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- (54) Benævnelse: **IKKE-IONISKE ASSOCIATIVE FORTYKNINGSMIDLER INDEHOLDENDE ALKOXYLEREDE CYCLOHEXYL-ALKYLER, ANVENDELSER DERAFF OG FORMULERINGER INDEHOLDENDE DISSE**
- (56) Fremdragne publikationer:
EP-A1- 2 327 732
EP-A1- 2 361 939
EP-A2- 1 566 393
WO-A1-99/11594

The present invention concerns new associative thickening agents belonging to the category of HEURs (Hydrophobically modified Ethylene oxide URethane). These products contain an original associative monomer with a base of alkyl cyclohexylol alkoxyates. Their thickening power is equal to or greater than that procured by HEUR
5 associative thickening agents of the prior art containing grafted alkyls phenols. An efficient substitute product is therefore available, which is free of alkyls phenols, matching current market demand.

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

The latter enables the rheology of the aqueous formulations into which it is introduced,
15 and notably aqueous paints, to be controlled, both at the manufacturing stage, and during transport or storage, or at the time of implementation. The wide variety of practical constraints in each of these stages relates to a multiplicity of different rheological behaviours.

Nevertheless, it is possible to summarise the requirement of the skilled man in the art in
20 obtaining an effect of the thickening of the aqueous formulation, both for reasons of stability over time, and for a possible application of the paint to a vertical surface, lack of spattering during implementation, etc. For this reason, additives have been designated which contribute to this regulation of the rheological behaviours under the
25 term "thickening agents".

Among these products, thickening agents known as "associative" thickening agents are distinguished, which are hydrosoluble polymers having insoluble hydrophobic groups. Such macromolecules have an associating character: when introduced into water, the
30 hydrophobic groups tend to assemble in the form of micellar aggregates. These aggregates are linked together by the hydrophilic parts of the polymers: a three-dimensional network is then formed which causes the viscosity of the medium to be increased.

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

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

These structures are well known to develop high viscosities, with a medium to low shearing 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, n° 4169, p 459, June 1986), which is equal respectively to the Stormer™ (KU) and Brookfield™ (mPa.s) viscosity measurements.

At the same time, document EP 1 566 393 describes a thickening agent of the HEUR type one of the essential characteristics of which is the presence of n-butyl-1-octanol, while its hydrophobic groups are based on fatty alcohols having 8 to 18 carbon atoms.

Document EP 1 013 264 describes a polyurethane thickening agent for cosmetic formulations, having an associative monomer functionalised by a hydrophobic group which may be linear or branched, but is preferentially linear, and having 12 to 24 carbon atoms.

Document WO 94/06840 proposes an associative thickening agent of the HEUR type, characterised by a certain density of hydrophobic groups, where the said groups are linear alkyl chains having 8 to 22 carbon atoms.

Document EP 1 584 331 proposes a hydrophobic terminal group having 6 to 34 carbon atoms for the associative monomer. To increase specifically the Brookfield™ viscosity.

5 Document EP 0 639 595 proposes linear hydrophobic groups having 4 to 36 carbon atoms.

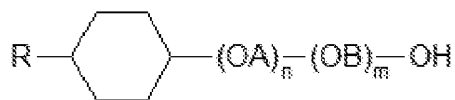
Document WO 02/102868 also makes reference to linear structures for the associative monomer.

10 Document EP 2 361 939 A1 describes thickening agents used in aqueous formulations. Example 1 describes the reaction between a polyether diol (PEG 8000), IPDI and the ethoxylated cardanol, which is an ethoxylated alkylphenol. Example 2 describes the reaction between a polyether diol (PEG 8000), IPDI and ethoxylated nonylphenol.

15 Independently of the particular rheological profiles provided by the variations described above, the HEURs with the most pronounced thickening power still remain molecules having alkyl phenols grafted on to their associative monomer. One of the representative products of this technology is Acrysol™ SCT-275, developed by the company DOW™. And alkyl phenols are currently widely suspected of being carcinogenic, and dangerous
20 for reproduction; although still tolerated in the paints industry, they nonetheless remain in the firing line of the legislative institutions, notably the European ones.

There is therefore a genuine requirement to develop a HEUR-type associative thickening agent, which is free of alkyls phenols, but which has an equivalent or even
25 improved thickening power.

Continuing its research along these lines, the Applicant observed in a completely surprising manner that the use of certain structures in place of the associative monomer led to such a result. This technological advance is based on the implementation, as an
30 associative monomer, of a compound the structure of which satisfies the following formula (I):



(I)

where:

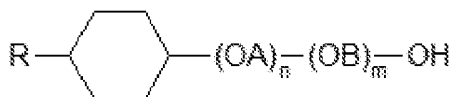
- m and n are integers of less than 150, at least one of which is non-zero,
- A and B designate alkyl groups which are different one from another, and having 2 to 4 carbon atoms, where group AO preferentially designates ethylene oxide, and group BO preferentially designates propylene oxide,
- R designates an alkyl group, whether linear or branched, containing 8 to 20 carbon atoms, and preferentially a linear alkyl group having 9 to 12 carbon atoms.

Such compounds have been identified as surfactants, and are obtained by alkoxylation of an alkyl phenol and hydrogenation of the product obtained. Reference may notably be made to the document US 6 111 146 which describes their synthesis. The resulting compounds are designated by the expression "alkyl cyclohexylol alkoxyates". It is important to add that the final structure is not that of an alkyl phenol, and that the resulting product will not be categorised as such.

The associative thickening agents which result from the polymerisation of this monomer of formula (I), of at least one polyalkylene glycol and at least one polyisocyanate, have no alkyls phenols; in an unexpected and particularly advantageous manner, they enable an aqueous paint to be thickened to a level of viscosity at least equal to that provided by HEURs of the prior art containing alkyl phenols. It is even demonstrated that it is possible to obtain for the invention a rheological profile similar to that proposed by the products of the state of the art for alkyl phenols. A product has therefore successfully been developed which is at least equivalent, and which overcomes the problem relating to the use of alkyl phenols.

Thus, a first object of the invention consists of hydrosoluble polyurethanes resulting from the condensation:

- a) of at least one polyalkylene glycol, and
 b) of at least one polyisocyanate, and
 c) of at least one monomer of formula (I) :



5

(I)

where:

- m and n are integers of less than 150, at least one of which is non-zero,
- 10 - A and B designate alkyl groups which are different one from another, and having 2 to 4 carbon atoms, where group AO preferentially designates ethylene oxide, and group BO preferentially designates propylene oxide,
- R designates an alkyl group, whether linear or branched, containing 8 to 20 carbon atoms, preferentially a linear alkyl group having 9 to 12 carbon atoms.

15

"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, the 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, 20 6,000, 10,000 and 20,000 g/mol (in the case of polyethylene glycol called PEG-1000, PEG-4000, PEG-6000, PEG 10000, 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.

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

30

The Applicant stipulates that the manufacture of these polyurethanes, which belong to the family of HEUR-type thickening agents, is known to the skilled man in the art, who can refer to the teaching of the documents cited above as the technological background of the present invention.

5

According to one embodiment of the present invention, these polyurethanes result from the condensation of, expressed as a % by weight of each of the monomers, where the sum of these %s is equal to 100%:

- 10 a) 90% to 99.5% of at least one polyalkylene glycol,
 b) 0.5% to 10% of at least one polyisocyanate and
 c) 90% to 99.5% of at least one monomer of formula (I).

According to one embodiment of the present invention, the polyalkylene glycol
15 constituting the polyurethane is polyethylene glycol,

According to another embodiment of the present invention, this is a polyethylene glycol of molecular mass of between 2,000 g/mole and 20,000 g/mole, for example between 8,000 g/mole and 15,000 g/mole, or for example between 8,000 g/mole and
20 12,000 g/mole.

According to one embodiment, the polyisocyanate constituting the polyurethane according to the invention is chosen from among toluene diisocyanate and its dimers and trimers, 1,4-butane diisocyanate, 1,6-hexane diisocyanate, isophorone diisocyanate,
25 1,3- and 1,4- cyclohexane diisocyanate, 4,4'-diisocyanatodicyclohexylmethane, 1-methyl-2,4-diisocyanatocyclohexane and its blend with 1-methyl-2,6-diisocyanatocyclohexane, the biuret of hexamethylene diisocyanate and its dimers and trimers and their blends.

30 A second object of the present invention consists of aqueous compositions containing water, at least one polyurethane according to the invention, together with at least one surfactant, and possibly at least one additive chosen from among a biocide, a solvent, an anti-foaming agent, a pH regulator, a coalescence agent, or 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.

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

10 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.

15 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.

20 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 condition(s) of application (for example a TMFF 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 2,2,4-trimethyl-1,3-pentanediol diisobutyrate may be cited.

25 According to one embodiment, the aqueous compositions of the invention contain, expressed as a % by weight of each of their constituents, where the sum of these %s is equal to 100%:

- 30
- 1) 5% to 45% of at least one polyurethane according to the invention,
 - 2) 5% to 30% of at least one surfactant,
 - 3) 25% to 75% of water,
 - 4) 0 to 5% of at least one additive chosen from among a biocide, a solvent, an anti-foaming agent, a pH regulator, a coalescence agent and their blends.

Another object of the present invention consists in the use of the said polyurethanes and of the said compositions, as thickening agents in aqueous formulations, where the said formulations are for example chosen from among aqueous paints, lacquers, varnishes, paper coating colors, cosmetic formulations and detergent formulations.

5

Another object of the present invention lies in the aqueous formulations containing the thickening agents or polyurethanes and the compositions according to the invention, where the said formulations are for example chosen from among aqueous paints, lacquers, varnishes, paper coating colors, cosmetic formulations and detergent formulations.

10

A final object of the present invention consists of a method for preparing a polyurethane according to the invention, consisting of a condensation of its different constituents.

15

The following examples enable the invention to be better understood, without however limiting its scope.

EXAMPLES

20

Example 1

This example illustrates the manufacture of an aqueous paint, in which a thickening agent of the prior art containing an alkyl phenol having 15 carbon atoms and a thickening agent according to the invention, the R group of which is a linear alkyl chain having 9 carbon atoms, are used: the corresponding hydrophobic group therefore contains 15 carbon atoms in this case.

25

Test n° 1:

This test illustrates the prior art. This corresponds to the implementation of an aqueous composition with 17.5% by dry weight of a polymer containing grafted alkyl phenols, which is Acrysol™ SCT-275 sold by the company Dow™.

30

Test n° 2:

This test illustrates the prior art. This corresponds to the implementation of an aqueous composition containing 17.5% by dry weight of a polymer consisting of, expressed as a % by weight of each of its monomers:

- 5
- a) 75% of polyethylene glycol of molecular mass by weight equal to 10,000 g/mole,
 - b) 5% of isophorone diisocyanate,
 - c) 15% by weight of a monomer of formula $\text{HO} - (\text{OE})_n - \text{R}$

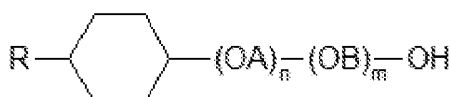
where OE is ethylene oxide, n is equal to 25 and R is the alkyl phenol group having 15 carbon atoms.

10

Test n° 3:

This test illustrates the invention. This corresponds to the implementation of an aqueous composition containing 17.5% by dry weight of a polymer consisting of, expressed as a % by weight of each of its monomers:

- 15
- a) 75% of polyethylene glycol of molecular mass by weight equal to 10,000 g/mole,
 - b) 5% of isophorone diisocyanate,
 - c) 15% by weight of a monomer of the following formula:



20

(I)

where $m = 0$ and $n = 25$ and R designates the linear alkyl group having 9 carbon atoms.

In each of the tests n° 1 to 3, 70.6 grams of Mowilith™ LDM 1871, 193.8 grams of bipermuted water and 32 grams of the composition to be tested are introduced into the beaker.

25

The pH is adjusted by using ammonium hydroxide (28%) to a value of between 8.6 and 8.9.

At 25°C, the Brookfield™ viscosities at 10 and 100 revolutions per minute (μ_{BK10} and μ_{BK100}) and the Stormer™ viscosities (μ_{S}) of the paint are measured.

30

The results are shown in table 1.

Test n°	1	2	3
Prior Art INvention	PA	PA	IN
μ_{Bk10}	13,600	12,200	13,800
μ_{Bk100}	8,700	6,800	8,850
μ_S	135	122	139

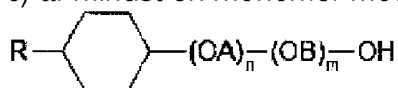
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Table 1

Patentkrav

1. Vandopløselige polyurethaner, som er opnået gennem kondensation:

- 5 a) af mindst én polyalkylenglycol,
 b) af mindst én polyisocyanat og
 c) af mindst én monomer med formel (I) :



(I)

hvor:

- 10 - m og n er heltal, som er mindre end 150, hvoraf mindst ét ikke er nul,
 - A og B betegner alkyl-grupper, som er indbyrdes forskellige, og som har 2 til 4 carbonatomer,
 - R betegner en lineær eller forgrenet alkylgruppe, som indeholder 8 til 20 carbonatomer.

15

2. Polyurethaner ifølge krav 1, hvor AO-gruppen betegner ethylenoxid, og BO-gruppen betegner propylenoxid.

20

3. Polyurethaner ifølge et hvilket som helst af de foregående krav, hvor R betegner en lineær alkylgruppe med 9 til 12 carbonatomer.

4. Polyurethaner ifølge et hvilket som helst af de foregående krav, hvor polyalkylenglycol er polyethylenglykol.

25

5. Polyurethaner ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** polyalkylenglycol er polyethylenglycol med en molekylmasse i vægt, som ligger mellem 2.000 g/mol og 20.000 g/mol.

30

6. Polyurethaner ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** polyalkylenglycol er polyethylenglycol med en molekylmasse i vægt, som ligger mellem 8.000 g/mol og 15.000 g/mol.

7. Polyurethaner ifølge et hvilket som helst af de foregående krav, **kendetegnet ved, at** polyisocyanat er udvalgt blandt toluendiisocyanat og dimerer

og trimerer deraf, 1,4-butandiisocyanat, 1,6-hexandiisocyanat, isophoron-diisocyanat, 1,3- og 1,4-cyclohexandiisocyanat, 4,4'diisocyanatodicyclohexylmethan, 1-methyl-2,4-diisocyanatocyclohexan og blanding deraf med 1-methyl-2,6-diisocyanatocyclohexan, hexamethylen-diisocyanat-biuret og dimerer og trimerer deraf og blandinger deraf.

5
8. Vandige sammensætninger, som indeholder vand, mindst én polyurethan ifølge et hvilket som helst af kravene 1 til 7 og mindst ét overfladeaktivt stof.

10 **9.** Vandig sammensætning ifølge krav 8, som yderligere indeholder et tilsætningsstof udvalgt blandt et biocid, et opløsningsmiddel, et antiskummiddel, en pH-regulator, et coalescence-middel eller blandinger deraf.

15 **10.** Sammensætninger ifølge krav 8 eller 9 **kendetegnet ved, at** de indeholder, udtrykt i vægt-% af hver af bestanddelene deraf, idet summen af disse %-dele er lig med 100 %:

- 20
- 1) 5 % til 45 % af mindst én polyurethan ifølge et hvilket som helst af kravene 1 til 7,
 - 2) 5 % til 30 % af mindst ét overfladeaktivt stof,
 - 3) 25 % til 75 % vand,
 - 4) 0 til 5 % af mindst ét tilsætningsstof udvalgt blandt et biocid, et opløsningsmiddel, et antiskummiddel, en pH-regulator, et coalescence-middel eller blandinger deraf.

25 **11.** Anvendelse af polyurethaner ifølge et af kravene 1 til 7 eller en sammensætning ifølge et af kravene 8 til 10 som fortykningsmidler i vandige formuleringer.

30 **12.** Anvendelse ifølge krav 11, hvor de vandige formuleringer er udvalgt blandt vandbaserede malinger, lakker, fernisser, papircoatingfarver, kosmetiske formuleringer eller rensformuleringer.

35 **13.** Vandige formuleringer, som indeholder polyurethaner eller sammensætninger ifølge et hvilket som helst af kravene 1 til 10, hvilke formuleringer er udvalgt blandt vandbaserede malinger, lakker, fernisser, papircoatingfarver,

kosmetiske formuleringer eller rensformuleringer.

14. Fremgangsmåde til fremstilling af en polyurethan ifølge et hvilket som helst af kravene 1 til 7, som består i en kondensation af de forskellige bestanddele deraf.