain metallurgical plants. Silicone dioxide powder is nonflammable and its temperature of melting is approx. 1600 °C.
It is generally known that the crystalline silicon can cause silicosis; however, in the additive according to this invention an amorphous silicone oxide is used, which is not considered harmful.

Fireproof additive with the microsilica according to this invention has unusually large surface of the grains of usually round shape. The additive is capable even in very thin layer to fill in the surface of the cavities and voids in the polyurethane, thereby preventing the access of the oxygen. Physical features of the microsilica - which in case of its application in the concrete mixtures ensure pozzolanic and rheological effect - in our case significantly ensure, after its connection with the surface of the polyurethane, its nonflammability. Silicone dioxide powder can contain crystalline form and alien admixtures pursuant to the method of the production of the microsilica. It can therefore contain calcium oxide, magnesium oxide, aluminum oxide, sodium oxide. The main part of microsilica (more than 50%) will be formed precisely by the amorphous silicone dioxide powder.

This invention ensures high fireproof effects, it uses non-toxic substances and it can be easily applied in the polyurethanes of various kinds.

**Examples of realization**

**Example 1**

In this example the fireproof additive is produced in following way: 1.5 kg of the powder pentaerythritol are mixed to 5 kg of water heated to 20 °C. The solution is continuously mixed and heated to the temperature of 65 °C, when we during intensive mixing slowly pour in 2 kg of the ammonium polyphosphate in the powder form. Then the solution is heated to 94 °C. After surpassing this temperature we mix 1.5 kg of the melamine into the solution and we heat it up to 100 °C. After achieving this temperature in the whole volume of the solution we finish heating and we let the solution cool below 65 °C, when we mix 2 kg of saccharose in the crystalline form into the solution.

Resulting solution is inserted into the polyurethane mixture, which contains triol (commercial name Alcupol R-1610) with mass share 60%, other polyls (TD) with mass share 20%, triethyl phosphate (TEP) in mass share of 15%, stabilizer of the foam (commercial name Struksilon 8006) in mass share 4% and catalyzer on the amine basis (commercial name DMDEE Jeffcat DMDLS) in mass share 1%.
After adding of the additive to the polyurethane mixture the saccharose forms 2% to 19% of the weight of the total mass from which the material is foamed out. In this example it is 10% of the mass share.

Example 2

Powder pentaerythritol is mixed in water with temperature of 25 °C. The liquid is heated to the temperature of 65 °C when the ammonium polyphosphate in the powder form is mixed into it. The liquid is heated to 92 °C and we maintain this temperature for at least 10 minutes. Then we mix in melamine while the monomeric reaction takes places. The liquid is heated to 100 °C; we mix it continuously and we maintain this temperature during normal pressure for at least 5 further minutes, during which a polymerization takes place. The amount of water can be chosen in the range of 30% to 95% of the mass share, based on the amount of the saccharose and additional melamine added later.

In this example saccharose presents 19% of the mass share, the additional melamine 10%, the copolymer of pentaerythritol, ammonium phosphate and melamine 10% of the mass share in the total weight of the polyurethane mixture. Other components forming the basis of the polyurethane mixture can vary.

Example 3

Fireproof additive in this example is supplied by amorphous silicone dioxide powder in the amount of 15% of the mass share.

Industrial applicability

Industrial applicability is obvious. According to this invention it is possible to industrially and repeatably produce and apply the fireproof additive as well as the polyurethane itself, which both lack the toxic components and which have strong fireproof effects. Additive and polyurethane with the additive can be advantageously used in construction, in manufacture of furniture, mattresses, paints and coatings, and sealants and in the automotive and aerospace industries.
PATENT CLAIMS

1. A fireproof additive to polyurethanes for slowing and/or preventing burning, where the polyurethane is based on polyols and/or triols and where the additive is to be added to a liquid mixture before foaming of a polyurethane material is characterized by the fact, that it includes a mixture of saccharose and copolymer with a pentaerythritol, an ammonium polyphosphate and a melamine in an aqueous solution.

2. The fireproof additive according to the claim 1 is characterized by the fact, that it contains an additional melamine.

3. The fireproof additive according to the claim 1 or 2 is characterized by the fact, that it contains a silicone dioxide powder with a fraction below 5 μm, preferably below 1 μm.

4. The fireproof additive according to any of the claims 1 to 3 is characterized by the fact, that it contains the saccharose in a mass share between 2 and 19%.

5. The fireproof additive according to the claim 4 is characterized by the fact, that it contains the melamine in the mass share between 10 and 60%.

6. The fireproof additive according to the claim 4 or 5 is characterized by the fact, that it contains the triol in the mass share between 40 and 80%.

7. The fireproof additive according to any of the claims 4 to 6 is characterized by the fact, that it contains the polyol in the mass share between 6 and 45%.

8. The fireproof additive according to any of the claims 4 to 7 is characterized by the fact, that it contains a triethyl phosphate in the mass share between 1 and 35%.
9. The fireproof additive according to any of the claims 4 to 8 is characterized by the fact, that it contains a stabilizer in an amount up to 3% of the mass share.

10. The fireproof additive according to any of the claims 4 to 6 is characterized by the fact, that it contains a catalyst on a basis of amines in the amount up to 3% of the mass share.

11. A method of production of a fireproof additive for slowing and/or preventing of a burning of a polyurethane foam is characterized by the fact, that:

- a pentaerythritol is added to a water; during continuous mixing a solution is gradually heated to a temperature between 52 and 68 °C,
- subsequently an ammonium polyphosphate is added to the solution during intensive mixing and the solution is gradually heated to the temperature above 92 °C,
- after surpassing this temperature a melamine is added to the solution and the solution is heated to the temperature between 98 and 100 °C, which is maintained for at least 5 minutes during which a polymerization takes place,
- and to the aqueous solution a saccharose is added and it is dissolved in it, preferably before a total cooling of the aqueous solution.

12. The method of the production of the fireproof additive according to the claim 11 is characterized by the fact, that the pentaerythritol is added to the water with temperature between 15 and 50 °C, preferably with temperature between 20 and 25 °C.

13. The method of the production of the fireproof additive according to the claim 11 or 12 is characterized by the fact, that all components added to water have powder and/or crystalline form.

14. The method of the production of the fireproof additive according to any of the claims 11 or 13 is characterized by the fact, that the
ammonium polyphosphate forms 5 to 90% of a mass share of the components added to the water.

15. The method of the production of the fireproof additive according to any of the claims 11 or 14 is characterized by the fact, that the pentaerythritol forms 5 to 90% of a mass share of the components added to the water.

16. The method of the production of the fireproof additive according to any of the claims 11 or 15 is characterized by the fact, that the melamine forms 5 to 90% of a mass share of the components added to the water.

17. The method of the production of the fireproof additive according to any of the claims 11 or 16 is characterized by the fact, that the saccharose forms 5 to 90% of a mass share of the components added to the water.

18. The method of the production of the fireproof additive according to any of the claims 11 or 17 is characterized by the fact, that the water, after the addition of all components, forms 30 to 95% of the mass share of the solution.

19. The method of the production of the fireproof additive according to any of the claims 11 or 18 is characterized by the fact, that after a finishing of the polymerization of the pentaerythritol, ammonium polyphosphate and melamine an additional melamine is added to the aqueous solution, whereby the amount of the additional melamine is at least twice the mass share of the saccharose, preferably four times the mass share of the saccharose.
PATENT CLAIMS

1. A fireproof polyurethane for slowing and/or preventing burning, where the polyurethane is based on polyols and/or triols and isocyanurate and where it also contains pentaerythritol, an ammonium polyphosphate and a melamine, is characterized by the fact, that it includes a mixture of saccharose and copolymer with a pentaerythritol, an ammonium polyphosphate and a melamine in an aqueous solution.

2. The fireproof polyurethane according to the claim 1 is characterized by the fact, that it contains the melamine in the mass share between 10 and 60%.

3. The fireproof polyurethane according to the claim 1 is characterized by the fact, that it contains an additional melamine.

4. The fireproof polyurethane according to any of the claims 1 to 3 is characterized by the fact, that it contains a silicone dioxide powder with a fraction below 5 μm, preferably below 1 μm.

5. The fireproof polyurethane according to any of the claims 1 to 4 is characterized by the fact, that it contains the saccharose in a mass share between 2 and 19%.

6. The fireproof polyurethane according to any of the claims 2 to 5 is characterized by the fact, that it contains the triol in the mass share between 40 and 80%.

7. The fireproof polyurethane according to any of the claims 2 to 6 is characterized by the fact, that it contains the polyol in the mass share between 6 and 45%.

8. The fireproof polyurethane according to any of the claims 2 to 7 is characterized by the fact, that it contains a triethyl phosphate in the mass share between 1 and 35%.
9. The fireproof polyurethane according to any of the claims 2 to 8 is characterized by the fact, that it contains a stabilizer in an amount up to 3% of the mass share.

10. The fireproof polyurethane according to any of the claims 2 to 6 is characterized by the fact, that it contains a catalyzer on a basis of amines in the amount up to 3% of the mass share.

11. A method of production of a fireproof additive for slowing and/or preventing of a burning of a polyurethane foam is characterized by the fact, that:

   a pentaerythritol is added to a water; during continuous mixing a solution is gradually heated to a temperature between 52 and 68 °C,

   subsequently an ammonium polyphosphate is added to the solution during intensive mixing and the solution is gradually heated to the temperature above 92 °C,

   after surpassing this temperature a melamine is added to the solution and the solution is heated to the temperature between 98 and 100 °C, which is maintained for at least 5 minutes during which a polymerization takes place,

   and to the aqueous solution a saccharose is added and it is dissolved in it, preferably before a total cooling of the aqueous solution.

12. The method of the production of the fireproof additive according to the claim 11 is characterized by the fact, that the pentaerythritol is added to the water with temperature between 15 and 50 °C, preferably with temperature between 20 and 25 °C.

13. The method of the production of the fireproof additive according to the claim 11 or 12 is characterized by the fact, that all components added to water have powder and/or crystalline form.

14. The method of the production of the fireproof additive according to any of the claims 11 or 13 is characterized by the fact, that the
ammonium polyphosphate forms 5 to 90% of a mass share of the components added to the water.

15. The method of the production of the fireproof additive according to any of the claims 11 or 14 is characterized by the fact, that the pentaerythritol forms 5 to 90% of a mass share of the components added to the water.

16. The method of the production of the fireproof additive according to any of the claims 11 or 15 is characterized by the fact, that the melamine forms 5 to 90% of a mass share of the components added to the water.

17. The method of the production of the fireproof additive according to any of the claims 11 or 16 is characterized by the fact, that the saccharose forms 5 to 90% of a mass share of the components added to the water.

18. The method of the production of the fireproof additive according to any of the claims 11 or 17 is characterized by the fact, that the water, after the addition of all components, forms 30 to 95% of the mass share of the solution.

19. The method of the production of the fireproof additive according to any of the claims 11 or 18 is characterized by the fact, that after a finishing of the polymerization of the pentaerythritol, ammonium polyphosphate and melamine an additional melamine is added to the aqueous solution, whereby the amount of the additional melamine is at least twice the mass share of the saccharose, preferably four times the mass share of the saccharose.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

INV. C08K3/36  C08K5/00  C08K5/17  C08K5/3492  C08K5/521
ADD. C08K5/1545

According to International Patent Classification (IPC) and both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C08K  C08L

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 , CHEM ABS Data, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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**Date of the actual completion of the international search**

14 July 2016

**Date of mailing of the international search report**

25/07/2016

**Name and mailing address of the ISA**

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016

**Authorized officer**

Schutte, Maya
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<td>US 9 097 Oil Bl (BARONE RICHARD J [US] ET AL) 4 August 2015 (2015-08-04) abstract; claims 1, 3, 9; table 1 column 2, lines 17-19, 30, 34-37 column 3, lines 32-35 column 4, lines 8-9, 50, 57 column 5, line 13 - column 6, line 24 column 7, line 17</td>
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