

NONIONIC ASSOCIATIVE THICKENERS CONTAINING CYCLOHEXYLOL ALKYLS, FORMULATIONS CONTAINING SAME AND USES THEREOF

5 The present invention concerns new associative thickeners belonging to the HEUR (Hydrophobically modified Ethylene oxide URethane) category. Used in aqueous formulations, they increase viscosity at low, medium and high shear gradient. Such a result derives in particular from the use of original groups based on alkyl cyclohexylols to manufacture the associative monomer of these thickeners.

10 Aqueous paint formulations containing mineral fillers consist of an aqueous phase, of one or more polymers in emulsion in the liquid phase referred to as binders, fillers and/or pigments, a dispersant and admixtures as diverse as surfactants, coalescent agents, biocides, and anti-foaming agents, and, finally, at least one thickening agent.

15 The latter allows a control of the rheology of aqueous formulations in which it is introduced, and in particular in aqueous paints, both at the manufacturing stage as well as during their transport, storage or in the course of their implementation. The diversity of practical constraints at the level of each of these steps reflects a multiplicity of different rheological behaviours.

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One can nevertheless summarize the need of the person skilled in the art to obtain a thickening effect in the aqueous formulation, both for reasons of stability over time as well as for a possible application of paint to a vertical surface, the absence of coating splash at the time of implementation, etc. This is why the additives which contribute to
25 this control of rheological behaviour are known as thickeners.

Among these products, there are the so-called "associative" thickeners which are water-soluble polymers with insoluble hydrophobic groups. Such macro-molecules have an associative characteristic: once introduced into water, the hydrophobic groups are
30 susceptible to association in the form of micellar aggregates. These aggregates are linked to one another by the hydrophilic parts of the polymers: there is then the formation of a three-dimensional network that causes the increase in the viscosity of the medium.

The operating mechanism and characteristics of associative thickeners are well known today and are described for example in the documents "Rheology modifiers for water-borne paints" (Surface Coatings Australia, 1985, pp. 6-10) and "Rheological modifiers
5 for water-based paints: the most flexible tools for your formulations" (Eurocoat 97, UATCM, vol. 1, pp 423-442).

Among these associative thickeners, there is the class of associative thickeners of the HEUR (Hydrophobically modified Ethylene oxide URethane) type. They designate
10 copolymers resulting from the synthesis between a compound of the polyalkylene glycol type, a polyisocyanate and a monomer or condensate called "associative" of the alkyl, aryl or aralkyl type consisting of a hydrophobic terminal group.

These structures are well known for developing high viscosities, for an average to low
15 shear gradient (j. of Applied Polymer Science, vol. 58, p 209-230, 1995 ; Polymeric Mat. Sci. and Engineering, vol. 59, p 1033, 1988; Polymeric Mat. Sci. and Engineering, vol. 61, p 533, 1989; Polymeric Paint Colour Journal, vol. 176, No. 4169, p 459, June 1986), which corresponds respectively to Stormer™ (KU) and Brookfield™ (mPa.s) measurements of viscosity.

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Beyond a simple increase in viscosity for the reasons already mentioned, the paint formulator sometimes expresses the need for a more complex rheology, a true compromise between application properties and the behaviour of the product in the can. On the one hand, one can seek to increase the ICI™ viscosity of the paint formulation:
25 this has the effect of improving the application properties of the product by limiting spatter (especially if the product is applied with a roller), sagging (if it is an application to walls or ceilings), and by an increase in the amount transferred from the application tool to the medium. On the other hand, an attempt will be made to optimize the tactile sensation of the paint when it is stirred or handled by increasing the medium shear rate
30 viscosity, the so-called Stormer™ viscosity. Finally, an attempt is made to concurrently increase the Brookfield™ viscosity: such a phenomenon ensures a satisfactory appearance and stability of the product in the can as well as a good loading of the application tool.

To resolve this triple technical problem, the person skilled in the art today has a very broad library of structures that differ essentially in the choice of the hydrophobic monomer.

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Document EP 1 566 393 describes a HEUR type thickener, one of the essential characteristic of which is the presence of n-butyl-1-octanol, while its hydrophobic groups are based on fatty alcohols with 8 to 18 carbon atoms.

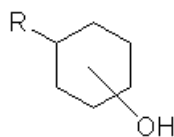
10 Document DE 10 206 023001 describes an associative non-ionic thickening agent of the HEUR type including a branched linear alcohol. Document EP 1 241 198 describes polyurethane-based thickening agents including a monoalcohol having 6 to 22 carbon atoms.

15 Document EP 1 013 264 describes a polyurethane thickener for cosmetic formulations with an associative monomer functionalized by a hydrophobic group that can be linear or branched, but preferentially linear and possessing 12 to 24 carbon atoms. Document WO 94/06840 proposes an associative thickener of the HEUR type characterized by a certain density of hydrophobic pendant groups by a urethane linkage, the said groups
20 being linear alkyl chains with 8 to 22 carbon atoms. Document EP 1 584 331 proposes a hydrophobic terminal group with 6 to 34 carbon atoms for the associative monomer. To specifically increase the Brookfield™ viscosity, document EP 0 639 595 proposes linear hydrophobic groups having 4 to 36 carbon atoms. Document WO 02/102868 also makes reference to linear structures for the associative monomer.

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However, none of the structures of the HEUR type of the prior art, classically based on associative monomers with linear alkyl groups, allow the simultaneous and sufficient increase in the ICI™, Stormer™ and Brookfield™ viscosities of the paint formulations in which they are used. Continuing her research in this regard, the Applicant found quite
30 surprisingly that the use of certain structures instead of the hydrophobic monomer resulted in an increase of these 3 viscosities for a number of carbon atoms that was identical or close to the linear alkyl structures of the prior art.

This technological advance is based on the use, as a hydrophobic monomer, of a compound whose structure corresponds to formula (I):

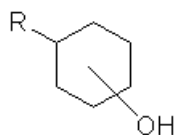


(I)

- 5 where R designates an alkyl group with 10 to 15 carbon atoms. Such compounds have been identified as surfactants and are obtained by hydrogenation of an alkyl phenol. In particular, reference can be made to document US 6 111 146 which describes their synthesis. The resulting compounds are referred by the expression "alkyl cyclohexylols". It is important to add that the final structure is not that of an alkyl
10 phenol, and that the resulting product will not be categorized as such.

These structures are therefore used to manufacture water-soluble polyurethanes resulting from the condensation:

- 15 a) of at least one monomer with the formula (I)



(I)

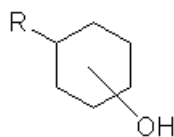
where R designates an alkyl group with 6 to 10 carbon atoms, preferentially 9 carbon atoms,

- 20 b) of at least one polyalkylene glycol, and
c) of at least one polyisocyanate.

It is these new polyurethanes that, for example, allow a thickening of a low, medium and high shear gradient paint formulation, this increase being measured against the
25 values obtained with linear alkyl structures of the prior art with a very similar number of carbon atoms.

Also, a first object of the present invention consists of water-soluble polyurethanes resulting from the condensation:

- a) of at least one monomer with the formula (I)



(I)

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where R designates an alkyl group with 6 to 10 carbon atoms, preferentially 9 carbon atoms,

- b) of at least one polyalkylene glycol
c) and, of at least one polyisocyanate.

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"Polyurethane" is understood to mean a urethane polymer, i.e. a compound produced by the reaction between an isocyanate and an alcohol.

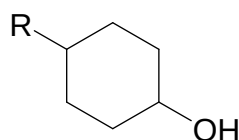
15 According to the invention, the term "alkyl" designates a linear or branched hydrocarbon radical with 6 to 10 carbon atoms, such as hexyl, heptyl, octyl, nonyl, decyl.

"Polyalkylene glycol" is understood to mean a polymer of an alkylene glycol derived from an olefinic oxide. The polyalkylene glycol according to the present invention is, for example, polyethylene glycol, polypropylene glycol, polybutylene glycol or a polyalkylene glycol containing a proportion of an ethylene-oxy group and/or a proportion of a propylene-oxy group and/or a proportion of a butylene-oxy group. The polyalkylene glycol according to the present invention can, for example, include a dominant proportion of an ethylene-oxy group in association with a secondary proportion of a propylene-oxy group. Specific examples of alkylene glycol polymers include: polyalkylene glycols having an average molecular weight of 1,000, 4,000, 6,000, 10,000 and 20,000 g/mol (in the case of polyethylene glycol called PEG-1000, PEG-4000, PEG-6000, PEG 10000 and PEG 20000); polyethylene polypropylene glycols having a percentage of ethylene oxide of between 20 and 80% by weight and a percentage of propylene oxide of between 20 and 80% by weight.

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"Polyisocyanate" is understood to mean a compound which includes at least 2 functional isocyanate groups -N=C=O .

According to one aspect of the present invention, the monomer of formula (I) has the following formula (II):



(II)

where R designates an alkyl group as defined above, i.e. having 6 to 10 carbon atoms.

According to another aspect of the present invention, monomer a) has a formula (I) or (II) where R designates a group having 9 carbon atoms.

The Applicant states that the manufacture of these polyurethanes, which belong to the HEUR type family of thickeners, is perfectly known to the person skilled in the art who can refer to the instructions of the documents cited previously in the technological background to the present invention.

According to one aspect of the present invention, the polyurethanes resulting from the condensation of:

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- a) 1% to 29% by weight of at least one monomer with the formula (I) or (II), and preferably 3% to 7% by weight,
- b) 70% to 98% by weight of at least one polyalkylene glycol, and preferably 86% to 94% by weight, and
- 25 c) 1% to 29% by weight of at least one polyisocyanate, and preferably 3% to 7% by weight,

where the sum of these mass percentages is equal to 100%.

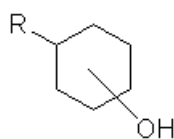
According to another aspect of the present invention, the polyurethanes result from the condensation of two monofunctional alcohols, a polyalkylene glycol and a polyisocyanate. In this case, one of two monofunctional alcohols has a formula (I) or

(II) where R designates an alkyl group having 6 to 10 carbon atoms, and preferably 9 carbon atoms, and the other monofunctional alcohol is of the aliphatic alcohol type, whether linear or branched, having between 6 et 20 carbon atoms, and preferably between 10 and 15 carbon atoms.

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According to yet another aspect of the present invention, the polyurethanes result from the condensation of:

a) 1 to 29% by weight of a monomer of formula (I) :



10

(I)

where R designates an alkyl group having between 6 and 10 carbon atoms, and preferably between 9 carbon atoms,

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b) 70% to 98% by weight of a polyalkylene glycol,

c) 1% to 29% by weight of a polyisocyanate, and

d) 1 to 29% by weight of an aliphatic alcohol having between 6 and 20 carbon atoms, and preferably between 10 and 15 carbon atoms,

where the sum of these mass percentages is equal to 100%.

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According to one aspect of the present invention, the polyurethanes result from the condensation notably of a polyalkylene glycol which is polyethylene glycol. This may relate, for example, to a polyethylene glycol the molecular mass of which varies between 2,000 g/mol and 20,000 g/mol, for example between 8,000 g/mol and 15,000 g/mol. As an example, polyethylene glycol of molecular mass 10,000 g/mol and 12,000 g/mol may be cited.

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According to another aspect of the present invention, the polyurethanes result from the condensation notably of a polyisocyanate which is chosen from the group consisting of toluene diisocyanate, the toluene diisocyanate dimers and the toluene diisocyanate trimers, 1,4-butane diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate, 1,3-

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cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, 4,4'-diisocyanatodicyclohexylmethane, 1-methyl-2,4-diisocyanatocyclohexane, a blend of 1-methyl-2,4-diisocyanatocyclohexane and 1-methyl-2,6-diisocyanatocyclohexane, the biuret of hexamethylene diisocyanate, the dimers of biuret of hexamethylene diisocyanate, the trimers of biuret of hexamethylene diisocyanate and a blend of at least two of these compounds.

A second object of the present invention relates to a method of preparing a polyurethane according to the invention, where the said method consists of a condensation of the various constituents of the polyurethane.

A third object of the present invention consists of an aqueous composition including a polyurethane according to the present invention.

According to one aspect of the invention, the said aqueous composition also includes water and at least one non-ionic surfactant. Thus, according to this aspect of the invention, the polyurethane is formulated in water in the presence of at least one non-ionic surfactant agent.

A "non-ionic surfactant" or "non-ionic surfactant agent" is understood to mean a non-ionic molecule consisting of at least a hydrophilic part and of at least a hydrophobic part.

According to one embodiment of the present invention, the said composition includes several surfactant agents, for example two, three or four.

According to another aspect of the present invention, the said aqueous composition also includes at least one additive selected from among the group consisting of a biocide, a solvent, an anti-foaming agent, a pH regulator, a coalescent agent and their blends.

A "biocide" is understood to mean a chemical substance intended to destroy, repel or make harmless harmful organisms, to prevent their action, or to oppose them in any other manner, through a chemical or biological action.

An "anti-foaming agent" is understood to mean a substance or a formulation intended to destroy air bubbles within a homogenous or heterogeneous liquid medium (or at its surface), or to prevent their formation.

- 5 A "pH regulator" or "pH regulating agent" is understood to mean a chemical compound which enables the pH to be adjusted to the expected value. For example, the pH regulating agent can increase the pH; this is the case with bases, such as NaOH. Alternatively, the pH regulating agent can reduce the pH ; this is the case with acids.
- 10 A "coalescent agent" is understood to mean an agent used in paints which enables the Minimum Film Formation Temperature (MFFT) of paint to be reduced to a temperature suitable for the desired conditions of application (for example a MFFT of 5°C for outside application). As an example of a coalescent agent according to the invention, propylene glycol, butyl glycol, 2,2,4-trimethyl-1,3-pentanediol monoisobutyrate or
- 15 2,2,4-trimethyl-1,3-pentanediol diisobutyrate may be cited.

According to yet another aspect, the aqueous composition of the present invention consists of:

- 20 1) 5% to 45% by weight of at least one polyurethane according to the invention, and preferably between 10 and 30% by weight,
- 2) 5% to 30% by weight of at least one surfactant, and preferably between 7 and 20% by weight,
- 3) 25% to 75% by weight of water, and
- 4) 0 to 5% by weight of at least one other additive chosen from the group
- 25 consisting of a biocide, a solvent, an anti-foaming agent, a pH regulator, a coalescent agent, and their blends,
- where the sum of these mass percentages is equal to 100%.

30 According to yet another aspect, the aqueous composition of the present invention consists of a polyurethane as described above, a surfactant, water, a biocide and an anti-foaming agent.

According to another aspect of the invention, the aqueous composition consists of a blend of 5 to 45% by weight of at least one polyurethane as described above, 5 to 30%

by weight of at least one surfactant, 25 to 75% by weight of water, 0.01 to 5% by weight of at least one biocide and 0.01 to 5% by weight of at least one anti-foaming agent.

- 5 A fourth object of the present invention relates to a method of preparation of an aqueous composition according to the invention, where the said method consists of blending different constituents of the aqueous composition.

10 A fifth object of the present invention consists of the use of a polyurethane according to the invention or an aqueous composition according to the invention to thicken an aqueous formulation, where the said formulation is selected from the group consisting of a paint, a lacquer, a varnish, a paper coating, a cosmetic formulation and a detergent formulation.

15 A sixth object of the present invention relates to an aqueous formulation including a polyurethane according to the invention or an aqueous composition according to the invention, where the said formulation is selected from the group consisting of a paint, a lacquer, a varnish, a paper coating, a cosmetic formulation and a detergent formulation.

20 According to one aspect of this object of the invention, the aqueous formulation is a paint and includes at least one dispersing agent, at least one mineral filler, at least one binder, at least one biocide, at least one anti-foaming agent, and possibly a coalescent agent.

25 A final object of the present invention relates to a method of preparation of an aqueous formulation according to the invention, where the said method consists of blending different constituents of the aqueous formulation.

30 The following examples allow a better understanding of the invention without however limiting its scope.

EXAMPLES

Example 1

- 5 This example describes a polyurethane according to the invention that uses a compound of formula (II) where R designates the linear alkyl group with 9 carbon atoms. Thus, we have here a hydrophobic monomer with the formula (II) with 15 carbon atoms.

At the same time, this example also illustrates 4 polyurethanes according to the prior art
10 that use linear fatty alcohols with 12, 14, 16 and 18 carbon atoms.

This example describes a polyurethane apart from the invention that uses a compound of formula (II) where R designates the linear alkyl group with 12 carbon atoms. Thus, we have here a hydrophobic monomer with the formula (II) with 18 carbon atoms.

15 All the polyurethanes are products that are the result of the condensation, expressed in % by weight of each of the constituents, of 90% polyethylene glycol with a molecular mass by weight equal to 10,000 g/mol, of 5% of a monomer terminated by a hydrophobic group, the nature of which will be specified later, and of 5% of isophorone
20 diisocyanate.

Finally, all these polyurethanes are formulated in water in the presence of a non-ionic surfactant (in this instance, a blend of commercially available branched alcoxylated C8 and C10 compounds) (ratio by weight: 30% polyurethane, 20% surfactant, 50% water).

25 An aqueous composition is obtained in this manner.

Test No. 1

This test illustrates a domain outside of the invention and corresponds to a formulation
30 in water at 30% by dry weight of a polyurethane with a molecular mass by weight equal to approximately 11,000 g/mol where the hydrophobic monomer has the formula (II), where R designates the linear alkyl group with 12 carbon atoms.

Test No. 2

This test illustrates the invention and corresponds to a formulation in water at 30% by dry weight of a polyurethane with a molecular mass by weight equal to approximately 11,000 g/mol where the hydrophobic monomer has the formula (II), where R designates
5 the linear alkyl group with 9 carbon atoms.

Test No. 3

This test illustrates the prior art and corresponds to a formulation in water at 30% by dry weight of a polyurethane with a molecular mass by weight equal to approximately
10 11,000 g/mol where the hydrophobic monomer is a linear alcohol with 12 carbon atoms marketed under the name NacolTM 12-96 by the SASOLTM company.

Test No. 4

This test illustrates the prior art and corresponds to a formulation in water at 30% by dry
15 weight of a polyurethane with a molecular mass by weight equal to approximately 11,000 g/mol where the hydrophobic monomer is a linear alcohol with 14 carbon atoms marketed under the name NacolTM 14-98 by the SASOLTM company.

Test No. 5

20 This test illustrates the prior art and corresponds to a formulation in water at 30% by dry weight of a polyurethane with a molecular mass by weight equal to approximately 11,000 g/mol where the hydrophobic monomer is a linear alcohol with 16 carbon atoms marketed under the name NacolTM 16-95 by the SASOLTM company.

Test No. 6

25 This test illustrates the prior art and corresponds to a formulation in water at 30% by dry weight of a polyurethane with a molecular mass by weight equal to approximately 11,000 g/mol where the hydrophobic monomer is a linear alcohol with 18 carbon atoms marketed under the name NacolTM 18-98 by the SASOLTM company.

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Test No. 7

This test illustrates the prior art and uses AcrysolTM RM 8 W marketed by the DOWTM company.

Example 2

5 This example illustrates the use of polyurethanes of example 1 as thickening agents for a flat paint.

The composition of the said paint is indicated in table 1, the mass of each constituent being indicated in grams.

The paint is formulated according to methods well known to the person skilled in the art.

10 In each test, 0.2% by dry weight of the polymer according to the invention is used in relation to the total weight of the paint formulation, i.e. approximately for 1 kg of formulation as defined below, 6.67 g of an aqueous composition as mentioned above.

Constituents	Mass (g)
Water	190
Ecodis™ P50 (Coatex™)	4
Acticide MBS (Thor™)	2
Tego™ 810 (Tego™)	1
NaOH (20 %)	1
Tiona™ 568 (Millenium™)	80
Durcal™ 2 (Omya™)	300
Omyacoat™ 850 OG (Omya™)	220
Acronal™ 290 D (BASF™)	130
Monopropylene glycol	10
Texanol™ (Eastman™)	10
Water	QS 1,000

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Table 1

The resulting viscosities are then determined at T = 24 hours at 25°C, at low shear rate, Brookfield™ viscosity at 10 RPM, designated μ_{Bk10} (mPa.s), at medium shear rate, Stormer viscosity, designated μ_s (KU), and at high shear rate, ICI viscosity, designated μ_{ICI} (Poise or P).

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The results are shown in table 2.

Test No.	1	2	3	4	5	6	7
PA/IN	OI	IN	PA	PA	PA	PA	PA
associative monomer	C18	C15	C12	C14	C16	C18	Acrysol RM8W
μ_{ICI} (P)	0.95	1.2	1.2	0.95	0.95	0.85	1.0
μ_S (KU)	128	102	96	106	125	116	103
μ_{Bk10} (mPa.s)	18,000	3,800	3,160	12,000	20,300	23,900	3,800

Table 2

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If the results obtained with the linear structures of the prior art are analysed, it will be apparent that the associativity of polymers disappears or decreases very significantly for more than 12 carbon atoms. At the same time, the Brookfield™ viscosity increases very significantly for 14 carbon atoms and more.

10 The polymers of the prior art of which the hydrophobic monomer is a linear C14, C16 or C18 are therefore not efficient enough in terms of ICI™ viscosity. As to the C12 polymer, it does not develop a sufficient Brookfield™ and Stormer™ viscosity.

However, surprisingly, the polymer according to the invention develops a totally unique rheology: it enables an equalling of the ICI™ viscosity obtained with the C12 polymer
15 while exceeding its Brookfield™ and Stormer™ viscosity levels.

It can even improve the performances obtained with the commercial polymer according to test No. 7, which produces a significant deficit in ICI™ viscosity.

Finally, test No. 1 demonstrates the importance of limiting the number of carbons in the hydrophobic monomer according to the invention. With 18 carbon atoms, the polymer
20 in test No. 1 is not effective enough at a high shear gradient (ICI™ viscosity).

Example 3

This example illustrates the use of the polyurethanes of example 1 as thickening agents
25 for another flat paint.

The composition of the said paint is indicated in table 3, the mass of each constituent being indicated in grams.

The paint is formulated according to methods well known to the person skilled in the art.

In each test, 0.36% by dry weight of the polymer according to the invention is used in relation to the total weight of the paint formulation.

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Constituents	Mass (g)
Water	277
Ecodis™ P50 (Coatex™)	4
Acticide MBS (Thor™)	2
Tego™ Airex 901 W (Tego™)	1
NaOH (20 %)	0.9
Tiona™ 568 (Millenium™)	81
Durcal™ 2 (Omya™)	300.1
Omyacoat™ 850 OG (Omya™)	133
Mowilith LDM 1871™ (Celanese™)	150
Tego™ 825 (Tego™)	10
Water	QS 1,000

Table 3

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The resulting viscosities are then determined at T = 24 hours at 25°C, at low shear rate, Brookfield™ viscosity at 10 RPM, designated μ_{Bk10} (mPa.s), at medium shear rate, Stormer viscosity, designated μ_s (KU), and at high shear rate, ICI viscosity, designated μ_{ICI} (Poise or P).

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The results are shown in table 4.

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Test No.	1	2	3	4	5	6	7
PA/IN	OI	IN	PA	PA	PA	PA	PA
associative monomer	C18	C15	C12 linear	C14 linear	C16 linear	C18 linear	Acrysol RM8W
μ_{ICI} (P)	0.7	1.1	1.1	0.75	0.65	0.6	0.75
μ_S (KU)	137	104	100	110	135	121	93
μ_{Bk10} (mPa.s)	25,000	10,200	8,800	20,000	36,000	45,000	9,700

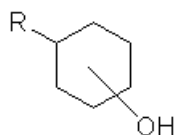
Table 4

The same conclusions are drawn from this table as those of the previous example.

CLAIMS

1 - Water soluble polyurethane resulting from the condensation:

- 5 a) of at least one monomer with the formula (I)



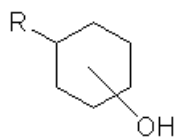
(I)

where R designates an alkyl group with 6 to 10 carbon atoms,

- b) of at least one polyalkylene glycol,
10 c) and of at least one polyisocyanate.

2 - Polyurethanes according to claim 1 resulting from the condensation of:

- a) a monomer of formula (I):



(I)

where R designates an alkyl group having 6 to 10 carbon atoms,

- b) a polyalkylene glycol,
c) a polyisocyanate, and
d) an aliphatic alcohol having between 6 and 20 carbon atoms.

20 3 - Polyurethanes according to claim 1, resulting from the condensation of:

- a) 1% to 29% by weight of at least one monomer of formula (I),
b) 70% to 98% by weight of at least one polyalkylene glycol, and
c) 1% to 29% by weight of at least one polyisocyanate

25 where the sum of these mass percentages is equal to 100%.

4 - Polyurethanes according to claim 1 or 3, resulting from the condensation of

- a) 3% to 7% by weight of at least one monomer of formula (I),
b) 86% to 94% by weight of at least one polyalkylene glycol, and
30 c) 3% to 7% by weight of at least one polyisocyanate

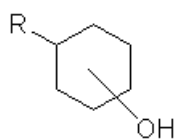
where the sum of these mass percentages is equal to 100%.

5 - Polyurethanes according to any of the previous claims, where the polyalkylene glycol is a polyethylene glycol the molecular mass by weight of which varies between
5 2,000 g/mol and 20,000 g/mol.

6 - Polyurethanes according to any of the previous claims, where the polyisocyanate is chosen from the group consisting of toluene diisocyanate, the toluene diisocyanate dimers, the toluene diisocyanate trimers, 1,4-butane diisocyanate, 1,6-hexane
10 diisocyanate, isophorone diisocyanate, 1,3-cyclohexane diisocyanate, 1,4-cyclohexane diisocyanate, 4,4'-diisocyanatodicyclohexylmethane, 1-methyl-2,4-diisocyanatocyclohexane, a blend of 1-methyl-2,4-diisocyanatocyclohexane and 1-methyl-2,6-diisocyanatocyclohexane, the biuret of hexamethylene diisocyanate, the dimers of the biuret of hexamethylene diisocyanate, the trimers of biuret of
15 hexamethylene diisocyanate, and a blend of at least two of these compounds.

7 - Polyurethanes according to any of the previous claims, where the said monomer a) has a formula (I) where R designates a group having 9 carbon atoms.

20 8 - Polyurethanes according to claim 1 or 2, resulting from the condensation of:
a) 1 to 29% by weight of a monomer of formula (I):



(I)

where R designates an alkyl group having between 6 and 10 carbon atoms,
25 b) 70% to 98% by weight of polyalkylene glycol,
c) 1% to 29% by weight of a polyisocyanate, and
d) 1% to 29% by weight of an aliphatic alcohol having between 6 and 20 carbon atoms,
where the sum of these mass percentages is equal to 100%.

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9 - Polyurethanes according to claim 8, resulting from the condensation of:

- a) 1% to 29% by weight of a monomer of formula (I), where R designates an alkyl group having between 6 and 10 carbon atoms,
b) 70% to 98% by weight of a polyalkylene glycol,
c) 1% to 29% by weight of a polyisocyanate, and
5 d) 1% to 29% by weight of an aliphatic alcohol having between 10 and 15 carbon atoms,
where the sum of these mass percentages is equal to 100%.

10 10 - An aqueous composition including a polyurethane according to any of claims 1 to 9,

11 - An aqueous composition according to claim 10, also including water and a non-ionic surfactant agent.

15 12 - An aqueous composition according to claim 10 or 11, also including at least one additive selected from the group consisting of a biocide, a solvent, an anti-foaming agent, a pH regulator, a coalescent agent and their mixtures

20 13 - An aqueous composition according to any of the claims 10 to 12, containing:

- 1) 5% to 45% by weight of at least one polyurethane according to any of the claims 1 to 9,
2) 5% to 30% by weight of at least one surfactant,
3) 25% to 75% by weight of water, and
25 4) 0 to 5% by weight of at least one other additive chosen from the group consisting of a biocide, a solvent, an anti-foaming agent, a pH regulator, a coalescent agent and their mixtures,

the sum of these mass percentages being equal to 100%.

30 14 - Aqueous formulation including a polyurethane according to any of claims 1 to 9, or an aqueous composition according to any of claims 10 to 13, the said formulation being

selected from among the group consisting of a paint, a lacquer, a varnish, a paper coating color , a cosmetic formulation and a detergent formulation.

15 - Use of a polyurethane according to any of claims 1 to 9, or an aqueous composition
5 according to any of claims 10 to 13 to thicken an aqueous formulation, the said formulation being selected from among the group consisting of a paint, a lacquer, a varnish, a paper coating color , a cosmetic formulation and a detergent formulation

16 - Process for the preparation of a polyurethane according to any of claims 1 to 9,
10 consisting of a condensation of its various constituents.