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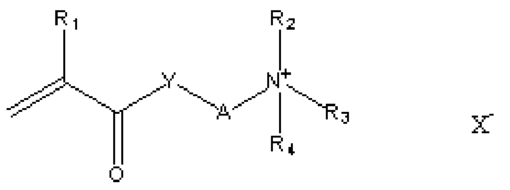
(54) Title: INVERSE EMULSIONS AS THICKENERS FOR COSMETICS



(I)

(57) Abstract: The present invention describes inverse emulsions useful as thickeners wherein the weight ratio between the aqueous phase and the organic phase is from 4:1 and 2:1 and characterised by containing from 20 to 70% by weight of an acrylic polymer obtained by inverse emulsion polymerisation of (i) from 90 to 99.9% by weight of an anionic acrylic monomer containing a strongly acidic functional group; (ii) from 0.1 to 10% by weight of a cationic acrylic monomer of the formula (I) wherein: R_1 is hydrogen or methyl; R_2, R_3, R_4 are, one independently of the others, hydrogen or C_1-C_4 alkyl; Y is NH or O; A is a C_1-C_6 alkylene; X is chloride.

WO 2006/067164 A1

Description

INVERSE EMULSIONS AS THICKENERS FOR COSMETICS.

[0001] The present invention relates to inverse emulsions useful as thickeners in cosmetic formulations and to the procedure for their preparation.

[0002] The inverse emulsions of the invention comprise a polymer obtained by polymerisation of an anionic acrylic monomer containing a strongly acidic functional group (and more specifically a sulfonic functional group), and one or more cationic monomers.

[0003] The inverse emulsions of the invention possess high skin and hair compatibility, which makes them particularly suited for the preparation of cosmetic formulations, and exhibit good thickening properties and stability over time.

[0004] With the expression “cosmetic formulations” we mean the products normally used for personal care, such as body and face creams, hair gels and lotions, hair colouring and bleaching creams, sunscreen compositions, make-up products, cleansing, moisturizing and perspiring fluids and other products for similar applications.

[0005] It is known that a technical problem often encountered in the cosmetic industry is to obtain high viscous formulations (pastes, gels) stable over time and exhibiting high compatibility with skin and hair.

[0006] An essential characteristic of the thickeners employed in cosmetic formulations is to manifest their thickening capability even when used in small amounts, without negatively altering the other properties of the formulations.

[0007] In the specialised literature many methods are reported to regulate the rheological properties of different formulations, often including the use of polymers in the form of inverse emulsion (an inverse emulsion is an emulsion containing both an oil-in-water emulsifier and a water-in-oil emulsifier, wherein the aqueous phase is dispersed in the organic phase in very small drops), but the synthetic thickeners for cosmetics of the present invention are never described.

[0008] We cite as an example:

- EP 503853, wherein an inverse emulsion containing a polymer comprising units deriving from acrylamide, 2-acrylamido-2-methylpropanesulfonic acid and a polyfunctional monomer is described; a disadvantage of the inverse emulsions of EP 503853 is the fact that they contain traces of acrylamide, a toxic substance which is unacceptable by the present European legislative trend;
- US 6,375,959 and US 6,197,287 wherein procedures for the preparation of cross-linked or branched polyelectrolytes based on strongly acidic monomers and other monomers, but not acrylamide, in the form of an inverse emulsion, are described;
- US 6,329,483, wherein copolymers of carboxylic acids and quaternary ammonium compounds and the preparation of gels and emulsions containing the same is described;
- US 2001/0023284, wherein copolymers of a neutral monomer (N-alkylacrylamide) with one or more monomers selected from cationic monomers, monomers bearing strongly acidic functional groups and monomers bearing weakly acidic functional groups are described.

[0009] The Applicant described in its international application PCT/IT03/00389 inverse emulsions for use as thickeners containing an acrylic polymer obtained from the inverse emulsion polymerisation of an anionic acrylic monomer containing a weakly acidic functional group, an anionic acrylic monomer having a strongly acidic functional group and a cationic acrylic monomer.

[0010] It is still desirable in the cosmetic field to have thickeners in the form of stable emulsions that are able to give stable cosmetic formulations, and that, in addition to a good thickening efficiency in different conditions and ease of use, exhibit an improved compatibility with skin and hairs.

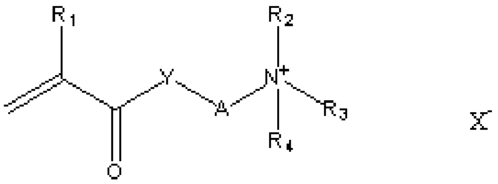
[0011] With the expression “stable emulsion” we mean an emulsion that in the normal storing conditions (from –10°C to 40°C) and for the usual lifetime (180-360 days) does not show phase separation, sediment, formation of floating pellicles and lumps.

[0012] With the expression “stable cosmetic product” we mean a cosmetic formulation that in the above said conditions and lifetime does not show phase separation, sediment, formation of floating pellicles and lumps.

[0013] By cosmetic product with high compatibility with skin and hair we mean a product that is easily absorbed through a keratinous substrate while making changes in the touch, in moisturisation and perspiration, and improving the general sensorial characteristics without altering the physiological pH.

[0014] In developing its research the Applicant has now found that it is possible to obtain excellent results by using in polymerisation exclusively anionic acrylic monomers containing a strongly acidic functional group and at least a cationic monomer of the formula (I)

[0015]



[0016] (I)

wherein:

R_1 is hydrogen or methyl;

R_2, R_3, R_4 are, one independently of the others, hydrogen or C_1-C_4 alkyl;

Y is NH or O;

A is a C_1-C_6 alkylene;

X is chloride.

[0017] The thus obtained inverse emulsions possess a stability which is perfectly suited for their industrial use in cosmetic formulations, even many months after their preparation; furthermore the inverse emulsions of the invention enable the preparation of cosmetic formulations with very good compatibility with skin and hair.

[0018] It is well known that the combined presence of two different functional groups in the same macromolecule, a cationic one and an anionic one, tends to be the cause of coagulation; coagulation can occur both in the step preceding the reaction (when monomers having opposed functionality are mixed together), and while the reaction takes place, during the polymer formation.

[0019] An insufficient distribution of the charges in the macromolecule itself increases its solubility in the oily phase and leads to its desorption from the water phase where the reaction takes place.

[0020] The polymer desorption and its consequent dissolution in the oily phase usually causes the coagulation of the dispersed system and gelation.

[0021] It has now surprisingly been observed that by exclusively using anionic acrylic monomers containing a strongly acidic functional group together with cationic monomers, and operating within the ratio of the present invention, it is still possible to prevent coagulation and gelation.

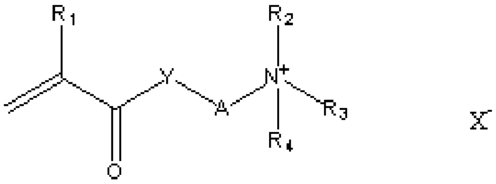
[0022] It is a fundamental object of the present invention an inverse emulsion for the preparation of cosmetic formulations wherein the weight ratio between the aqueous phase and the organic phase is from 4:1 to 2:1 and containing from 20 to 70% by weight of an acrylic polymer obtained by inverse emulsion polymerisation of

(i) from 90 to 99.9% by weight of an anionic acrylic monomer containing a strongly acidic functional group;

(ii) from 0.1 to 10% by weight of a cationic acrylic monomer of the formula (I)

[0023]

[0024]



[0025] (I)

wherein:

R_1 is hydrogen or methyl;

R_2, R_3, R_4 are, one independently of the others, hydrogen or C_1-C_4 alkyl;

Y is NH or O;

A is a C_1-C_6 alkylene;

X is chloride.

[0026] The anionic acrylic monomer containing a strongly acidic functional group is selected among the monomer of this kind that are normally employed for the preparation of polymeric synthetic thickeners for cosmetic use; among those monomers, 2-acrylamido-2-methylpropanesulfonic acid is preferred for the realisation of the present invention.

[0027] Preferably the cationic acrylic monomer of the formula (I) is selected from acryloyloxyethyl-trimethylammonium chloride and methacryloyloxyethyl-trimethylammonium chloride.

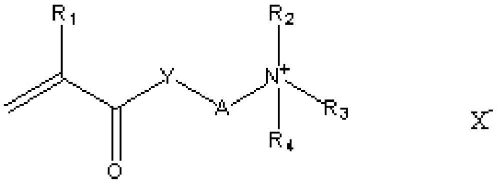
[0028] According to a fundamental aspect of the invention the acrylic polymer obtained by inverse emulsion polymerisation is cross-linked with from 0.01 to 1% by weight of a compound containing two or more ethylenic groups, preferably with methylene-bis-acrylamide.

[0029] It is a further object of the present invention a procedure for the preparation of an inverse emulsion for cosmetic formulations characterised by:

a. preparing a composition consisting of from 40 to 60% by weight of water, and for the remaining weight percentage of a mixture of acrylic monomers consisting of:

(i) from 90 to 99.9% by weight of an anionic acrylic monomer containing a strongly acidic functional group;

(ii) from 0.1 to 10% by weight of a cationic acrylic monomer of the formula (I)



[0030] (I)

wherein:

R_1 is hydrogen or methyl;

R_2, R_3, R_4 are, one independently of the others, hydrogen or C_1-C_4 alkyl;

Y is NH or O;

A is a C_1-C_6 alkylene;

X is chloride;

[0031] b. adding to the composition prepared in a. an aqueous solution of an alkali to adjust the pH between 4 and 7, a cross-linking agent and an initiator of radical polymerisation, maintaining the temperature between 3 and 7°C;

[0032] c. preparing an organic phase containing one or more water-in-oil emulsifiers;

[0033] d. introducing the mixture obtained in b. into the organic phase prepared in c. and emulsifying the two phases by vigorous stirring;

[0034] e. initiating the polymerisation and completing it maintaining the temperature between 55 and 95°C under vigorous stirring;

[0035] f. cooling the reaction mixture to 35-45°C and adding an oil-in-water emulsifier.

[0036] As it was previously said about the inverse emulsion of the invention, the anionic acrylic monomer containing a strongly acidic functional group is selected among the monomers that are normally employed for the preparation of polymeric synthetic thickeners for the cosmetic use; among those monomers, 2-acrylamido-2-methylpropanesulfonic acid is particularly preferred for the realisation of the present invention.

[0037] Preferably the cationic acrylic monomer of the formula (I) is selected from acryloyloxyethyl-trimethylammonium chloride and methacryloyloxyethyl-trimethylammonium chloride.

[0038] In the procedure of the invention, normally, the alkali used is NaOH.

[0039] According to another aspect of the invention, the acrylic polymer obtained by inverse emulsion polymerisation is cross-linked with from 0.01 to 1% by weight of a compound containing two or more ethylenic groups, preferably with methylene-bis-acrylamide.

[0040] Among the initiators of radical polymerisation utilisable for the realisation of the present invention are ammonium, potassium or sodium persulfate, and water-soluble organic peroxides, such as hydrogen peroxide and peracetic acid.

[0041] In the inverse emulsions of the invention the organic phase consists of mineral oils containing saturated hydrocarbons or of vegetable oils or of mixture thereof, having boiling point from 150 to 300°C.

[0042] Preferably the organic phase is a C_{20} hydrogenated polydecene.

[0043] The water-in-oil and the oil-in-water emulsifiers are those normally used for this purpose.

[0044] We cite among the utilisable water-in-oil emulsifiers: sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan monooleate; among the utilisable oil-in-water emulsifiers we cite the linear or branched ethoxylated alcohols.

[0045] To initiate the polymerisation of the acrylic monomers advantageously an aqueous solution of sodium metabisulfite is used.

[0046] The inverse emulsions of the invention may further additionally contain the common additives used in radical polymerisation, by way of example sequestering agents such as sodium diethylenetriaminepentaacetate .

[0047] As it was previously observed, the inverse emulsions of the present invention are particularly suited for the treatment of hair and skin, in body and face creams, hair gels and lotions, hair colouring and bleaching creams, sunscreen compositions, make-up products, cleansing, moisturizing and perspiring fluids.

[0048] In the following examples the preparation of an inverse emulsion according to the invention and of a cosmetic formulation containing it is reported.

[0049] The examples illustrate the present invention without limiting it, or the kind of application of the inverse emulsions.

[0050] Example 1.

[0051] The following ingredients are loaded into a 1.5 l pirex reactor equipped with a steel anchor stirrer:

693 g aqueous solution (50% by weight) of sodium 2-acrylamido-2-methylpropane sulfonate;

3 g ADAMQUAT MC 80 (80% by weight acryloyloxyethyl-trimethyl ammonium chloride sold by Atofina).

[0052] At about 0°C, the following ingredient are slowly added while stirring:

10 g aqueous solution (2% by weight) of methylene-bisacrylamide;

0.5 g aqueous solution (40% by weight) of sodium diethylenetriaminepentaacetate;

5 g aqueous solution (4% by weight) of ammonium persulfate.

[0053] In the meantime, the organic phase is prepared inside a 500 ml beaker adding under stirring:

16.2 g sorbitan monooleate;

204 g C_{20} hydrogenated isodecene.

[0054] The aqueous phase is slowly added into the organic phase and subsequently the mixture is efficiently stirred with a high shear dispersing machine (ultra-turrax IKA).

[0055] The emulsion is then reloaded in the pirex reactor and the reaction is started. The first operation is to insufflate nitrogen directly in the bulk of the product for about 10 minutes. This is a key step, because it enables to lower and control the amount of oxygen dissolved in the emulsion and to adjust the induction times. The second phase takes place only after the emulsion temperature is warmed up to 20°C. After that, 10 g of a 1% by weight aqueous solution of sodium metabisulfite is quickly loaded drop-wise through an addition funnel. The third phase is the radical reaction. The reaction proceeds spontaneously raising gradually the temperature to about 50 °C in 50 minutes. The stirring is maintained as fast as possible and cool water re-circulates inside the reactor jacket. After this period of time the emulsion is heated to 60°C and maintained at this temperature for about one hour to complete the monomers conversion, consuming the residual monomers. Subsequently a cooling down period is required to reach a temperature of 35-40°C. The final step is the addition of 22 g of isotridecylic alcohol 9.5 moles ethoxylated.

[0056] The mixture is rapidly stirred till homogeneity is reached; the final emulsion (Emulsion 1) is then unloaded and stored for at least 24 hours before the evaluation of its properties takes place.

[0057] Properties evaluation of Emulsion 1.

[0058] Samples of Emulsion 1 are stored at different temperatures.

[0059] The emulsion stability is evaluated at different temperatures by visually checking possible phase separation or settling on the bottom of the vessel using a glass stick.

[0060] In the following table (Table 1) the test temperatures and minimal stability times of the emulsion are shown.

Table 1

Temperature	5°C	20°C	45°C
Stability (days)	>360	>180	>30

[0061] The thickening properties are instead evaluated as follows and are shown in Tables 2 and 3.

[0062] A 2% by weight aqueous solution of Emulsion 1 is prepared in deionized water with high stirring in a 1 litre beaker.

[0063] Subsequently the viscosity is measured at 20°C, at different pH values (see Table 2, Brookfield Viscosity in mPa.s, spindle 6, after 24 h).

[0064] The pH was adjusted by additions of an aqueous solution (50%) of citric acid.

Table 2

5 rpm	pH
52000	7,4
50100	7,1
21000	6,7
4500	6,5
950	4,3

[0065] rpm= rounds per minute

[0066] Example 2.

[0067] A viscous facial freshener for dry skins was prepared with Emulsion 1, with the following ingredients:

[0068]

[0069]

[0070]

[0071]

Table 3

Ingredients	%
Phase A	
Water	to 100
Glycerin	2
Euphr officinalis aqua	5
Punica granatum (and) propylene glycol (and) water	1,5
Diazolidinyl urea	0,25
Emulsion 1	1
Phase B	
Persea Gratissma oil	1,9
Bisabolol	0,1
Fase C	
Fragrance	0,1

[0072] Phase A is mixed at room temperature and homogenised using a high shear turbo emulsifier. Phase B is prepared, added to Phase A while stirring with the turbo emulsifier. Phase C is added and the mixture is stirred to homogeneity.

[0073] Features of the obtained cream:

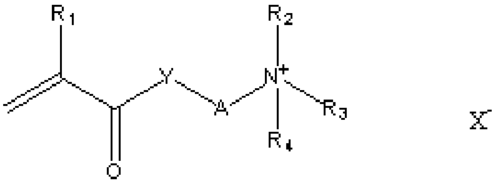
[0074] Viscosity = 12600 mPa.s (5 rpm, 20°C); pH=6.7; Stability= no separation after centrifugation at 6000 rpm for 30 minutes at 25°C

[0075] The product shows high spreadability when used. The stoutness of the product and its long lasting effect helps the active substances absorption

[0076]

Claims

1. Inverse emulsion wherein the weight ratio between the aqueous phase and the organic phase is from 4:1 to 2:1 and characterised by containing from 20 to 70% by weight of an acrylic polymer obtained by inverse emulsion polymerization of
   (i) from 90 to 99.9% by weight of an anionic acrylic monomer containing a strongly acidic functional group;
   (ii) from 0.1 to 10% by weight of a cationic acrylic monomer of the formula (I)



(I)

wherein:

R_1 is hydrogen or methyl;

R_2, R_3, R_4 are, one independently of the others, hydrogen or C_1-C_4 alkyl;

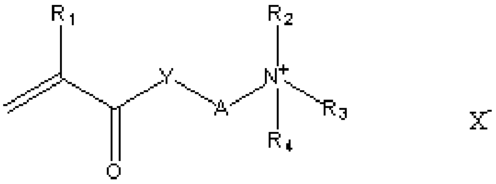
Y is NH or O;

A is a C_1-C_6 alkylene;

X is chloride.

2. Inverse emulsion according to claim 1., wherein the anionic acrylic monomer containing a strongly acidic functional group is 2-acrylamido-2-methylpropanesulfonic acid.
3. Inverse emulsion according to claim 2., wherein the cationic acrylic monomer of the formula (I) is selected from acryloyloxyethyl-trimethylammonium chloride and methacryloyloxyethyl-trimethylammonium chloride.
4. Inverse emulsion according to any of the preceding claims, wherein the acrylic polymer obtained by inverse emulsion polymerisation is cross-linked with from 0.01 to 1% by weight of a compound containing two or more ethylenic groups.

5. Inverse emulsion according to claim 4., wherein the acrylic polymer obtained by inverse emulsion polymerisation is cross-linked with methylene-bis-acrylamide.
6. Procedure for the preparation of an inverse emulsion characterised by:
   a. preparing a composition consisting of from 40 to 60% by weight of water, and for the remaining weight percentage of a mixture of acrylic monomers consisting of:
   (i) from 90 to 99.9% by weight of an anionic acrylic monomer containing a strongly acidic functional group;
   (ii) from 0.1 to 10% by weight of a cationic acrylic monomer of the formula (I)



(I)

wherein:

R_1 is hydrogen or methyl;

R_2, R_3, R_4 are, one independently of the others, hydrogen or C_1-C_4 alkyl;

Y is NH or O;

A is a C_1-C_6 alkylene;

X is chloride;

   b. adding to the composition prepared in a. an aqueous solution of an alkali to regulate the pH between 4 and 7, a cross-linking agent and an initiator of radical polymerisation, maintaining the temperature between 3 and 7°C;
   c. preparing an organic phase containing one or more water-in-oil emulsifiers;
   d. introducing the mixture obtained in b. into the organic phase prepared in c. and emulsifying the two phases by vigorous stirring;
   e. initiating the polymerisation and completing it maintaining the temperature between 55 and 95°C under vigorous stirring;

   f. cooling the reaction mixture to 35-45°C and adding an oil-in-water emulsifier.

7. Procedure for the preparation of an inverse emulsion according to claim 6., wherein the anionic acrylic monomer containing a strongly acidic functional group is 2-acrylamido-2-methylpropanesulfonic acid.
8. Procedure for the preparation of an inverse emulsion according to claim 7., wherein the cationic acrylic monomer of the formula (I) is selected from acryloyloxyethyl-trimethylammonium chloride and methacryloyloxyethyl-trimethylammonium chloride.
9. Procedure for the preparation of an inverse emulsion according to any of the claims from 6. to 8., wherein the acrylic polymer obtained by inverse emulsion polymerisation is cross-linked with from 0.01 to 1% by weight of a compound containing two or more ethylenic groups.
10. Procedure for the preparation of an inverse emulsion according to claim 9., wherein the acrylic polymer obtained by inverse emulsion polymerisation is cross-linked with methylene-bis-acrylamide.
11. Use of an inverse emulsion according to any of the claims from 1. to 5., for the preparation of cosmetic formulations.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2005/057001

A. CLASSIFICATION OF SUBJECT MATTER
C08F220/00

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)
C08F

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.
A	US 2003/223951 A1 (GEARY NICHOLAS WILLIAM ET AL) 4 December 2003 (2003-12-04) the whole document -----	1-11
A	FR 2 802 936 A (SOCIETE D'EXPLOITATION DE PRODUITS POUR LES INDUSTRIES CHIMIQUES SEPPI) 29 June 2001 (2001-06-29) the whole document -----	1-11
A	WO 2004/063228 A (LAMBERTI SPA; POLOTTI, GIANMARCO; BENETTI, ARIANNA; FEDERICI, FRANCO;) 29 July 2004 (2004-07-29) the whole document -----	1-11

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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Date of the actual completion of the international search 16 March 2006	Date of mailing of the international search report 07/04/2006
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2005/057001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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