

**ALKALI-SWELLABLE ACRYLIC EMULSIONS COMPRISING ACRYLIC
ACID, USE THEREOF IN AQUEOUS FORMULATIONS AND
FORMULATIONS CONTAINING SAME**

5 The present invention relates to new methacrylic acid-free alkali swellable thickener emulsions: this monomer was until then indispensable in this type of emulsion, which made manufacturers dependent on this raw material. These new emulsions contain a certain quantity of 2-acrylamido-2-methylpropane sulfonic acid (or AMPS®, CAS No: 40623-75-4). They may also be made in the absence of a surfactant, which prevents the
10 formation of foam. Finally, they are effective for thickening aqueous media, including media with a pH between 5 and 6, such as the skin.

Aqueous formulations are found that may contain mineral fillers in very many domains: those of aqueous paints, paper coating dispersions, mineral suspensions, detergents,
15 cosmetic formulations, or of concretes and cements.

Controlling their rheology is a necessity, 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
20 rheological behaviours. In the case of a paint, for example, the need of the person skilled in the art can be summarized as that of obtaining a thickening effect, both for reasons of stability over time as well as for a possible application of the paint to a vertical surface, the absence of splashing when using it, or sagging after its use, etc.

25 Indeed, products that contribute to this control of rheological behaviour have been designated as thickeners. Among these thickeners, the person skilled in the art has long known the particular category of alkali swellable acrylic emulsions which are polymers that are emulsified in water using surfactants, the said polymers consisting of at least one non water-soluble monomer and at least one neutralisable alkali water-soluble monomer,
30 including methacrylic acid.

The Applicant states that the expression "direct emulsion of a polymer in water" refers to a stable and homogeneous dispersion of polymer particles in water (it does not refer here to oil in water or water in oil type emulsions which involve the existence of two distinct

phases, one aqueous and the other oily). As to the expression "swellable alkali polymer", it means that the said polymer is capable, when the medium is alkaline, of incorporating a quantity of water such that there is the formation of a gel.

5 There are 2 major families of alkali swellable acrylic thickeners: thickeners of the ASE (Alkali Swellable Emulsion) type and those of HASE (Hydrophobically modified Alkali Swellable Emulsion) type. The first designate copolymers of methacrylic acid with a non-water soluble ester of this acid, and the second designate methacrylic acid based
10 so-called "associative" hydrophobic groups. In addition, these copolymers can be cross-linked.

The mechanisms of action of these products differ. Polymers of the ASE type only thicken in the neutralized state, hence the expression "alkali swellable": an ionic
15 repulsion mechanism is then induced between the various carboxylate groups on the polymer chain. These ionized groups polarize the water molecules which causes the increase in the viscosity of the medium. In addition to the above-mentioned ionic phenomenon, polymers of the HASE type bring into play interactions between their associative hydrophobic groups which also contributes to thickening the medium. These
20 mechanisms, in particular the alkali swellable nature of these emulsions and their ability to thicken an aqueous medium at a pH close to neutrality, have been described in documents WO 2007 / 144721 and "Practical guide to associative thickeners" (Proceedings of the Annual Meeting Technical Program of the FSCT, 2000, 78th, 644-702).

25 There are many applications that can be found for these thickeners in paint, coating dispersions or cosmetics (see patent applications FR 2 693 203 A1, FR 2 872 815 A1, FR 2 633 930 A1, FR 2 872 815 A1). In addition, they exist in the commercial form, particularly through the range of products Rheocarb™, Rheocoat™, Thixol™,
30 Rheotech™, Polyphobe™ and Viscoatex™ marketed by the company COATEX S.A.S.

Returning to the constitution of ASE and HASE type emulsions, methacrylic acid appears today as an unavoidable monomer which constitutes at least 20% by weight of these thickener polymers. Due to its carboxylic acid function, it participates in the increase in

viscosity of the medium through an already described ionic phenomenon, and it is easily polymerizable in an aqueous emulsion in the presence of surfactants with hydrophobic monomers, including the associative monomers.

5 These polymerizations in emulsion are widely illustrated in the scientific literature. Reference can be made to the publications "Synthesis of an alkali-swella-
ble emulsion and its effect on the rate of polymer diffusion in poly (vinyl acetate-butyl acrylate) latex
films" (Journal of Polymer Science, Part A: Polymer Chemistry, 2005, 43 (22), pp. 5632-
5642), "Structural and rheological properties of hydrophobically modified alkali-soluble
10 emulsion solutions" (Journal of Polymer Science, Part B: Polymer Physics, 2002, 40 (18),
pp. 1985-1994) "Viscoelastic properties of hydrophobically modified alkali-soluble
emulsion in salt solutions" (Polymer, 1999, 40 (23), pp. 6369-6379), "Dissolution
behaviour in water of a model hydrophobic alkali-swella-
ble emulsion polymer with C₂₀H₄₁ groups" (Canadian Journal of Chemistry (1998), 76(11), pp. 1779-1787), and to
15 patent applications EP 0 089 213 A1, EP 0 646 606 A1, EP 0 979 833 A1, for the ASEs,
and EP 0 013 836 A1, WO 93 / 2454 A1, US 4 268 641 A1, US 4 421 902 A1, US
3 915 921 A1 for the HASEs.

Today, methacrylic acid is considered an indispensable monomer in ASE and HASE type
20 emulsions: This data is to a large extent integrated into the industrial world, and is not
questioned by the person skilled in the art. But it is precisely the mandatory nature of
methacrylic acid that is a problem. We live in an era when the shortage of raw materials
and their cost fluctuation indexed to that of a barrel of crude oil are recurring data in the
chemical industry. Therefore, a technology attached exclusively to a material becomes
25 strategically risky for its manufacturers and users.

It is to address this major drawback that the Applicant has undertaken research with the
aim of substituting acrylic acid for methacrylic acid in ASE and HASE type emulsions.
However, no document on the state of the art discloses a technique for the direct
30 polymerization of acrylic acid in an emulsion without methacrylic acid and in the
presence of a hydrophobic monomer, the acrylic acid in such a case representing at least
20% by weight of the monomers to be polymerized.

The applicant was able to demonstrate that such a direct polymerization in emulsion was possible, to the extent that use was made of a certain quantity of a particular monomer which is 2-acrylamido-2-methylpropane sulfonic acid (or AMPS®, CAS No: 40623-75-4). In a completely surprising and beneficial way, true emulsions of the ASE and HASE type, free of methacrylic acid, were thus manufactured.

Now the acrylic acid based thickeners known to the person skilled in the art are cross-linked acrylic acid polymers obtained by precipitation in a solvent (see document EP 0 584 771 A1), or polymers that are cross-linked or hydrophobically modified in reverse water-in-oil emulsions (see documents FR 2 873 126 A1 and FR 2 782 086 A1), or finally, high molecular weight polymers (greater than 10,000,000 g/mol) obtained in solution in water and dried (known by the name of superabsorbent polymers or SAPs; see in particular documents EP 0 371 421 A1 and US 5 221 722 A1). Nothing exists in the state of the art for the production of alkali swellable emulsions containing at least 20% by weight of acrylic, and free of methacrylic acid.

In addition, the process which is the object of the present Application, has a preferential variant that produces other benefits: It can be implemented without a surfactant or solvent other than water. Now, it is well known that these latter generate many problems in the implementation of emulsions of the ASE and HASE type in an aqueous formulation.

In the case of a paint, there may be the creation of inhomogeneities, and even an alteration in the properties of the final product, that is, of the dry film of paint resulting from the drying of the aqueous formulation. The formation of "craters" or insoluble particles that are heterogeneities that harm the aesthetic appearance and properties of the film surface can also be observed (the mechanical aspect, but also the optical properties and the condition of the surface). Finally, it is well known that the presence of surfactants in a paint formulation will ultimately degrade the washable property of the dry film (see "Effect of surfactants used for binder synthesis on the properties of latex paints", Progress in Organic Coatings, 2005, 53 (2), pp. 112-118).

Other advantages of the new methacrylic acid-free ASE and HASE type emulsions reside in the fact that they have a commercial dry extract (greater than 25% by dry weight of

active ingredient), are stable over time and are characterized by particle sizes similar to the emulsion of the prior art. Finally, their thickening effectiveness is demonstrated.

Another object of the present invention lies in the use of the aforementioned emulsions as thickening agents in aqueous formulations, these constituting the final object of the present invention.

Also, a first object of the present invention consists of a direct manufacturing process in an aqueous emulsion of a polymer, characterized in that said process involves the polymerization reaction of, expressed in % by weight of each of the monomers:

- a) 20% to 80% by weight of acrylic acid,
 - b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
 - c) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
 - d) 0 to 1% by weight of at least one crosslinking monomer,
- the _total_a) + b) + c) + d) being equal to 100%.

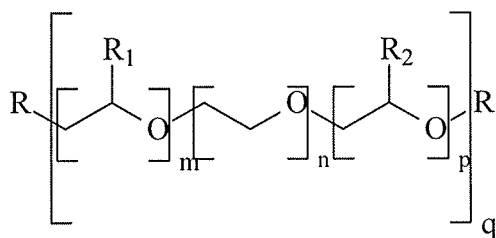
or

- a) 20% to 80% by weight of acrylic acid,
 - b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
 - c) 10% to 25% by weight of a monomer containing a hydrophobic group,
 - d) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
 - e) 0 to 1% by weight of at least one crosslinking monomer,
- the _total_a) + b) + c) + d) being equal to 100%,

The other characteristics of this process (temperature, choice of catalytic system, use of a transfer agent, employment of a possible crosslinking agent) are those described in the state of the art, including the above documents to which the person skilled in the art can refer.

This process is also characterized in that the ester of (meth)acrylic acid is chosen from ethyl acrylate, butyl acrylate, methyl methacrylate, and their mixtures.

This process is also characterized in that the monomer containing a hydrophobic group has the general formula:



where:

- m, n, p and q are integers and m, n, p are less than 150, q is greater than 0 and at least one integer from among m, n and p is non-zero.
- 5 - R contains a polymerizable vinyl function,
- R₁ and R₂ are identical or different and represent hydrogen atoms or alkyl groups,
- R' is a hydrophobic group with at least 6 and not more than 36 carbon atoms.

10 This process is also characterized in that the crosslinking monomer is chosen from among ethylene glycol dimethacrylate, trimethylolpropane triacrylate, diallyl phthalate, allyl acrylate, the allyl maleates, methylene-bis-acrylamide, methylene-bis-methacrylamide, tetralyloxyethane, the triallyl cyanurates, the allylic ethers obtained from polyols.

15 This process is also characterized in that the aqueous emulsion presents a dry extract that is between 10% and 50% by dry weight of polymer with respect to its total weight.

This process is also characterized in that the emulsion has a particle size between 50 nm and 500 nm.

20 This process is also characterized in that the polymer presents a mean molar mass by weight of between 20,000 g/mol and 1,000,000 g/mol.

In a preferred variant, this process does not use surfactants or solvents other than water.

25 Another object of the present invention consists of the use in a manufacturing process of an emulsion of the ASE or HASE type, of 2-acrylamido-2-methylpropane sulfonic acid as an agent enabling the complete substituting of methacrylic acid by acrylic acid.

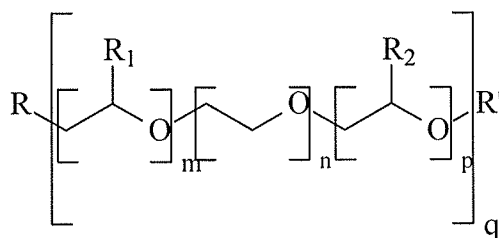
Another object of the present invention is a direct aqueous emulsion of a polymer characterized in that it consists of, expressed in % by weight of each monomer:

- 5 a) 20% to 80% by weight of acrylic acid,
 b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
 c) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
 d) 0 to 1% by weight of at least one crosslinking monomer,
 the $a + b + c + d$ being equal to 100%.

10 or

- a) 20% to 80% by weight of acrylic acid,
 b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
 c) 10% to 25% by weight of a monomer containing a hydrophobic group,
 15 d) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
 e) 0 to 1% by weight of at least one crosslinking monomer,
 the $a + b + c + d$ being equal to 100%.

20 This emulsion is also characterized in that the monomer containing a hydrophobic group has the general formula:



where:

- m, n, p and q are integers and m, n, p are less than 150, q is greater than 0 and at least one integer from among m, n and p is non-zero.
- 25 - R contains a polymerizable vinyl function,
- R₁ and R₂ are identical or different and represent hydrogen atoms or alkyl groups,
- R' is a hydrophobic group with at least 6 and not more than 36 carbon atoms.

This emulsion is also characterized in that the crosslinking monomer is chosen from among ethylene glycol dimethacrylate, trimethylolpropane triacrylate, diallyl phthalate, allyl acrylate, the allyl maleates, methylene-bis-acrylamide, methylene-bis-methacrylamide, tetrallyloxyethane, the triallyl cyanurates, the allylic ethers obtained
5 from polyols.

This emulsion is also characterized in that it presents a dry extract of between 10% and 50% by dry weight of polymer in relation to its total weight.

10 This emulsion is also characterized in that it has a particle size between 50 nm and 500 nm.

This emulsion is also characterized in that the polymer presents a mean molar mass by weight of between 20,000 g/mol and 1,000,000 g/mol.

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In a preferred variant, this emulsion is characterized in that it is free of surfactants and solvents other than water.

Another object of the present invention lies in the use of the above-mentioned emulsion
20 as a thickening agent for an aqueous formulation. Concretely, the emulsion is introduced into the medium to be thickened, the pH of which is maintained close to neutral, in order to obtain the thickening effect. The person skilled in the art, using routine experiments, will be able to find the pH starting from which the phenomenon of thickening is observed.

25

This use is also characterized in that said formulation is selected from an aqueous paint, a paper coating dispersion, an aqueous suspension of mineral substances, a detergent, a cosmetic formulation, or containing a hydraulic binder, and finally a cosmetic formulation, more specifically, a cosmetic formulation to be applied to the skin or a
30 region of the body where the pH is between 5 and 6.

A final object of the present invention resides in an aqueous formulation containing the above mentioned emulsion, the said formulation being selected from an aqueous paint, a paper coating dispersion, an aqueous suspension of mineral substances, a detergent, a

cosmetic formulation, or containing a hydraulic binder, a cosmetic formulation to be applied to the skin or a region of the body where the pH is between 5 and 6.

EXAMPLES

Example 1

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Test No. 1 according to the invention

This test concerns the manufacture of an ASE type emulsion containing a copolymer consisting of, expressed in % by weight of each of its monomers:

10

- a) 36.4% acrylic acid,
- b) 62.4% ethyl acrylate,
- c) 1.2% AMPS

15 Into a 1 litre reactor equipped with mechanical agitation and an oil bath type heating system, introduce 550 g of biperemuted water and 7.0 g of an AMPS solution (55% solution of AMPS in water neutralized with sodium hydroxide, marketed by the LUBRIZOL™ company under the name AMPS 2405).

20 The medium is heated to 78°C and then the catalytic system, consisting of 0.96 g of ammonium persulfate dissolved in 10 g of biperemuted water and 0.096 g of sodium metabisulphite dissolved in 10 g of biperemuted water is introduced using a funnel.

25 Next, 236 g of ethyl acrylate and 85 g of acrylic acid (90%) is introduced in a continuous and progressive manner.

For the entire duration of the addition, the temperature of the reaction medium is maintained at 78°C (±2).

30 Once the addition is completed, the pump is rinsed with 20 g of biperemuted water and the reaction is allowed to continue for 30 minutes at 78°C (±2).

Then 0.10 g of ammonium persulfate dissolved in 25 g of water is added in 30 minutes while maintaining the temperature at 80°C (±2) and the reaction is allowed to continue for 1 hour at 87°C (±2).

An emulsion is thus obtained that contains 32.4% by dry weight of active ingredient, and whose particle size, measured by Dynamic Light Scattering is equal to 99 nm.

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Comparative tests

First, an attempt was made to produce the same polymer as in test 1, but without using AMPS, that is, a polymer consisting of 36.5 per cent by weight of acrylic acid and 63.5%
10 by weight of ethyl acrylate.

To do this, the same protocol as above was used, except for the initial introduction of AMPS. After letting the reaction proceed at 87°C for 1 hour, the formation of a cloudy precipitate in solution was observed, a part of which settled at the level of the axis of the reactor (riprap). The size of the particles formed exceeded 500 nm. The medium, very
15 inhomogeneous and rich in large particles, does not lend itself to handling, and particularly to pumping operations. In addition, storage risks increasing the sedimentation of the product.

A quantity of AMPS greater than 22% by weight of the total mass of the monomers
20 employed was then used according to an operating procedure identical to that described in test No. 1, the copolymer then being constituted, expressed in % by weight of each of its monomers of:

- a) 36.5 % acrylic acid,
- 25 b) 38.5% ethyl acrylate,
- c) 25.0% AMPS.

The formation of insoluble species which precipitated in the medium was then observed.

30 Next, the AMPS (1.2%, weight/weight) was then replaced by another monomer used in ASE and HASE emulsions: ethyl acrylate. The creation of homogeneous emulsions was not realised; the observations are the same as the previous ones, with the formation of a precipitate, the riprap phenomenon and the harmful consequences which result from it.

The AMPS was then substituted (always 1.2% weight/weight) by styrene, lauryl methacrylate, 2-sulfoethyl methacrylate, sodium styrene sulfonate, the sodium salt of 1-allyloxy-2-hydroxypropyl sulfonate (Sipomer COPS 1) for the identical results (presence of insolubles and the riprap phenomenon).

5

Tests No. 2 through 11 according to the invention

Tests No. 2 through 11 concern the synthesis of other emulsions illustrating the invention according to the same operating procedure as described above.

10

Tests Nos. 2-8 illustrate other monomer compositions with an AMPS mass level fixed at 1.2%, while tests Nos. 9-11 illustrate other AMPS levels (a constant mass ratio between ethyl acrylate and acrylic acid was maintained).

15 The characteristics of the emulsions obtained are given in table 1.

Test No.	Monomer composition (% mass)	ES (%)	Particle diameter (nm)
1	1,2 AMPS / 62,4 AE / 36,4 AA	32,4	99
2	1,2 AMPS / 68,7 AE / 30,1 AA	32,8	115
3	1,2 AMPS / 74,6 AE / 24,2 AA	29,6	153
4	1,2 AMPS / 80,4 AE / 18,4 AA	32,2	102
5	1,2 AMPS / 28,35 ABu / 70,45 AA	37,6	287
6	1,2 AMPS / 74,1 AE / 18,4 AA / 6,3 MAM	33,2	96
7	1,2 AMPS / 67,8 AE / 18,4 AA / 12,6 MAM	32,4	106
8	1,2 AMPS / 53,25 AE / 35,8 AA / 9,75 MethC22OE25	33,1	185
9	10 AMPS / 57,9 AE / 32,1 AA	29,6	175
10	15 AMPS / 55,4 AE / 29,6 AA	29,6	215
11	20 AMPS / 52,9 AE / 27,1 AA	29,6	276

Table 1

20 In this table, MethC22OE25 designates a monomer of formula (I) in which R designates the methacrylate function, $m = p = 0$, $n = 25$, and R' refers to a methyl group, EA designates ethyl acrylate, BuA butyl acrylate, MEM methyl methacrylate, AA and MA acrylic and methacrylic acid.

Example 2

- 5 This example demonstrates the thickening power of emulsions according to the invention implemented in water so as to have an active ingredient content of 5% in dry polymer. After introduction in water, the medium is neutralized by the addition of sodium hydroxide at a pH between 4.9 and 5.5, and the Brookfield™ viscosity of the medium is measured at 25°C and 100 RPM, the values of which are reported in table 2

10

Emulsion according to Test No.	Brookfield™ viscosity (mPa.s) of the gel at 5%
1	3320
9	2830
10	1750
11	1310

Table 2

- 15 The thickening character of the emulsions manufactured is thus demonstrated from the moment they are placed under alkaline conditions.

Moreover, it is surprising to note that the thickening effect occurs at such a low pH; usually, emulsions of the ASE and HASE type thicken in a pH ranging from 6 to 7.

- 20 This "low pH" thickening is particularly difficult to obtain, and is quite interesting in the cosmetics domain, where a thickening effect is sought at a pH in the range of the skin, i.e. in a range between 5 and 6 pH units. This is reported in document EP 2 027 169 A1.

25 **Example 3**

This example illustrates the implementation in the formulation of a concrete, of thickening emulsions of the commercial ASE type (containing surfactants) and of an emulsion according to the invention that is free of surfactants.

To do so, a concrete is prepared according to the techniques that are well described in the literature, consisting of:

- 300 kg of CEM I 52.5 N cement;
- 5 - 880 of large 10/20 stones;
- 110 kg of 0/4 sand;

where the water to cement ratio W/C is set at 0.5, and into which is introduced, in relation to the dry weight of the cement:

- 1.23% by weight in the capacity of a dispersant marketed by the COATEX™
- 10 company under the name Ethacryl™ 1030;
- 1% by weight in the capacity of a defoamer marketed by the HUNTSMANN™
- company under the name Empilan PF 7169.

Tests A, B, C and D respectively implement in the formulation of concrete 0.7% by

15 weight in the capacity:

- of an ASE type emulsion containing surfactants and marketed by the COATEX™
- company under the name Viscoatex™ 730;
- of an ASE type emulsion containing surfactants and marketed by the COATEX™
- company under the name Rheocoat™ 35;
- 20 - of a HASE type emulsion containing surfactants and marketed by the COATEX™
- company under the name Rheocoat™ 66;
- of an emulsion according to the invention, which is described in test No. 1.

For each of the tests A, B, C and D, the occluded air was measured according to standard

25 EN 12350-7. The results obtained were 9.5%, 12.0%, 12.5% and 3.0% respectively.

The thickening emulsion according to the invention thus considerably reduces the amount of air introduced into the formulation. In the end, there is thus a more compact product with improved resistance.

CLAIMS

1 - Direct manufacturing process in an aqueous emulsion of a polymer, characterized in that said process involves the polymerization reaction of, expressed in % by weight of
5 each of the monomers:

- a) 20% to 80% by weight of acrylic acid,
 - b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
 - c) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
 - 10 d) 0 to 1% by weight of at least one crosslinking monomer,
- the $\text{total_a} + \text{b} + \text{c} + \text{d}$ being equal to 100%.

or

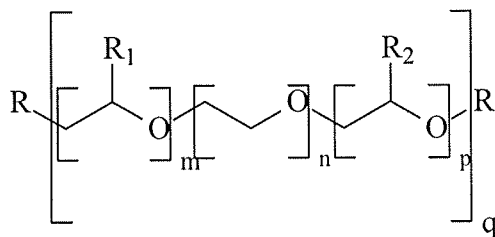
- 15 a) 20% to 80% by weight of acrylic acid,
- b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
- c) 10% to 25% by weight of a monomer containing a hydrophobic group,
- d) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
- e) 0 to 1% by weight of at least one crosslinking monomer,
- 20 the $\text{total_a} + \text{b} + \text{c} + \text{d} + \text{e}$ being equal to 100%,

and in that the aqueous emulsion presents a dry extract that is between 10% and 50% by dry weight of polymer with respect to its total weight

25 2 - Process according to claim 1 characterized in that the ester of (meth)acrylic acid is chosen from ethyl acrylate, butyl acrylate, methyl methacrylate, and their mixtures.

3 - Process according to claims 1 or 2 characterized in that the monomer containing a hydrophobic group has the general formula:

30



where:

- m, n, p and q are integers and m, n, p are less than 150, q is greater than 0 and at least one integer from among m, n and p is non-zero.
 - R contains a polymerizable vinyl function,
 - 5 - R₁ and R₂ are identical or different and represent hydrogen atoms or alkyl groups,
 - R' is a hydrophobic group with at least 6 and not more than 36 carbon atoms.
- 4 - Process according to one of claims 1 to 3 characterized in that the crosslinking monomer is chosen from among ethylene glycol dimethacrylate, trimethylolpropane triacrylate, diallyl phthalate, allyl acrylate, the allyl maleates, methylene-bis-acrylamide, methylene-bis-methacrylamide, tetrallyloxyethane, the triallyl cyanurates, the allylic ethers obtained from polyols.
- 10
- 5 - Process according to one of claims 1 to 4 characterized in that the emulsion has a particle size between 50 nm and 500 nm.
- 15
- 6 - Process according to one of claims 1 to 5 characterized in that the polymer presents a mean molar mass by weight of between 20,000 g/mol and 1,000,000 g/mol.
- 20
- 7 - Process according to one of claims 1 to 6 characterized in that it does not use a surfactant or solvent other than water.
- 8 - Direct aqueous emulsion of a polymer characterized in that it consists of, expressed in % by weight of each monomer:
- 25
- a) 20% to 80% by weight of acrylic acid,
 - b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
 - c) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
 - d) 0 to 1% by weight of at least one crosslinking monomer,

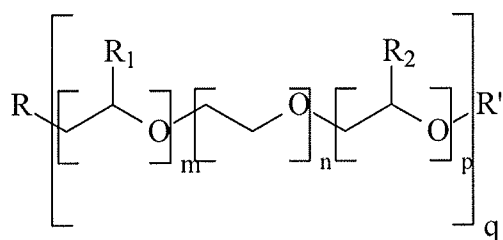
the total $a) + b) + c) + d)$ being equal to 100%.

or

- 5 a) 20% to 80% by weight of acrylic acid,
b) 10% to 90% by weight of at least one ester of (meth)acrylic acid,
c) 10% to 25% by weight of a monomer containing a hydrophobic group,
d) 0.05% to 22% by weight of 2-acrylamido-2-methylpropane sulfonic acid,
e) 0 to 1% by weight of at least one crosslinking monomer,
10 the total a) + b) + c) + d) + e) being equal to 100%,

and in that the aqueous emulsion presents a dry extract that is between 10% and 50% by dry weight of polymer with respect to its total weight

- 15 9 - Emulsion according to claim 8 characterized in that the monomer containing a
hydrophobic group has the general formula:



where:

- 20
- m, n, p and q are integers and m, n, p are less than 150, q is greater than 0 and at least one integer from among m, n and p is non-zero.
 - R contains a polymerizable vinyl function,
 - R₁ and R₂ are identical or different and represent hydrogen atoms or alkyl groups,
 - R' is a hydrophobic group with at least 6 and not more than 36 carbon atoms.

- 10 - Emulsion according to one of claims 8 or 9 characterized in that the crosslinking monomer is chosen from among ethylene glycol dimethacrylate, trimethylolpropane triacrylate, diallyl phthalate, allyl acrylate, the allyl maleates, methylene-bis-acrylamide, methylene-bis-methacrylamide, tetrallyloxyethane, the triallyl cyanurates, the allylic ethers obtained from polyols.

11 - Emulsion according to one of claims 8 to 10 characterized in that it has a particle size between 50 nm and 500 nm.

5 12 - Emulsion according to one of claims 8 to 11 characterized in that the polymer presents a mean molar mass by weight of between 20,000 g/mol and 1,000,000 g/mol.

13 - Emulsion according to one of claims 8 to 12 characterized in that it is free of surfactants and solvents other than water.

10

14 - Use of the emulsion according to one of claims 8 to 13 as a thickening agent of an aqueous formulation.

15 15 - Use according to claim 14 characterized in that said formulation is selected from an aqueous paint, a paper coating dispersion, an aqueous suspension of mineral substances, a detergent, a cosmetic formulation or containing a hydraulic binder, more specifically, a cosmetic formulation to be applied to the skin or a region of the body where the pH is between 5 and 6.

20 16 - Aqueous formulation containing the emulsion according to one of claims 8 to 12, the said formulation being selected from an aqueous paint, a paper coating dispersion, an aqueous suspension of mineral substances, a detergent, a cosmetic formulation, or containing a hydraulic binder, a cosmetic formulation to be applied to the skin or a region of the body where the pH is between 5 and 6.

25