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(54) **Title:** NEW POLYOL COMPOSITIONS AND USE THEREOF

(57) **Abstract:** The present invention relates to a settlement-stable composition of a modified organoclay in polyols, wherein said composition includes at least one polyol compound; at least one organoclay modified by the intercalation of quaternary ammonium groups and at least one organic phosphate or phosphonate. Said stable composition comprises a weight percentage of modified organoclay of between 0.5% and 10%; a weight percentage of polyol compound or compounds of 30% to 70% and a weight percentage of organic phosphate or phosphonate of between 30% and 70%. The invention also relates to a polyol component for polyurethane foam formulations comprising the stable composition of modified organoclay in polyols and to the polyurethane foams produced.

DESCRIPTION

"NEW POLYOL COMPOSITIONS AND USE THEREOF"

Technical field of the invention

The present invention relates to new polyol compositions and modified organoclays and to the use of said compositions as the polyol component of a polyurethane system. The invention also relates to formulations for rigid and flexible polyurethane foams comprising the new polyol component.

Background of the invention

Polyurethane foam is obtained by reacting a polyisocyanate compound with a polyol compound. A polyol is a compound that comprises several hydroxyl groups in its molecular structure and the most commonly used in formulations of polyurethane foams tend to be polyethers and/or polyesters.

The reaction medium used to produce polyurethane is designed to include: flame retardants, catalysts of the polymerisation reaction between the polyisocyanate compound and the polyol compound (or gelling catalysts), catalysts of the reaction between the polyisocyanate compound and water (or foaming catalysts), silicone surfactants and physical foaming agents (e.g. HFC) and chemical foaming agents (water). All these elements that are present in the reaction medium tend to be mixed together with the polyol compound in which it is known as the polyol component or formulated polyol.

Together, the polyisocyanate component plus the polyol component is known as a polyurethane system.

In order to improve the properties of polyurethane foams, such as their resistance to fire or their mechanical and surface properties, in addition to improving the nucleation effects, additives such as modified organoclays have recently begun to be used, which, if correctly exfoliated in the polyurethane matrix, favour said improvements.

The organoclays used are clays modified by the intercalation of quaternary ammonium groups. They come from clays, i.e. from minerals consisting mainly of hydrated aluminosilicates whose structure includes cations and which are structured in many ways, e.g. in sheets. One example of clay or phyllosilicate is montmorillonite (MMT). In modified MMT, the Na^{+} and Ca^{2+} cations that are situated between the layers of silicate in its original structure have been chemically substituted for quaternary ammonium compounds that enable expansion between the sheet layers of silicate. The state of the art in the use of such materials in polyurethane foams has recently been described by X. Cao (Polymer 46,2005, 775-783) and L. James Lee (Composites Science and Technology 65,2005, 2344-2363).

There are also some patents in the state of the art that disclose compositions adapted for polyurethane foam systems containing organoclays modified by the intercalation of quaternary ammonium groups.

EP 1209189 discloses a rigid polyurethane foam composition, containing up to 10% organoclays modified by the intercalation of quaternary ammonium groups dispersed in a foaming agent selected from the hydrofluorocarbon (HFC), hydrochlorofluorocarbon (HCFC) and hydrocarbon group. To produce the rigid polyurethane foam, the foaming agent is mixed with the polymer composition or its precursors, so that some of the components used to produce the foam contain up to 10% organoclay in relation to the total weight of the polymer. Preferably, the organoclay is dispersed in the foaming agent solution using an ultrasonic bath. It is possible to produce rigid polyurethane foams with a composition of this type; however, it is not suitable for industrial production due to the use of ultrasound and the lack of stability of the mixture with the foaming agent. Furthermore, the mixture with the organoclays is not included in the polyol component.

It can be inferred from WO 2005/082993 that organoclay modified by the intercalation of quaternary ammonium groups is in the isocyanate component and in order to achieve a homogeneous dispersion they must also be subjected to sonication by ultrasound. The organoclay is not stable in the isocyanate component, producing an increase in viscosity during storage. The use of sonication makes its application difficult on an industrial scale.

WO 2006/003421 explains a mixture to form polyurethane foams that consists of the necessary agents to form such foams together with particles of organoclays modified by the intercalation of quaternary ammonium groups and at least one coupling agent of the neoalkoxy titanate or neoalkoxy zirconate type, such as Lica 12. The mixture also comprises a flame retardant agent, such as triethyl phosphate or tris(chloropropyl) phosphate. To produce the final mixture, it must be stirred vigorously by mechanical stirring, assisted by the use of ultrasound. The use of ultrasound makes its application difficult on an industrial scale, in addition to the high cost of these coupling agents.

Another of the documents that mentions the use of modified organoclay in some of the components needed to produce polyurethane foams is the German patent DE 10351268, which claims the use of organoclays modified by the intercalation of quaternary ammonium groups, wherein at least two of such groups are carboxylic, such as Nanofil 784, produced by Süd Chemie. Subsequently, the Nanonfil 784 is modified again by the esterification of these carboxyl groups with diols or polyols. Although this document discloses mixtures for polyurethane, where the polyol component comprising the organoclay is theoretically stable, they can only be produced on a laboratory scale, as Nanofil 784 is not marketed and the complexity of its production and its high cost make it unsuitable for it industrial use, cyclopentane also being used as a foaming agent.

The compositions disclosed in WO 03059817 are intended for producing elastomers, i.e. thermoplastic non-foamed materials, and they are not applicable to rigid foams that must be sprayed. Furthermore, it must be emphasised that the compositions disclosed in this patent present problems of stability, specifically, settling of the modified organoclay and they require a great deal of stirring to be mixed properly.

In all the documents mentioned so far, the basic problem is the settling of the organoclay modified by the intercalation of quaternary ammonium groups, dispersed in one of the components that is used for the reaction that produces polyurethane foams.

To prevent it from settling, as is disclosed in JP 2005-248146, the modified organoclay must be mixed with the polyol component just before performing the reaction with the isocyanate component. This makes the system complex, complicating the preparation of the mixture that must finally react to produce the desired foam.

In the cases where settling does not occur, e.g. as disclosed in DE 10351268, equipment and stages must be used in the production process of these compositions that make its extrapolation to an industrial scale impracticable, e.g. the use of an ultrasonic bath.

The compositions that are the object of the present invention do not present the problems posed by the state of the art because they are stable compositions and they also make it possible to produce polyurethane foams with greatly improved properties.

Explanation of the invention

The compositions of organoclayss modified by the intercalation of quaternary ammonium groups in polyols that are the object of the invention are characterised in that they are surprisingly stable, i.e. they do not present the problems of the state of the art and they are also characterised in that they comprise at least one polyol compound, at least one organoclay or phyllosilicate modified by the intercalation of quaternary ammonium groups and at least one organic phosphate or phosphonate.

The stable composition according to the invention is also characterised in that the weight percentage of the polyol compound or compounds is between 30% and 70%; the weight percentage of modified organoclay is between 0.5% and 10%; and the weight percentage of organic phosphate or phosphonate is between 30% and 70%.

The organoclays modified by the intercalation of quaternary ammonium compounds or groups used are preferably organoclays of the montmorillonite (MMT) type modified by the intercalation of quaternary ammonium groups where the substituents of the nitrogen atom are hydrogenated fat, methyl, methyl and benzyl.

The stable composition according to the invention is characterised in that the polyol compound is independently chosen from a non-alkoxylated polyester, polyether or Mannich base.

According to another characteristic of the settlement-stable compositions that are the object of the invention, the organic phosphate or phosphonate is independently chosen preferably from triethyl phosphate (TEP) and tris(2-butoxyethyl) phosphate (TBEP).

Another object of the present invention is a polyol component for polyurethane foam systems, characterised in that it comprises a stable composition of organoclay in polyols, which is formulated with at least one polyol compound, at least one organoclay or phyllosilicate modified by the intercalation of quaternary ammonium groups and at least one organic phosphate or phosphonate.

Essentially, the polyol component comprises a stable composition of organoclays in polyols that represents a weight percentage, in relation to the total polyol component, of 10% to 70%.

Said stable dispersion of organoclays in polyols, in turn, contains between 30% and 70% by weight of polyol compound or compounds, between

0.5% and 10% by weight of organoclay and between 30% and 70% by weight of organic phosphate or phosphonate.

The organic phosphate in said polyol component is independently chosen from triethyl phosphate (TEP) or tris(2-butoxyethyl) phosphate (TBEP).

According to another characteristic of the polyol component that is the object of the invention, the composition of organoclays in polyols preferably comprises as the organoclay montmorillonite (MMT) modified by the intercalation of quaternary ammonium groups where the substituents of the nitrogen atom are hydrogenated fat, methyl, methyl and benzyl.

Another object of the present invention is a formulation for rigid polyurethane foams, characterised in that it comprises a polyisocyanate component and a polyol component, wherein said polyol component is a stable composition of modified organoclay in polyols, which is formulated with at least one polyol compound, at least one modified organoclay, also referred to as phyllosilicate, modified by the intercalation of quaternary ammonium groups, and at least one organic phosphate or phosphonate.

Essentially, the polyol component of the formulation for rigid polyurethane foams comprises a stable composition of organoclays in polyols that represents a weight percentage, in relation to the total polyol component, of 10% to 70%. Said stable dispersion of organoclays in polyols, in turn, contains between 30% and 70% by weight of polyol compound or compounds, between 0.5% and 10% by weight of organoclay, and between 30% and 70% by weight of organic phosphate.

Preferably, the formulation for rigid polyurethane foams is used for foams that must be applied by spraying.

Another object of the present invention is a formulation for flexible polyurethane foams, characterised in that it comprises a polyisocyanate component and a polyol component, wherein said polyol component is a stable composition of organoclay in polyols, which is formulated with at least one polyol compound, at least one organoclay, also referred to as phyllosilicate, modified by the intercalation of quaternary ammonium groups, and at least one organic phosphate or phosphonate.

Essentially, the polyol component of the formulation for flexible polyurethane foams comprises a stable composition of organoclays in polyols that represents a weight percentage, in relation to the total polyol component, of 10% to 70%. Said stable dispersion of organoclays in polyols, in turn, contains between 30% and 70% by weight of polyol compound or compounds, between 0.5% and 10% by weight of organoclay, and between 30% and 70% by weight of organic phosphate.

Preferably, the formulation for flexible polyurethane foams is used to produce microcellular flexible foams.

The formulation for microcellular flexible foams is for footwear.

Preferably, the formulation for flexible polyurethane foams is applicable to microcellular flexible foams with a density of less than 300 grams/litre.

Brief description of the Figures

Two figures are provided below by way of a non-limiting example: a graph and an image, respectively, which aim to show that the stabilised modified organoclay in a polyol composition according to the invention is suitably exfoliated in polyurethane foams.

Thus, Fig. 1 shows a graph with X-ray diffraction curves for sprayed polyurethane foams produced using formulations comprising a polyol component with a settlement-stable composition of modified organoclay in polyols according to the invention; and

Fig. 2 shows a scanning electronic microscopy (SEM) image at 50 X, achieved using a voltage of 15 V, which aims to show that stable compositions with modified organoclays present a smaller cell size.

Detailed description of the invention.

Detailed description of stable dispersions (compositions of organoclays in polyols)

Three examples of stable dispersions and their properties are presented below to exemplify the stability of the compositions of organoclays modified by the intercalation of quaternary ammonium groups in polyols that are the object of the invention, which comprise at least one polyol compound such as polyol polyester, at least one type of modified organoclay and at least one organic phosphate or phosphonate.

The raw materials used for Examples 1 to 3 are listed below:

Polyester 1: Hoopol F-1398 polyester, produced by Synthesia Española S.A., with an IOH (hydroxyl index) of 230-250 mg KOH/g and a viscosity of 200 cps at 60° C.

Polyester 2: Hoopol FR-441 polyester, produced by Synthesia Española S.A., with an IOH of 75-80 mg KOH/g and a viscosity of 1000 cps at 60° C.

Nanofil 2 and Nanofil 32: organoclays modified by the intercalation of quaternary ammonium groups, produced by Süd Chemie. These are organoclays of the modified montmorillonite type in which the sodium and calcium atoms have been replaced by quaternary ammonium groups or compounds where the substituents of the nitrogen atom are hydrogenated fat, methyl, methyl and benzyl.

Example 1

562.5 g of triethyl phosphate and 62.5 g of Nanofil 2 were mixed in a 2-litre spherical reactor. The mixture was heated, stirring at 500 RPM at 90° C. It was then kept at 90° C for 1 hour, subsequently adding 375 grams of the Hoopol F 1398 polyol polyester (polyester 1), simultaneously cooling it to reach a temperature of 30° C.

The dispersion of modified organoclay in polyol achieved had a hydroxyl index (IOH) of 90 mg KOH/g and a viscosity of 300 cps at 25° C. The dispersion is stable at 3000 RPM for half an hour, with no settling.

Example 2

320 g of triethyl phosphate, 80 g of Nanofil 32 and 300 grams of Hoopol F 1398 (polyester 1) were mixed in a 2-litre spherical reactor. It was heated, stirring at 500 RPM at 90° C. It was then kept at 90° C for 1 hour, subsequently adding 300 grams of the Hoopol F 1398 polyol polyester, simultaneously cooling it to reach a temperature of 30° C.

The dispersion achieved had an IOH of 144 mg KOH/g and a viscosity of 500 cps at 25° C. The dispersion is stable at 3000 RPM for half an hour, without any settling at all.

Example 3

84.3 g of tris(2-butoxyethyl) phosphate and 9.37 g of Nanofil 2 were mixed in a 2-litre spherical reactor. The mixture was heated, stirring at 500 RPM at 90° C. It was then kept at 90° C for 1 hour, subsequently adding 56.25 g of the Hoopol FR441 polyol polyester (polyester 2), simultaneously cooling it to reach a temperature of 30° C.

The dispersion achieved had an IOH of 30 mg KOH/g and a viscosity of 640 cps at 25° C. The dispersion is stable at 3000 RPM for half an hour, without any settling at all.

The compositions in Examples 1 to 3 produced polyol components for polyurethane foam systems that were used in formulations for rigid foams and for flexible foams. Said polyol component is commonly referred to as a charge-stabilised polyol component, meaning by charge the dispersions of modified organoclays included therein.

These polyol components in the examples comprised, in addition to the above-described dispersions of organoclay modified by the intercalation of quaternary ammonium groups in polyols, compounds already known by persons skilled in the art, such as polyethers, compounds with flame retardant properties; surfactants; foaming and gelling catalysts, foaming agents, etc.

The organoclays that can preferably be used in the settlement-stable compositions of modified organoclay in polyols are those that have particle sizes of 8 to 35 microns and that, as has been previously mentioned, have been produced by chemical modification or the intercalation of quaternary ammonium groups that substitute the original sodium ions of the montmorillonite.

For example, modified organoclays produced by the company Süd Chemie can be used, such as: Nanofil 2, Nanofil 5, Nanofil 8, Nanofil 9, Nanofil 15, Nanofil 32, Nanofil 106, Nanofil 919, Nanofil 948, Nanofil SE3000 or Nanofil SE3010.

It is also possible to use modified nanoclays such as those produced by the company Southern Clay, with intercalated groups of a similar nature such as: Cloisita 10A, Cloisita 11B, Cloisita 15A, Cloisita 20A, Cloisita 25A, Cloisita 30B and Cloisita 93A.

Those that have undergone a sodium ion exchange for a quaternary ammonium group are considered most suitable, where the substituents of the nitrogen atom are: hydrogenated fat, methyl, methyl and benzyl. Nanofil 2, Nanofil 32 (which differ from Nanofil 32 in terms of their particle size), Cloisita 10A and Cloisita 11B have these characteristics. More preferably, Nanofil 2 is chosen.

The polyol compound or compounds of the stable compositions of organoclay in polyols can be of the polyether type or polyester type.

Those of the polyether type are addition products of propylene oxide or ethylene oxide, or mixtures of both, catalysed in a base medium, on a polyhydroxylated compound that acts as a primer. The molecular weight of the polyethers used in the present invention is between 250 and 12000, and they are prepared by alkoxylation following methods that are widely referred to and described in specialist literature. It is also possible to use non-alkoxylated polyols known as Mannich bases.

The polyesters can be all the products resulting from the reaction between a polycarboxylic acid, or a mixture of them, and polyhydroxylated compounds, preferably using dicarboxylic acids and glycols (dihydroxylated compounds), although it is possible to add different proportions of tri- or tetrafunctional components to achieve a functionality of more than two, which is advisable for certain applications. It is also possible to use polyesters based on recycled PET and polyols based on vegetable oils. The molecular weight of the polyesters used in the present invention is between 400 and 5000, and they are prepared by a fusion procedure or by any other methods that are widely referred to and described in specialist literature.

These polyols (polyethers and polyesters) are described in "The Huntsman Polyurethanes Book", published by D. Randall and S. Lee, pages: 89-112, John Wiley (2002).

According to another characteristic of the stable composition of organoclays in polyols that is the object of the invention, the organic phosphate or phosphonate is of the type used in fire retardants for rigid polyurethane foams, such as triethyl phosphate (TEP), dimethyl-propyl-phosphonate (DMPP), dihydroxyethyl-methyl-amino-diethyl-phosphonate, *TCPP*. Likewise, chlorine-free materials such as cresyl diphenyl phosphate and tris(2-butoxyethyl) phosphate (TBEP) are suitable phosphate or phosphonate materials, which can be successfully used in flexible foams for footwear. Triethyl phosphate (TEP) is preferred for rigid foams and tris(2-butoxyethyl) phosphate (TBEP) is preferred for flexible foams.

Detailed description of formulations for polyurethane foams made with stable dispersions from examples 1 to 3.

<u>Example 4</u>

Formulation and properties of a flexible microcellular foam made with the dispersion of example 3.

Raw materials used:

Polyester 1: Hoopol F2441 polyester, produced by Synthesia Española S.A., with an IOH of 75-80 and a viscosity at 60° C of 900 cps.

Polyester 2: Hoopol F110-1000 polyester, produced by Synthesia Española S.A., with an IOH of 56 and a viscosity at 60° C of 1100 cps.

Prepolymer 1: 4,4' MDI (methylene diphenyl diisocyanate) prepolymer modified with polyester with a functionality of more than 2 and NCO content = 22.2 – 23.3, such as P-822 isocyanate produced by Synthesia Española S.A.

Table 1 lists the components of a formulation for a microcellular flexible foam identified as (1).Table 1

Components	1
Polyester 1	45
Polyester 2	25
Example 3	20
Ethylene glycol	18
Catalyst	1
Silicone surfactants	1.2
Triethanolamine	0.4
Water	0.7
Prepolymer (NC0 22.2-23.2)	Prepolymer 1
Index	98-100
Free foam density (g/l)	150
Density of the moulded piece (g/l)	300
Asker C hardness	56
Elongation %	340
Demoulding	3 min

The data in table 1 show Asker hardness results for microcellular foam that are higher than those that would be achieved without the addition of a stable modified organoclay composition in soles of an equivalent density.

Important advantages have also been observed in demoulding with conventional mould release agents, and in the appearance, skin and stability of the moulded piece. It is important to point out that a formulation of this type cannot be made and collapses without the composition described in example 3, which is the object of this invention.

Example 5:

Formulation and properties of a sprayed rigid foam made with the dispersions (stable compositions of modified organoclay in polyols) of Example 1 or Example 2.

Table 2 lists the compounds that make up several polyol components (1) and (2), which are adapted to react with a respective compound with isocyanate groups in order to produce a rigid polyurethane foam that is adapted to be applied by spraying.

In said Table 2, the formulated polyol component 1 contains the composition described in example 1. The formulated polyol 2 contains the composition described in example 2. Furthermore, both formulated polyols contain a Mannich base type polyol with a hydroxyl index of 490 mg KOH/g (Synthanol MT-480, a commercial product by Synthesia Española), a PET (polyethylene terephthalate) initiated aromatic polyester with a hydroxyl index of 240 mg KOH/g (Hoopol F-1394, a commercial product by Synthesia Española), a glycerine initiated propoxylated polyether with a hydroxyl index of 380 (e.g. Voranol CP-450 produced by The Dow Chemical Company), a flame retardant (e.g. tris(2-chloropropyl) phosphate, TCPP), glycerine, a standard silicone surfactant to stabilise rigid polyurethane foam (e.g. Tegostab B-8453, produced by Degussa), foaming catalysts (aromatic or aliphatic tertiary amines: pentamethyl diethylene triamine (PMDTA), dimethyl cyclohexylamine (DMCHA) and dimethyl benzylamine (DMBA)), a gelling catalyst (tin dibutyldilaureate), a hydrofluorocarbon (365mfc/227ea) and water.

Table 2

Components		1	2	Standard
Example 1		28.5	-	-
Example 2		-	40.0	-
Synthanol MT-480		14.5	13.2	20.0
Hoopol F-1394		29.1	6.0	34.7
Propoxylated polyether		10.0	14.7	11.0
Glycerine		0.8	1.0	-
Flame retardant		-	8.0	15.9
Silicone surfactant		1.0	1.0	1.0
Catalysts		2.6	2.6	3.9
Water		2.5	2.5	2.5
365mfc/227ea		11.0	11.0	11.0
Viscosity at 23° C (mPa·s)*		350	480	410
Creaming time (sec)*		1.9	2.1	2.3
Gelling time (sec)*		5.1	6.1	7.6
Free foam density (Kg/m3)*		30.5	30.2	29.7
Appearance of foam		OK	OK	OK
Applied density (Kg/m^3)*		41.0	38.0	36.4
Dimensional stability (%vol.)*	-20°C	-0.7	-0.5	-1.0
	80°C	-7.0	-4.0	-9.0
Resistance to	Perp.	185	257	195

Components		1	2	Standard
compression (Kpa)*	Paral.	145	135	110
Initial heat conductivity (mW/m.K)*		21.7	21.3	21.0
Reaction to fire (Euroclass)*		E	E	E
Flame height (cm)		10	8	13

*Parameters calculated in accordance with the UNE 92120-1:1998 guideline and its amendment UNE 92120-1:1998/1M:2003.

As can be inferred from Example 5 (Table 2, components 1 and 2), the new stable compositions of organoclays in polyols that do not settle, preferably using commercially available modified montmorillonite, such as Nanofil 2 and Nanofil 32 produced by Süd Chemie, make it possible to produce formulations of rigid polyurethane foams that comply with the Spanish regulations in terms of parameters such as reaction to fire (UNE-EN ISO 13501-1, EUROCLASS E), or with lower flame heights than in the state of the art (EN-ISO 11925-2), as can be seen in table 2. Furthermore, the properties and appearance of the foam produced are better, presenting a greater dimensional stability and resistance to compression than the same formula without a dispersion of organoclay.

As can be seen in Fig. 1, the X-ray diffraction curves (WAXD) achieved with a Siemens D_500 X-ray diffractometer, mean that it can be assumed that the modified organoclay type charge has been properly exfoliated in the foam matrix. Therefore, the absence of diffraction peaks in curves (b) (0.9 % of modified organoclay in the foam) and (c) (1.6 % of modified organoclay in the foam) is an indication of the exfoliation of the charge (organoclay) compared to the pure modified organoclay described by curve (a).

As can be seen in Fig. 2, which shows an image achieved by scanning electronic microscopy (SEM) at 50 X, rigid foams applied by spraying that comprise a polyol component with compositions that include dispersions or compositions of modified organoclays in polyols, present a finer cell structure than those made without said dispersions. This proves the significant nucleation effect of such stable dispersions, which bring about a reduction in the cell size.

The advantage of introducing the stable compositions of organoclay modified by the intercalation of quaternary ammonium groups in polyols, such as those described in Example 5 (Table 2, components 1 and 2), in rigid polyurethane foams applied by spraying can therefore be summarised as: good resistance to fire, better mechanical properties (resistance to compression), better dimensional stability, reduction of flame height, reduction of smoke generation, reduction of cell size, evidence of exfoliation of the charge in the foam matrix.

CLAIMS

1.- Settlement-stable composition of a modified organoclay in polyols, which comprises at least one polyol compound; at least one organoclay modified by the intercalation of quaternary ammonium groups and at least one organic phosphate or phosphonate.

2.- Stable composition according to claim 1, characterised in that the weight percentage of the polyol compound or compounds is between 30% and 70%; the weight percentage of organoclay modified by the intercalation of quaternary ammonium groups is between 0.5% and 10%; and the weight percentage of organic phosphate or phosphonate is between 30% and 70%.

3.- Stable composition according to claim 1 or 2, characterised in that the organoclay is montmorillonite (MMT) modified by the intercalation of quaternary ammonium groups where the substituents of the nitrogen atom are hydrogenated fat, methyl, methyl and benzyl.

4.- Stable composition according to claim 1 or 2, characterised in that the polyol compound is independently chosen from a non-alkoxylated polyester, polyether or Mannich base.

5.- Stable composition according to claim 1 or 2, wherein the organic phosphate is triethyl phosphate.

6.- Stable composition according to claim 1 or 2, wherein the organic phosphate is tris(2-butoxyethyl) phosphate.

7.- Polyol component for polyurethane foam systems, characterised in that it comprises a stable composition of a modified organoclay in polyols according to any of claims 1 to 6 above.

8.- Polyol component for polyurethane foam systems according to claim 7, characterised in that it comprises a stable composition of organoclay modified by the intercalation of quaternary ammonium groups in polyols according to any of claims 1 to 6 above in a weight percentage of 10% to 70% in relation to the total of the polyol component.

9.- Formulation for rigid polyurethane foams, characterised in that it comprises a polyisocyanate component and a polyol component, wherein said polyol component consists of the component according to any of claims 7 to 8 above.

10.- The formulation for rigid polyurethane foams according to claim 9, characterised in that it can be applied by spraying.

11.- Formulation for flexible polyurethane foams, characterised in that it comprises a polyisocyanate component and a polyol component, wherein said polyol component consists of the component according to any of claims 7 to 8 above.

12.- The formulation for flexible foams according to claim 11, characterised in that it is applicable to microcellular flexible foams.

13.- The formulation for flexible foams according to claim 12, characterised in that it is applicable to microcellular flexible foams for footwear.

14.- The formulation for flexible foams according to claim 13, characterised in that it is applicable to microcellular flexible foams with a density of less than 300 grams/litre.

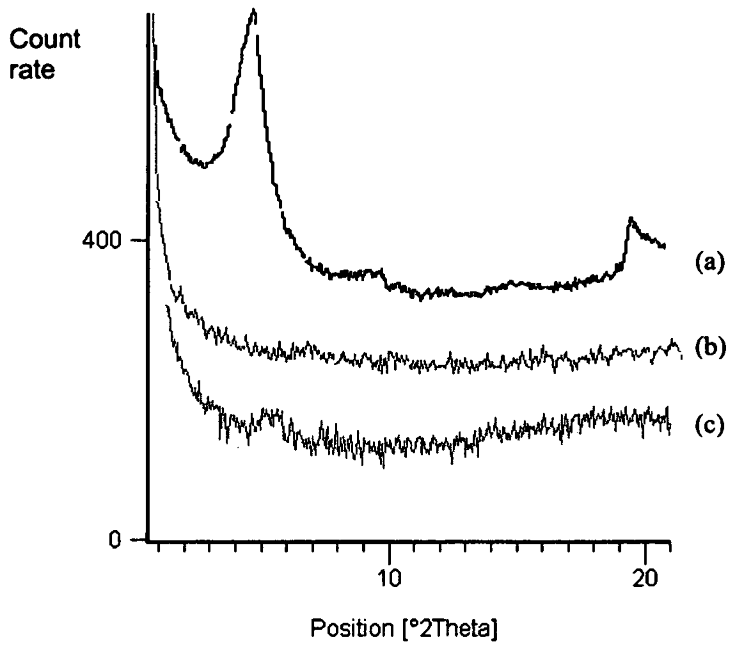
Count rate
400
0
10
20
Position [°2Theta]
(a)
(b)
(c)

Fig. 1

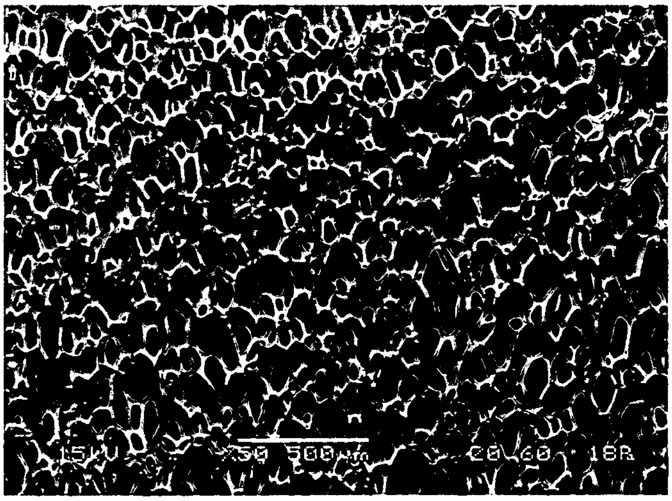
15kU X50 500µm 20 60 18R

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2007/002492

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08K3/34 C08K5/521 C08K9/04
ADD. C08G101/00

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)
C08K C08G

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 practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	WO 2006/060174 A (HONEYWELL INT INC [US]; BIBB CAROLINE [US]; ZHU ZHEN [US]; WILLIAMS DA) 8 June 2006 (2006-06-08) paragraphs [0006], [0029], [0032] - [0034]; claims 6-8	1,2,7-9, 11
X	EP 0 361 764 A (ICI PLC [GB]) 4 April 1990 (1990-04-04) page 3, line 23 - page 4, line 14	1,3,4,7, 9,11
Y	example 5	2,5,6,8

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[X] Further documents are listed in the continuation of Box C.

[X] 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

"E" earlier document but published on or after the international filing date

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"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 June 2007	04/07/2007

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Krätzschmar, Ulrike

Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 2006/003421 A (UNIV STRATHCLYDE [GB]; LIGGAT JOHN [GB]; PETHRICK RICHARD A [GB]; RHON) 12 January 2006 (2006-01-12) cited in the application page 7, line 24 - page 11, line 14 page 17, lines 7-24 page 28, line 23 - page 29, line 19; examples 93-95	1,3,4,7, 11
Y	claims 1-15,60	2,5,6,8
A	CAO X ET AL: "Polyurethane/clay nanocomposites foams: processing, structure and properties" POLYMER, ELSEVIER SCIENCE PUBLISHERS B.V, GB, vol. 46, no. 3, 26 January 2005 (2005-01-26), pages 775-783, XP004705996 ISSN: 0032-3861 cited in the application the whole document	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2007/002492

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