(12) PATENT ABRIDGMENT (11) Document No. AU-B-24699/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 609897

(54) Title
LYOTROPIC LIQUID CRYSTALLINE COMPOSITIONS

International Patent Classification(s)
(51)⁴ **C09K 019/52**

(21) Application No. : **24699/88** (22) Application Date : **04.11.88**

(30) Priority Data

(31) Number	(32) Date	(33) Country
4974/87	**06.11.87**	**HU HUNGARY**
4975/87	**06.11.87**	**HU HUNGARY**

(43) Publication Date : **11.05.89**

(44) Publication Date of Accepted Application : **09.05.91**

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(56) Prior Art Documents
EP 271375
GB 1439244

(57) Claim

1. A graft lyotropic liquid crystalline composition having a viscosity less than 10 Pa.s. comprising 0.5 to 50% by mass of solid material(s) or the mixture thereof having a surface free energy of 18 to 240 mN/m and a grain size of ∠100 µm, 5 to 55% by mass of surfactant material(s) or the mixture thereof having at least 8 carbon atoms, optionally 0.01 to 40% by mass of polymer the value of a of which - characteristic of the tangly structure and of penetrability by the medium - is at least 0.6 to 67% by mass of water or aqueous solution of non-surfactant materials, 0 to 40% by mass of water immiscible, miscible or partly miscible solvents or the mixture

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thereof, or the water immiscible or partly miscible organic solvent solution of non-surface active materials, 0 to 60% by mass of co-surfactant materials or the mixture thereof and optionally other additives and the total amount of water, water immiscible, miscible or partly miscible solvents and co-surfactant materials used as auxiliary materials is 15 to 94.5% by mass.

11. Process for the preparation of a composition as claimed in Claim 1, comprising grafting the solution or suspension containing, related to the total mass of composition, optionally 0.01 to 40% by mass of polymer the value of a of which - characteristic of the tangly structure and of penetrability by the medium - is at least 0.6, 5 to 55% by mass of surfactant material(s) or the mixture thereof having at least 8 carbon atoms, 0 to 67% by mass of water or the aqueous solution of non-surfactant materials, 0 to 40% by mass of water immiscible, miscible or partly miscible solvents or the mixture thereof, 0 to 60% by mass of co-surfactant material(s) or the mixture thereof and optionally other additives and the total amount of water, water immiscible, miscible or partly miscible solvents and co-surfactant materials used as auxiliary materials is 15-94.5% by mass, with a solid material having a surface free energy of 18 to 240 mN/m and a grain size of < 100 μm.

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

609897

Class

Int. Class

Application Number:
Lodged:

This document contains the amendments made under Section 49 and is correct for printing.

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

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Complete Specification for the invention entitled:

MULTIPHASE SYSTEMS

The following statement is a full description of this invention, including the best method of performing it known to : us

MULTIPHASE SYSTEMS

The invention relates to lyotropic liquid crystalline compositions wherein the formation of liquid crystalline structure is the result of an interaction (grafting) with the solid surface.

It is generally characteristic of the liquid crystalline systems that they contain a large amount of amphipatic molecules (containing both hydrophobic and hydrophilic groups) beside the solvent. For example Moucharafieh and Frieberg ("First comparison between aqueous and nonaqueous lyotropic liquid crystals": Mol. Cryst. Liq. Cryst. 49 Letters 231-238, 1979) describe such regular systems wherein the amount of amphipatic material is 55% by mass if water is used as solvent and more than 45% by mass if ethylene glycol is the solvent (the balance is solvent).

Similar results were obtained in the course of our experiments. A large amount of surfactant material seems to be necessary independently on the ionogenic character of the amphipatic material. According to Tiddy et al. (J. Chem. Soc. Faraday Trans. I. 77 "Structure of liquid-crystalline phase formed by sodium dodecyl sulfate and water as determined by optical microscopy, X-ray diffraction and nuclear magnetic resonance spectroscopy") the sodium dodecyl sulfate (as a typical anionic surfactant material) forms a liquid crystalline system with water in a concentration of > 67% by mass.

In addition to the large amount of the surfactant material further problems arise in connection with the liquid crystalline systems. Heusch ("Flüssig-kristalline Eigenschaften von Tensiden" Proc. VII. Intern. Congr. on Surfactants, Moscow, 1978. pp. 911-940) examined anionic, cationic and non-ionic surfactants and found that the viscosity (measured by Höppler viscosimeter) of systems having lyotropic liquid crystalline structure exceeded the upper measuring limit of the viscosimeter (= 50,000 mPa.s). The system having such high viscosity cannot be used in the practice or they are applicable only in some extreme fields, e.g. as cleaning gel.

A lot of efforts has been made to develop liquid crystalline system having a surfactant content below the lower limit of the above mentioned concentration range of 45 - 70% by mass. The common feature of these compositions is that they contain another amphipatic material, called co-surfactant, capillaractive material or amphiphil, next to the surfactant. Danielson investigates ("The association of alkyl-chain salts in apolar media", Proc. VII. Intern. Congr. on Surfactants, Moscow, 1978. pp. 1010-1037), after Ekwall, systems containing sodium octanoate as surfactant material in an amount of 6 - 27% by mass, 5 - 33% by weight of water and decanol as co-surfactant in an amount of 70 - 95% by mass. Regarding that the decanol is a transition between the surfactant and co-surfactant materials, the result obtained is not surprising. James and Heathcock arrive at the same conclusion ("Electron and optical microscopy study of the lamellar mesophase region of the water /sodium octanoate/ decanol ternary system", J. Chem. Soc. Faraday Trans. I. 77, 2857-2865 1981).

The formation of liquid crystalline structure is very advantageous as it assures the thermodynamic stability of the composition and the sedimentation stability of the material dispersed therein. The advantageous properties of the known liquid crystalline systems, however, cannot be utilized partly due to economic reasons (attributed to the high concentration of the surfactant and/or co-surfactant materials), partly due to the extremely high viscosity (several hundred thousand mPa.s) of these compositions.

The aim of our invention is to obtain liquid crystalline systems which can assure the liquid crystalline structure by the use of a relatively low amount of surfactant and/or co-surfactant material and the viscosity of which does not exceed the value of 10 Pa.s applicable in practice. Further aim of our invention is to obtain such liquid crystalline system the crystalline structure of which is locally maintained for a long time upon dilution.

It has been found that a liquid crystalline structure can be formed using a significantly lower amount of surfactant and/or co-surfactant materials compared to the known liquid crystalline systems containing surfactant materials, optionally co-surfactant materials and/or another solvent immiscible and/or partially miscible and/or totally miscible with the solvent, if the mixture (or solution or dispersion) of the aforementioned materials is grafted with a solid material having a surface free energy of 18 to 240 mN/m and preferably a grain size of <100 /um. Surprisingly it has been found that the viscosity of liquid crystalline system obtained by grafting is considerably lower than that of the conventional lyotropic systems. It has been found further that the lyotropic liquid crystalline layer is maintained for a long period after the dilution of the system and the decomposition thereof is slow if the system contains a polymer in an amount of 0.01 - 40% by mass and which polymer is in a relative stretched state and is partly or totally penetrable by the medium: $\underline{a} > 0.6$.

The amount of the solid grafting material is between 0.5 and 50% by mass.

The penetrability of said polymer (i.e. the rate of its tangly structure can be characterized by the $\underline{a}$ exponent of Kuhn, Mark, Houwink' relation existing between the intrinsic viscosity and the molar mass (see Rohrsetzer, S: Colloidal Chemistry, Textbook Publisher, 1986 and Shaw, D. J.: Introduction into the Colloidal and Surface Chemistry, Technical Publisher, 1986).

The liquid crystalline composition according to the invention is characterized in that it contains 0.5 to 50% by mass of solid material(s) or the mixture thereof having a surface free energy of 18 to 240 mN/m and a grain size of $<$ 100 /um, 5 to 55% by mass of surfactant material(s) or the mixture thereof having at least 8 carbon atoms, optionally 0.01 to 40% by mass of polymer the value of a of which - characteristic of the tangly structure and of penetrability by the medium - is at least 0.6, 0 to 67% by mass of water or aqueous solution of non-surfactant materials, 0 to 40% by mass of water immiscible, miscible or partly miscible solvents or the mixture thereof or the water immiscible or partly miscible organic solvent solution of non-surfactant materials, 0 to 60% by mass of co-surfactant materials or the mixture thereof and optionally other additives and the total amount of water, water immiscible, miscible or partly miscible solvents and co--surfactant materials used as auxiliary materials is 15 to 94.5% by mass.

The composition according to the invention may be prepared by grafting the solution or suspension containing, related to the total mass of composition, optionally 0.01 to 40% by mass of polymer the value of a of which - characteristic of the tangly structure and of penetrability by the medium - is at least 0.6, 5 to 55% by mass of surfactant material(s) or the mixture thereof having at least 8 carbon atoms, 0 to 67% by mass of water or the aqueous solution of non-surfactant materials 0 to 40 % by mass of water immiscible, miscible or partly miscible solvents or the mixture thereof, 0 to 60% by mass of co--surfactant material(s) or the mixture thereof and optionally other additives and the total amount of water, water immiscible, miscible or partly miscible solvents and co-surfactant materials used as auxiliary materials is 15 to 94.5% by mass, with a solid material having a surface free energy of 18 to 240 mN/m and a grain size of ≤ 100 μm.

The material having a surface free energy of 18 to 240 mN/m may be prepared in the system in situ.

Alternatively the composition according to the invention may be prepared by carrying out the dissolution of the auxiliary materials and/or co-surfactants and the grafting with the solid materials simultaneously.

According to the invention the following surfactants can be used:

Anionic materials: carboxylic acid salts, e.g. fatty acid soaps; sulfates, e.g. alkyl sulfates, preferably sodium dodecyl sulfate; sulfonic acid salts, e.g. alkyl benzene-sulfonates; phosphates, e.g. alkyl phosphates and their salts; esters of ethoxylated fatty alcohols prepared with inorganic acids, preferably with sulfuric acid, phosphoric acid, and their salts, etc.

Cationic materials: ammonium salts, e.g. cetyl-trimethyl-ammonium halides; quaternary nitrogen compounds, e.g. N--alkyl pyridinium salts; alkyl amines or the salts of alkyl amides - ethylene oxide adducts, e.g. ethoxylated coconut fatty acid amide.

Non-ionic materials: fatty acid esters of polyhydric alcohols, ethoxylated-dianhydrosorbitol-stearates, o-phosphoric acid--trialkyl esters; ethyleneoxide adducts, e.g. fatty acid - polyethylene glycol esters, fatty alcohol - ethylene oxide adducts, adducts of alkyl phenols and ethylene oxide, preferably alkyl phenol -polyglycol ether; adducts of alkyl amines or alkyl amides with ethylene oxide; adducts of polypropylene glycols with ethylene oxide; o-phosphoric acid triesters of alkyl polyethylene glycol ethers, etc.

Amphoteric materials: preferably internal salts of betains or phosphoric acid derivatives formed with choline.

In the compositions according to the invention the following solvents may be used: water, aliphatic and/or aromatic solvents, e.g. mineral oils, low molecular ketones, mono- or polyhydric alcohols and ethers; vegetable and animal oils, saturated or unsaturated carboxylic acid having 1 to 6 carbon atoms or unsaturated carboxylic acids having more than 6 carbon atoms.

As co-surfactants alcohols, ketones and esters containing one or more polar groups; fatty alcohols, e.g. iso-octanol, dodecanol may be used.

As polymer polyelectrolytes, neutral polymers, natural macromolecules and derivatives thereof, polypeptides having an <u>a</u> value higher than 0.6, may be used.

As solid material having a surface free energy of 18 to 240 mN/m natural material, e.g. quartz, anatase; synthetic materials, e.g. plastic materials, basic materials of paints, etc. may be used. If the solid materials used possess biological activity, the composition according to the invention may preferably be used in the field of human and veterinary therapeutics and plant protection.

The results given in the following Examples have been obtained by using the following two methods:

- the liquid crystalline structure of the compositions has been proved by polarizing microscope using crossed polarizer and analyzer, gypsum I red plate;
- the degradation of structure after dilution has been followed by measuring the quantity of the released surfactant material. The degradation has also been followed by a comparative method, i.e. measuring the surface tension of the diluted composition according to the invention and that of a composition diluted to the same concentration but containing no grafting material, as a function of time.

It has been found that in each case the amount of the surfactant remaining back on the surfac of the solid material exceeds the rate of the adsorption by several orders of magnitude. This is proved by the difference between the measured surface tension values and by the change of the surface tension in time. We have found that the liquid crystalline layer adhered to the solid surface influences advantageously the aggregation and sedimentation stability of the solid material.

The following non-limiting Examples illustrate the compositions according to the invention.

Example 1

Sodium dodecyl sulfat	27% by mass
Water	53% by mass
PVC K70 powder (47 mN/m; grain size d=20-50 μm)	20% by mass

(η = 2.03 Pa.s)

The above composition shows a liquid crystalline structure at 33.75% by mass surfactant content, related to the liquid phase, proved by polarizing microscope. The known system containing sodium dodecyl sulfate shows liquid crystalline structure at a sodium dodecyl sulfate concentration above 67% by mass.

Example 2

Nonyl phenol polyglycol ether (10 EO)	30% by mass
Water	60% by mass
Anatase (85 mN/m; d= 12-20 μm)	10% by mass

(η = 1.18 Pa.s)

The above composition shows a lyotropic liquid crystalline structure at 33.33% by mass of surfactant content (related to the liquid phase), proved by polarizing microscope. According to literature data the nonyl phenol polyglycol ether (10 EO) forms a liquid crystalline structure in water at a concentration of 55% , according to our experiment at a concentration of 58% by mass.

Example 3

Ethoxylated anhydrosorbitol monostearate	32.5% by mass
Lead (240 m/Nm; d = 10 - 75 μm)	0.5% by mass
Water	67% by mass

(η = 1.67 Pa.s)

The above composition shows a liquid crystalline structure at 32.7% by mass of surfactant related to the medium, which is proved by microscope. The surfactant forms liquid crystalline structure without grafting at a concentration above 40% by mass.

Example 4

Sodium dodecyl sulfate	51% by mass
Water	29% by mass
Polytetrafluorethylene (PTFE) (Teflone ^{R}) (18 mN/m; d = 5-8 μm)	20% by mass

(η = 2.17 Pa.s)

The sodium dodecyl sulfate forms a liquid crystalline structure in water at a concentration $>$ 67% by mass, while the above composition shows the requested liquid crystalline structure at a concentration of 63.7% by mass.

Example 5

Ethoxylated C_{12}-C_{16} fatty alcohol (EO=4)	20% by mass
Water	32% by mass
n-Hexadecane	8% by mass
Quartz (120 mN/m; d = 1-5 μm)	40% by mass

(η = 2.70 Pa.s)

The system used as control contains 40% by mass of above ethoxylated fatty alcohol, 50% by mass of water and 10% by mass of n-hexadecane. The above composition contains 33.3% by mass of surfactant 53.3% by mass of water and 13.3% by mass of n-hexadecane, related to the liquid phase. The liquid crystalline structure can be proved by microscope.

Example 6

Sodium dodecyl sulfate	20% by mass
N-dodecyl alcohol	20% by mass
n-Dodecane	20% by mass
Water	20% by mass
PVC K70 powder (47 mN/m; d = 20-56 μm)	20% by mass

(η = 1.13 Pa.s)

The system without grafting shows the liquid crystalline structure at the following composition: 40% by mass of sodium dodecyl sulfate, 20% by mass of n-dodecyl alcohol, 20% by mass of n-dodecane, 20% by mass of water. The above composition according to the invention contains only 20% by mass of each mentioned component. The liquid crystalline structure is proved in both cases by microscope.

Example 7

Ethoxylated anhydrosorbitol monostearate	5% by mass
Sodium dodecyl sulfate	5% by mass
Ethanol	40% by mass

n-Hexanol	5% by mass
n-Dodecanol	5% by mass
Quartz (120 mN/m; d = 1-5 μm)	40% by mass

(η = 2.18 Pa.s)

The composition of the system without grafting and having a liquid crystalline structure is as follows: 20% by mass of ethoxylated anhydrosorbitol monostearate, 13% by mass of sodium dodecyl sulfate, 10% by mass of n-hexanol, 10% by mass of dodecanol and 47% by mass of ethanol. The above composition(calculated for the liquid phase) contains 8.3% by mass of each surfactant and co-surfactant and 66.7% by mass of ethanol. Both structures are proved by microscope.

Example 8

Cetyl-trimethylammonium bromide	35% by mass
Water	45% by mass
Quartz (120 mN/m; d = 1-5 μm)	20% by mass

(η = 0.59 Pa.s)

The cetyl-trimethylammonium bromide forms in water liquid crystalline structure at a concentration of 56% by mass, while the above composition forms the lyotropic system at a concentration of 43.7% by mass, calculated for the liquid phase.

Example 9

Ethoxylated anhydrosorbitol tristearate	10% by mass
Isooctanol	60% by mass
Ethylene glycol	10% by mass
Anatase (85 mN/m, d = 12-20 μm)	20% by mass

(η = 1.76 Pa.s)

The ethoxylated anhydrosorbitol tristearate forms liquid crystalline phase in the mixture of isooctanol and ethylene glycol only at the concentration of 40% by mass. The above composition contains 12.5% by mass of surfactant calculated for the liquid phase.

Example 10

Ethoxylated anhydrosorbitol tristearate	3% by mass
Sodium dodecyl sulfate	3% by mass
Water	20% by mass
n-Dodecanol	24% by mass
Quartz (120 mN/m; d = 1-5 μm)	50% by mass

(η = 1.28 Pa.s)

The mixture of sodium dodecyl sulfate and ethoxylated anhydrosorbitol tristearate (1:1) forms a lyotropic liquid crystalline system with water in the presence of n-dodecanol without grafting with quartz only at a concentration of $>$ 24% by mass.

Example 11

Ethoxylated castor oil (EO=35)	20% by mass
Calcium dodecyl benzenesulfonate	35% by mass
n-Butanol	25% by mass
Paraffin oil (pharmacopeia)	10% by mass
PTFE (18 mN/m; d = 5-8 /um)	10% by mass

(η = 0.78 Pa.s)

The above composition has a liquid crystalline structure, which is proved by microscope. A composition without PTFE forms only a regular structure if the amount of the ethoxylated castor oil is increased by 10% by mass.

Example 12

Ethoxylated anhydrosorbitol tristearate	10% by mass
Water	10% by mass
Cholesterol	5% by mass
n-Dodecane	50% by mass
Anatase (85 mN/m; d = 12-20 /um)	15% by mass

(η = 1.59 Pa.s)

The cholesterol is added to the system dissolved in the water. The composition is a lyotropic liquid crystal showing under the microscope a lamellar liquid crystalline structure.

Example 13

Ethylene oxide-propylene oxide block oligomer (corresponding to the typ of Genapol PF 10)	13% by mass

Water	65% by mass
Coffein	7% by mass
Polyethylene (21 mN/m; d = 10-30 /um) (η = 1.5 Pa.s)	15% by mass

The coffein is dissolved in the water and the other ingredients are admixed in this solution. The composition thus obtained shows under microscope a radially arranged lyotropic liquid cristalline structure.

Example 14

Ethoxylated anhydrosorbitol tristearate	10% by mass
Water	20% by mass
Cholesterol	5% by mass
n-Dodecane	30% by mass
Butyl acetate	20% by mass
Anatase (85 mN/m; d = 12-20 /um)	15% by mass

The cholesterol is dissolved in the mixture of n-dodecane and butyl acetate and the solution thus obtained is added to the system. The composition obtained is a lyotropic liquid crystal showing under the microscope a lamellar lyotropic liquid crystalline structure.

Example 15

Sodium dodecyl sulfate	25% by mass
Water	54% by mass
Polyvinylpyrrolidone (M = 25,000; a = 0.85)	1% by mass
PVC K70 powder (47 mN/m; d = 20-56 /um)	20% by mass

Example 16 (counter Example)

Sodium dodecyl sulfate	25% by mass
Water	54% by mass
Polyvinylpyrrolidone ($M = 1 \times 10^6$, $a = 0.52$)	1% by mass
PVC K70 powder (47 mN/m; d = 20-56 µm)	20% by mass

Both compositions are lyotropic liquid crystals, but the composition of the counter Example does not show a liquid crystal layer bound to the solid particles after a dilution with water to a concentration of 5% by mass. In case of the composition of Example 25, diluted to the same concentration, however, 65% of the surfactant remains bound 60 minutes after the dilution.

Example 17

Ethoxylated anhydrosorbitol monostearate	5% by mass
Water	44.99% by mass
Poly(L) glutamic acid ($M = 10{,}000$, $a = 1.115$)	0.01% by mass
Quartz (120 mN/m; d = 1-5 µm)	50% by mass

The above composition is a lyotropic liquid crystal, the adhered layer contains the 28% of the starting tenzide after 60 minutes.

Example 18

Nonyl phenol polyglycol ether (EO = 10)	10% by mass
Water	40% by mass
Polyethylene oxide ($M = 1{,}000$, $a = 0.82$)	40% by mass
PTFE (18 mN/m; d = 5-8 µm)	10% by mass

Example 19 (counter Example)

Nonyl phenol polyglycol ether	10% by mass
Water	40% by mass
Polyethylene oxide (M = 1,000, a = 0.82)	40% by mass
PTFE (18 mN/m; d = 5-8 μm)	10% by mass

In case of the composition of Example 18 the adhered layer contains the 72% of the surface tension reducing components after 60 minutes a 20-fold dilution with water, while the composition according to the counter Example retains only less than 10% of the surfactant.

Example 20

Octadecyl trimethylammonium bromide	16% by mass
Water	50% by mass
Polyethylene oxide (M = 1,000, a = 0.82)	25% by mass
Polyvinylalcohol (M = 18,000, a = 0.77)	5% by mass
Isopropanol	4.5% by mass
Lead (240 mN/m; d = 10-76 μm)	0.5% by mass

The composition is a liquid lyotropic crystal. In the diluted system (5 ml composition dispersed in 100 ml water) the amount of the bound surfactant material is 65% 60 minutes after the dilution.

Example 21

Ethoxylated C_{12}-C_{16} fatty alcohol (EO=15)	15% by mass
Water	67% by mass
Polyacrylic acid sodium salt (M = 25,000, a=1.08)	5% by mass
Anatase (85 mN/m; d = 12-20 μm)	13% by mass

The composition is a lyotropic liquid crystal. In the diluted system (5 g composition dispersed in 100 ml of water) the amount of the bound surfactant material is 90% 60 minutes after the preparation.

Example 22

Ethoxylated anhydrosorbitol monostearate	9.5% by mass
Water	40% by mass
Isopropanol	20% by mass
Ethylene glycol	20% by mass
Polyvinylalcohol (M = 78,000, a = 0.77)	0.25% by mass
Polyvinylpyrrolidone	0.25% by mass
PVC K70 powder (47 mN/m; d = 20-56 /um)	10% by mass

The composition is a lyotropic liquid crystal which retains the 55% of the surfactant material 60 minutes after 3-fold dilution with water.

Example 23

Ethoxylated castor oil (EO = 35)	15% by mass
n-Hexanol	40% by mass
n-Dodecanol	20% by mass
n-Dodecane	20% by mass
Polyethylene imine (M = 12,000, a = 0.89)	2% by mass
Quartz (120 mN/m; d = 1-5 /um)	3% by mass

The composition is a lyotropic liquid crystal. 60 minutes after a 20-fold dilution with water the 30% of the surfactant material remains adhered to the solid surface.

Example 24

Sodium dodecyl sulfate	51% by mass
Water	42% by mass
Polyacrylic acid (M = 50,000, a = 0.91)	0.25% by mass
Oligodextrane (M = 2,000, a = 0.60)	0.25% by mass
PVC K70 powder (47 mN/m; d = 20-56 µm)	6.5% by mass

The composition is a lyotropic liquid crystal. 60 minutes after a 20-fold dilution with water the 25% of the surfactant remains bound.

Example 25

Ethoxylated anhydrosorbitol tristearate	20% by mass
Water	40% by mass
Polyacrylamide (M = 10,000, a = 0.84)	10% by mass
Quartz (120 mN/m; d = 1-5 µm)	20% by mass

The composition is a lyotropic liquid crystal. 60 minutes after a 20-fold dilution the 70% of the surfactant remains bound.

Example 26

Ethoxylated tallow amine (EO = 25, amine value : 0.75)	10% by mass
Water	49.5% by mass
Polyacrylamide (M = 5 x 10^6, a = 0.80)	0.5% by mass
Quartz (120 mN/m; d = 1-5 µm)	40% by mass

The composition is a lyotropic liquid crystal. 60 minutes after a 20-fold dilution with water the 92% of the surfactant remains bound.

Example 27

Ethylene oxide - propylene oxide block oligomer (corresponding to the typ of Genapol PF 10)	10% by mass
Water	68% by mass
Coffein	5% by mass
Oligodextrane (M = 2,000, a = 0.6)	2% by mass
Polyethylene (21 mN/m; d = 30 μm)	15% by mass

The composition is a lyotropic liquid crystal. The lyotropic structure remains on the surface of the solid material after a 6-fold dilution with water. 60 minutes after the dilution the 55% of the surfactant is in a bound state. When preparing the composition the aqueous solution of coffein was used as starting material.

Example 28

Ethoxylated anhydrosorbitol tristearate	10% by mass
Ethylene glycol	20% by mass
Dodecane	50% by mass
Cholesterol	5% by mass
Polyethylene oxide - propylene oxide (M = 10,000, a = 0.84)	5% by mass
Anatase (85 Mn/m; d = 12-30 μm)	10% by mass

When preparing the composition the aqueous solution of cholesterol was used as starting material. Under microscope the composition shows a lamellar lyotropic structure. After dilution with water (1 : 25) the bound structure remains on the surface of the particles. 60 minutes after the dilution the 40% of the surfactant is bound.

Example 29

Ethoxylated anhydrosorbitol tristearate	10% by mass
Ethylene glycol	20% by mass
Dodecane	50% by mass
Cholesterol	5% by mass
Polyethylene oxide - propylene oxide (M = 10,000, a = 0.84)	5% by mass
Anatase (85 mN/m; d = 12-30 μm)	10% by mass

When preparing the composition the ethylene glycol solution of cholesterol was used as starting material. Under microscope the composition shows a lamellar lyotropic structure. After dilution with water (1 : 25) the bound structure remains on the surface of the particles. 60 minutes after the dilution the 40% of the surfactant is bound.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A graft lyotropic liquid crystalline composition having a viscosity less than 10 Pa.s. comprising 0.5 to 50% by mass of solid material(s) or the mixture thereof having a surface free energy of 18 to 240 mN/m and a grain size of $<$100 μm, 5 to 55% by mass of surfactant material(s) or the mixture thereof having at least 8 carbon atoms, optionally 0.01 to 40% by mass of polymer the value of a of which - characteristic of the tangly structure and of penetrability by the medium - is at least 0.6 to 67% by mass of water or aqueous solution of non-surfactant materials, 0 to 40% by mass of water immiscible, miscible or partly miscible solvents or the mixture thereof, or the water immiscible or partly miscible organic solvent solution of non-surface active materials, 0 to 60% by mass of co-surfactant materials or the mixture thereof and optionally other additives and the total amount of water, water immiscible, miscible or partly miscible solvents and co-surfactant materials used as auxiliary materials is 15 to 94.5% by mass.

2. A composition as claimed in Claim 1, comprising a water soluble polymer in an amount of 1 to 40% by mass.

3. A composition as claimed in Claim 1, comprising a ~~the~~ mixture of non-ionic polymers the total amount of which is 0.5 to 30% by mass.

4. A composition as claimed in Claim 1, comprising totally dissociated ionic polymer in an amount of 0.01 - 5% by mass.

5. A composition as claimed in Claim 1, comprising partly dissociated water soluble polymer(s) or the mixture thereof in an amount of 0.5 to 20% by mass.

6. A composition as claimed in Claim 1, comprising ~~the~~ a mixture of non-ionic polymers in an amount of 0.5 - 20% by mass.

7. A composition as claimed in Claim 1, comprising non-ionic surfactant material(s) or the mixture thereof in an amount of 5 to 35% by mass as surfactant material.

8. A composition as claimed in Claim 1, comprising ionic surfactant material(s) or the mixture thereof in an amount of 20 to 51% by mass as surfactant material.

9. A composition as claimed in Claim 1, comprising ~~the~~ a mixture of ionic and non-ionic surfactant materials in an amount of 6 to 55% by mass as surfactant material.

10. A composition as claimed in Claim 1, comprising ~~the~~ a mixture of amphoteric and ionic and/or non-ionic surfactant materials in an amount of 6 to 55% by mass as surfactant material.

11. Process for the preparation of a composition as claimed in Claim 1, comprising

grafting the solution or suspension containing, related to the total mass of composition, optionally 0.01 to 40% by mass of polymer the value of a of which - characteristic of the tangly structure and of penetrability by the medium - is at least 0.6, 5 to 55% by mass of surfactant material(s) or the mixture thereof having at least 8 carbon atoms, 0 to 67% by mass of water or the aqueous solution of non-surfactant materials, 0 to 40% by mass of water immiscible, miscible or partly miscible solvents or the mixture thereof, 0 to 60% by mass of co-surfactant material(s) or the mixture thereof and optionally other additives and the total amount of water, water immiscible, miscible or partly miscible solvents and co-surfactant materials used as auxiliary materials is 15-94.5% by mass, with a solid material having a surface free energy of 18 to 240 mN/m and a grain size of < 100 µm.

12. Process as claimed in Claim 11, wherein the solid material having a surface free energy of 18 to 240 mN/m and a grain size of < 100 µm, is prepared in situ in the system.

13. Process as claimed in Claim 11, wherein the dissolution of the auxiliary material(s) and the grafting with the solid material is carried out simultaneously.

DATED this 3rd day of November 1988.
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