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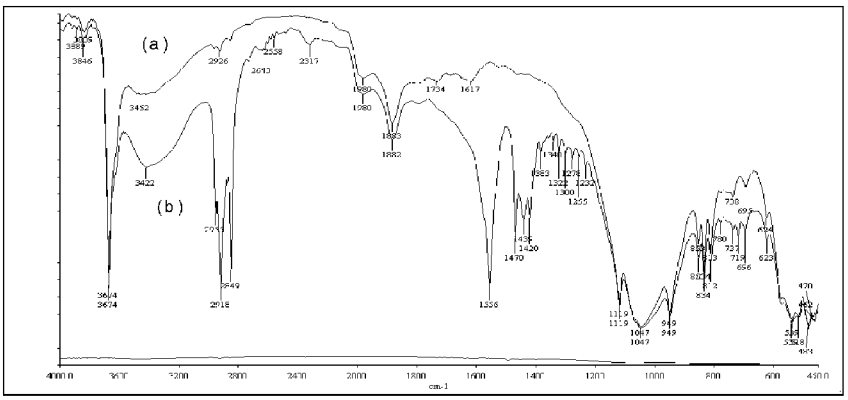
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(54) Title: A PROCESS TO PREPARE A CLAY DERIVATIVE

Figure 1/4



(57) Abstract: This invention relates to a process to prepare fatty acid derivatives of certain selective clay particles. These derivatised clay particles are useful in many applications especially as emulsifier particularly in personal cleansing compositions. It is an object of the invention to provide an alternative process suitable for derivatising the clay particle with fatty acids which salts are substantially water insoluble which the present inventors have found are not viable by the process in aqueous media. It has been found that reacting an asymmetric 1:1 or 2:1:1 clay particles having alternating tetrahedral and octahedral sheets terminating with a tetrahedral sheet at one external surface plane and an octahedral sheet at another external surface plane, with a fatty acid, a fatty acid chloride or derivatives thereof in the presence of an organic solvent solves the problem.

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A PROCESS TO PREPARE A CLAY DERIVATIVE

Technical Field

This invention relates to a process to prepare fatty acid derivatives of certain selective clay particles. These derivatised clay particles are useful in many applications especially as emulsifier particularly in personal cleansing compositions.

Background and Prior Art

Cleansing compositions have been formulated with detergent actives for ensuring the cleansing action. Popular detergent actives which have been used are soaps and synthetic surfactants. Soaps are salts of fatty acid of which alkali metal salts have been more commonly used. Synthetic surfactants are usually made from materials of petroleum origin. Synthetic surfactants are classified into anionic, cationic, non-ionic, amphoteric and zwitterionic classes. All of the above classes have been included in personal cleansing compositions. Popular synthetic surfactants include primary alcohol sulphates (PAS), alkylbenzene-sulphonates (LAS), sulphates of ethoxylated aliphatic alcohols containing 1-12 ethyleneoxy groups, Sodium Lauryl ethoxy sulphate (SLES), the reaction product of fatty acids esterified with isethionic acid and neutralised with alkali, alkyl betaines (e.g. Cocobetaine), alkyl amidopropylbetaines (e.g. Coco amidopropyl betaine - CAPB), sorbiton mono stearate, sorbiton mono oleate, ethoxylated SLES, Cetyl trimethyl ammonium halide among a host of other surfactants, many of which are commercially available under various brand names.

Many of the above mentioned soaps and synthetic surfactants are expensive. It is believed that the surfactants are not effectively utilised and there is scope for better utilisation, thereby reducing wastage and cost to both the manufacturers and the consumers. Further, conventional surfactants mentioned above are believed to be non-biodegradable and therefore a burden to the environment. Thus, development of alternative surface active materials which are more environmentally friendly will be welcomed not only by the Governments but by the manufacturers and consumers at large. Conventional surfactants are also perceived by some consumers to be harsh on the skin, to leave an unpleasant feel on the skin and have problems with ease of rinsing. Thus, there is a need for providing milder, more skin friendly and easily rinseable detergent actives in personal cleansing compositions.

Certain highly absorbent materials like clay e.g. bentonite, attapulgite, kaolinite etc which are known to absorb oils have been used in cleansing compositions, but have had limited usefulness when incorporated in personal cleansing compositions.

There has been further work on functionalising particulate material. Examples of design and synthesis of such particles using the above strategy are described in a review by Perro et al, J. Material Chem., 2005, 15, p3745-3760. One of the approaches used in the past is disclosed in US4715986 (Th. Goldschmidt AG, 1987) which describes particles for stabilizing or destabilizing emulsions of a size less than 100 microns, comprising fragments having on one side thereof hydrophilic group and on the other side thereof hydrophobic groups such that the hydrophilic and the hydrophobic groups are anisotropically distributed in a non-statistical manner. One of the methods for obtaining such fragments is by communition of hollow microspheres. In all the methods that are described, precursor materials have homogeneous distribution of surface groups, e.g. silica, alumina, hollow

microspheres, microgel, carbon and starch. Thus, particles are disclosed in this publication are formed by breaking particles that are uniformly tagged on the outside into pieces, thereby providing particle fragments that contain a reacted surface (the former outside) and an unreacted surface (the former inside). The drawbacks of these particles and the method to produce them is that the surface reaction to the particles as disclosed will be uniform, not limited to one of the external surface planes, which causes un-necessary binding on sites where no binding is required and therefore loss of chemicals. Also the tags on some sites will be bound stronger and more reactive/functional than other sites. Additionally there will be a wide variety of particles present in the mixture of smashed particles, some bipolar, some with no reacted surface at all. Processes starting with asymmetric particles such as 1:1 clays are not described, while particles tagged by selective surface reaction remain to be desired.

US 3211565 relates to hydrophobic organophilic particulate matter and discloses particles that made by treating clay particles with an organic diamine, and thereafter reacted with oleic acid. However, the treatment of the clay particle with the diamine, takes away the bipolar character of the particle and cause the reaction with oleic acid to be uniform.

US 5,688,315 discloses particles that are tagged with an oleate. However, the disclosed processes only provide for uniform surface reaction with calcium oleate, leading to homogeneously tagged particles.

The present inventors have been working on solving this problem of providing alternative materials having enhanced surface active properties. They have, during the course of their research, developed novel materials starting from 1:1 or 2:1:1 clays that give the materials enhanced properties by virtue of tailoring

functionalities to selected surfaces of these clay particles. A co-pending Indian Patent Application 668/MUM/2008 discloses the novel particle. It also discloses a process to prepare an embodiment of the novel particle i.e. a specific fatty acid derivatised clay particle. The process disclosed comprises reaction of the clay with a fatty acid in aqueous medium and this process is suitable for derivatisation with fatty acids whose salts are substantially water soluble. Preferred substantially water soluble fatty acids salts which are suitable to derivatise clay by the aqueous route by the process disclosed in said copending application are oleates and laurates. The present invention is an alternative process carried out in a non-aqueous organic solvent media which is especially suitable for derivatising the clay particle with fatty acids whose salts are substantially water insoluble which the present inventors have found are not viable by the process in aqueous media. While the process of the present invention can be used to derivatise clay with fatty acids whose salts are substantially water soluble, the present process is especially suitable for derivatising clays with fatty acids whose salts are generally considered water insoluble. Examples of such fatty acids are palmitic acid and stearic acid.

It is an object of the present invention to provide for a process to prepare a novel material which is an alternative to conventional surfactant.

Summary of the Invention

According to the present invention there is provided a process to prepare a fatty acid derivative of asymmetric 1:1 or 2:1:1 clay particles comprising the steps of

(i) reacting asymmetric 1:1 or 2:1:1 clay particles having alternating tetrahedral and octahedral sheets terminating with

a tetrahedral sheet at one external surface plane and an octahedral sheet at another external surface plane, with a fatty acid, a fatty acid chloride or derivatives thereof in the presence of an organic solvent;

(ii) Filtering the particles from the reaction media and washing them to be substantially free of unreacted reactants; and

(iii) Drying the particles

Detailed Description of the Invention

The present invention relates to process to prepare a fatty acid derivative of specific clay particles which act as a novel material having surface active properties. The material is prepared from precursor particles which are asymmetric 1:1 or 2:1:1 clay particles having alternating tetrahedral and octahedral sheets terminating with a tetrahedral sheet at one external surface plane and an octahedral sheet at another external surface plane. The precursor clay is treated to have bipolar topospecific characteristics which is achieved by having a fatty acid of carbon chain length preferably 10 and higher attached to coordinating cation on one of the exterior surface planes i.e. either the external surface plane having the tetrahedral sheet or the external surface having the octahedral sheet.

The precursor of the treated particle with bipolar topospecific characteristics according to the present invention is an asymmetric 1:1 or 2:1:1 clay particle having alternating tetrahedral and an octahedral sheets terminating with a tetrahedral and an octahedral sheet at exterior surface planes. Particle of 1:1 clay is particularly preferred as precursor.

1:1 clays preferred according to the present invention include kaolinite and serpentine subgroups of minerals. The species

included within kaolinite subgroup are particularly preferred viz. kaolinite, dickite, halloysite and nacrite.

The species included within serpentine subgroup are chrysolite, lizardite, and amesite.

2:1:1 clays preferred according to the present invention include chlorite group of minerals. Chlorite is also referred as 2:2 clay by some mineralogists. The chlorite comprises tetrahedral-octahedral-tetrahedral sheets like 2:1 clays, with extra weakly bound brucite like layer.

The tetrahedral sheet preferably comprises coordinating tetrahedral cation of silicon. The tetrahedral sheet may also comprise isomorphously substituted coordinating tetrahedral cations which are not silicon. Isomorphously substituted coordinating tetrahedral cations include, but are not limited to cations of aluminium, iron or boron.

The octahedral sheet preferably comprises coordinating octahedral cation of aluminium. The octahedral sheet may also comprise isomorphously substituted coordinating octahedral cations which are not aluminium. Isomorphously substituted coordinating octahedral cations include cations of magnesium or iron.

The chemical group is attached to coordinating cations on the exterior side of one of the external surface sheets. Accordingly, the chemical group may be attached to coordinating cations on the exterior side of the tetrahedral sheet. Alternatively, the chemical group is attached to coordinating cations on the exterior side of the octahedral sheet which is the more preferred aspect.

The treated particle prepared by the process of the present invention is believed to have the property of anisotropic

hydrophobicity which is possibly the reason for providing the surface active property responsible for the cleansing action. By anisotropic hydrophobicity is meant that the particle has two spatially distinct exterior faces having distinct surface characteristics wherein one of the distinct exterior faces is relatively more hydrophilic and the other distinct exterior face is relatively more hydrophobic.

The treated particle with bipolar topospecific characteristics of the present invention can be used in cleansing compositions and enables formulation of the treated particles in relatively more stable emulsions as compared to untreated particles at same particle loading. Thus, the treated particles also act as useful emulsifying agent in compositions made from the treated particle prepared as per the process of the invention.

The process of the present invention is used to prepare modified clay particles that are expected to be used as emulsifying agents, to structure water containing systems, as rheology modifiers to modify viscosity characteristics of a system, and as oil removal agents. The derivatised particles prepared by the process of the present invention finds use in formulations ranging from paints, adhesives, inks, oil-well muds, and in personal care formulations. The cost of the derivatised particle of the present invention is low.

Preferred fatty acids which are used for reaction with the clay include lauric, myristic, pentadecanoic, palmitic, palmitoilic, margaric, stearic, oleic, linoleic, linolenic or arachidic acids and derivatives therof. Most preferred fatty acids include lauric, myristic, palmitic, stearic or oleic acid. Similarly the fatty acid chlorides which are preferred for use in the reaction include lauroyl, myristoyl, palmitoyl, heptadecanoyl, stearoyl, or

oleoyl chlorides. Most preferred fatty acid chlorides include lauroyl, myristoyl, palmitoyl or stearoyl chlorides.

The reaction is carried out in the presence of an organic solvent. Preferred organic solvents are those whose Hansen Solubility parameter is in the range of 10 to 30. Preferred organic solvents include benzene, toluene, xylene, ethylbenzene, tetrahydrofuran, di-isopropyl ether, methyl-ethyl ketone, di-methy furan, n-heptane, cyclohexane, ligroin, dimethyl ketone, methanol, ethanol, isopropyl alcohol, n-butanol, n-propyl alcohol, cyclo hexanol, ethylene glycol and ethylene dichloride. More preferred organic solvents are benzene, toluene, xylene, ethylbenzene, cyclohexane, methanol, ethanol, isopropyl alcohol, n-butanol, cyclo hexanol, ethylene glycol and ethylene dichloride

When the process comprises reacting the clay with a fatty acid, the most preferred organic solvent is xylene or isopropyl alcohol. Further, when the process comprises reacting the clay with a fatty acid, it is preferred that the clay is acid treated prior to reacting with said fatty acid. Preferred acid is a mineral acid. Acids which may be contacted with the precursor are preferably selected from sulphuric acid, nitric acid or hydrochloric acid, hydrochloric acid being preferred. Preferred concentrations of acids are in the range of 0.1 to 0.5 N. The acid treated clay is then washed with sufficient amount of water to be made substantially free of free acid.

When the process comprises reacting the clay with a fatty acid chloride, the most preferred organic solvent is toluene. Further, when the process comprises reacting the clay with a fatty acid chloride, it is preferred that the clay is alkali treated prior to reacting with the fatty acid chloride. The alkali used for the treatment is preferably alkali metal hydroxide, carbonate or bicarbonate, preferred alkali metal being sodium or potassium.

Preferred concentration of alkali is from 0.01 to 0.5 N. The alkali treated clay is then washed with sufficient amount of water to be made substantially free of free alkali.

The step of reacting the asymmetric 1:1 or 2:1:1 clay particle with the fatty acid or fatty acid chloride is preferably carried out in the presence of a phase transfer catalyst. Preferred phase transfer catalysts include quaternary ammonium salts. Preferred quarternary ammonium salts useful as phase transfer catalysts are

Tetrabutylammonium chloride; Tetrabutylammonium bromide; tributylmethylammonium chloride; tetrabutylammonium hydrogen sulphate,
tetraethylammonium chloride; tetraethylammonium hydrogen sulphate;
tetraethylammonium bromide; tetrabutylammonium iodide; tetraoctylammonium bromide; tetrakis(decyl)ammonium bromide; tetrahexylammonium bromide; ethylhexadecyldimethylammonium bromide. More preferred phase transfer catalysts are tetrabutyl ammonium bromide, tetra butylammonium chloride and tetrabutyl ammonium hydrogen sulphate and in particular, tetrabutyl ammonium bromide.

The phase transfer catalyst, when used, is preferably present in an amount in the range of 0.1 to 5%, more preferably in the range of 0.3 to 0.7% by weight of the asymmetric 1:1 or 2:1:1 clay particles.

The reaction is preferably carried out at a temperature in the range of 40 to 110 °C, more preferably in the range of 65 to 90 °C. The reaction is preferably carried out for a time of 0.5 to 12 hours, more preferably from 1 to 6 hours, further more preferably 2 to 6 hours. The reaction mixture after the completion of reaction is usually filtered. Filtration is

preferably carried out under vacuum. The filter cake is usually washed to be made substantially free of unreacted reactants. This is preferably done with sufficient amount of methanol and possibly other solvents. The filter cake is then dried preferably in an oven.

The invention will now be illustrated with the help of the following non-limiting examples.

Description of the figures

Figure 1 shows IR Spectra of acid treated kaolinite (a) IR Spectra of palmitic acid derivatised kaolinite as per Example – 1 (b).
Figure 2 shows IR Spectra of acid treated kaolinite (a) IR Spectra of palmitic acid derivatised kaolinite as per Example – 2 (b).
Figure 3 shows IR Spectra of acid treated kaolinite (a) IR Spectra of stearic acid derivatised kaolinite as per Example – 3 (b)
Figure 4 shows IR Spectra of alkali treated kaolinite (a) IR Spectra of stearoyl chloride derivatised kaolinite as per Example – 5 (b)

Examples

Example – 1: Kaolinite derivatised with palmitic acid as per the invention

Kaolinite which is a 1:1 clay was first acid treated as per the following protocol:

Acid treatment protocol:

A ~50% (w/v) dispersion of Kaolinite and ~2% (w/v) Hydrogen peroxide (30%) was heated to about 40-45°C under stirring for about four hours. The reaction mixture was then acidified using 4N HCl to pH 4, refluxed further for an hour. The dispersion was then filtered through a Buchner funnel. The filter cake was washed twice with water and finally filtered and washed till the filtrate

was found to be neutral . The treated Kaolinite was then dried at 80°C for 4 hours till constant weight was reached.

The acid activated Kaolinite (10 grams) was taken along with 2 g of sodium hydroxide in 25 ml methanol and 25 ml Xylene and a phase transfer catalyst (0.05 g) tetra butyl ammonium bromide was added to the reaction mixture and heated to 60 °C. Palmitic acid (6.5 g) dissolved in 25 ml Methanol was then added drop wise to the reaction mixture which was then refluxed for 4 hours at 72°C after which it was cooled to room temperature. The mixture was then filtered, washed with about 50 ml of methanol and further washed three times with 50 ml water till the filtrate had a pH of about 7. The filter cake was then further washed three times with 50 ml methanol and filtered. The filter cake was air dried and then finally dried in oven at about 60°C.

The IR spectra of the derivatised clay as per Example - 1 is shown in Figure - 1. The spectra indicates that a palmitic acid derivative of a 1:1 clay has been prepared by the process of the invention. The derivative is selective in that the fatty acid is appended to the octahedral sheet of the clay particle.

Example - 2: Kaolinite derivatised with palmitic acid as per the invention

An experiment similar to Example - 1 was carried out except that iso propyl alcohol was used instead of xylene. The procedure was as follows:

Kaolinite clay was first acid treated as per the protocol described in Example - 1.

Palmitic acid (0.64 gm) was taken in 50 ml Isopropyl alcohol to which 0.1 gm of sodium hydroxide was added. To this, 0.05gm of the PTC i.e. tetra butyl ammonium bromide in 50 ml, heated to

about 86°C was added, till a clear solution resulted. This was followed by addition of 52.6 g of the acid treated clay. The mixture was then slowly heated to reflux for 5 hours. The reaction mixture was then filtered and washed with 100 ml water two times followed by washing two times with 50 ml methanol and then filtered. The filter cake was then air dried followed by drying in oven at about 55°C for 4 hours.

The IR spectra of the derivatised clay as per Example - 2 is shown in Figure - 2. The spectra indicates that a palmitic acid derivative of a 1:1 clay has been prepared by the process of the invention. The derivative is selective in that the fatty acid is appended to the octahedral sheet of the clay particle.

Example - 3: Kaolinite derivatised with stearic acid as per the invention

Kaolinite clay was first acid treated as per the protocol described in Example - 1.

The acid activated Kaolin (5 g) was taken in 25 ml methanol to which was added 0.9g sodium hydroxide and 25 ml xylene. To this was added 0.025g of the PTC i.e tetra methyl ammonium bromide. The mixture was then heated to about 60°C after which 12.37 g of stearic acid which was dissolved in 25 ml methanol and 25ml xylene was added drop wise and refluxed for 4 hours at about 72°C. The reaction mixture was then cooled to room temperature. The reaction mixture was then filtered, and washed with 25 ml methanol and then with 50 ml water three times till the filtrate attained a pH of about 7. It was then washed three times with 50 ml methanol and then filtered to form a cake which was air dried and finally dried in oven at 60°C.

The IR spectra of the derivatised clay as per Example - 3 is shown in Figure - 3. The spectra indicates that a stearic acid derivative of a 1:1 clay is prepared by the process of the

invention. The derivative is selective in that the fatty acid is appended to the octahedral sheet of the clay particle.

Example – 4: Reaction carried out in aqueous media

Kaolinite particles (about 1 gram) was taken in a 250 ml beaker. After that, 100 ml of 0.1 N hydrochloric acid was prepared and added to the clay particles and stirred for 15 minutes. Sodium hydroxide (0.4 grams) made as a 0.1 N solution was then added and stirred for about 15 minutes. Thereafter sodium stearate (9 grams) was added to the mixture. This mixture was heated for about 6 hrs. at 90°C. The mixture was then neutralised with 1N hydrochloric acid to get a final pH of about 6.7.

It was observed that after neutralization, the particle and the fatty acid together form lumps and it was difficult to separate out individual particles using conventional procedure such as filtration and centrifugation. Further, washing with solvent was also found to be not a viable option. Thus, Example – 4 indicates that the process of the present invention has advantages in derivatising clays when the salt of the fatty acid to be derivatised is substantially water insoluble e.g. stearic acid.

Example – 5: Kaolinite derivatised with stearoyl chloride as per the invention

Kaolinite which is a 1:1 clay was first alkali treated as per the following protocol:

Alkali treatment protocol:

A ~ 50% (w/v) dispersion of Kaolinite in ~ 2% (w/v) Hydrogen peroxide (30%) was prepared and heated to about 40-45°C. The mass was stirred for about 4 hours. To the reaction mixture sodium hydroxide was added to adjust the pH to 10-11 and refluxed for about an hour. After the alkali treatment, the reaction mass was neutralized with 1N hydrochloric acid, refluxed for 10 min and

filtered in a Buchner funnel. The filter cake was washed sufficiently with water till the filtrate was found to be neutral. The alkali activated clay was then dried at 80°C for about 4 hours till a constant weight was achieved.

The alkali treated clay was then derivatised with stearoyl chloride using the following procedure:

5.8g potassium carbonate solution and 150 ml toluene were mixed and heated to reflux and water was azeotropically distilled out along with 50 ml toluene. This was cooled to about 70 °C. To this was added 10 g of alkali activated kaolinite and 13 g stearoyl chloride and heated to reflux for 3 hours. The reaction mixture was then cooled to room temperature, filtered, and washed three times with 200 ml water. This was then washed with 50 ml acetone, filtered and washed again with 25 ml methanol and filtered. The filter cake was air dried for 2 hours and then dried in oven at 60°C.

The IR spectra of the derivatised clay as per Example – 5 is shown in Figure – 4. The spectra indicates that a 1:1 clay is derivatised with a fatty acid chloride (stearoyl chloride) by the process of the invention. The derivative is selective in that the fatty acid is appended to the octahedral sheet of the clay particle.

Claims:

1. A process to prepare a fatty acid derivative of asymmetric 1:1 or 2:1:1 clay particles comprising the steps of:
   (i) reacting asymmetric 1:1 or 2:1:1 clay particles having alternating tetrahedral and octahedral sheets terminating with a tetrahedral sheet at one external surface plane and an octahedral sheet at another external surface plane, with a fatty acid, a fatty acid chloride or derivatives thereof in the presence of an organic solvent;
   (ii) filtering the particles from the reaction media and washing them to be substantially free of unreacted reactants; and
   (iii) drying the particles.

2. A process as claimed in claim 1 wherein said asymmetric 1:1 clay particle is kaolinite, halloysite, dickite or nacrite.

3. A process as claimed in claim 2 wherein said asymmetric 1:1 clay particle is kaolinite.

4. A process as claimed in any one of the preceding claims wherein said fatty acid is chosen from lauric, myristic, palmitic, stearic or oleic acid.

5. A process as claimed in claim 4 wherein said organic solvent is xylene or isopropyl alcohol.

6. A process as claimed in claim 4 or 5 wherein said asymmetric 1:1 or 2:1:1 clay particle is acid treated prior to reacting with said fatty acid.

7. A process as claimed in any one of the preceding claims 1 to 3 wherein said fatty acid chloride is chosen from lauroyl, myristoyl, palmitoyl or stearoyl chloride.

8. A process as claimed in claim 7 wherein said organic solvent is toluene.

9. A process as claimed in claim 7 or 8 wherein said asymmetric 1:1 or 2:1:1 clay particle is alkali treated prior to reacting with said fatty acid chloride.

10. A process as claimed in any one of the preceding claims wherein the step of reacting the asymmetric 1:1 or 2:1:1 clay particle with the fatty acid or fatty acid chloride or derivative thereof is carried out in the presence of a phase transfer catalyst.

Figure 1/4

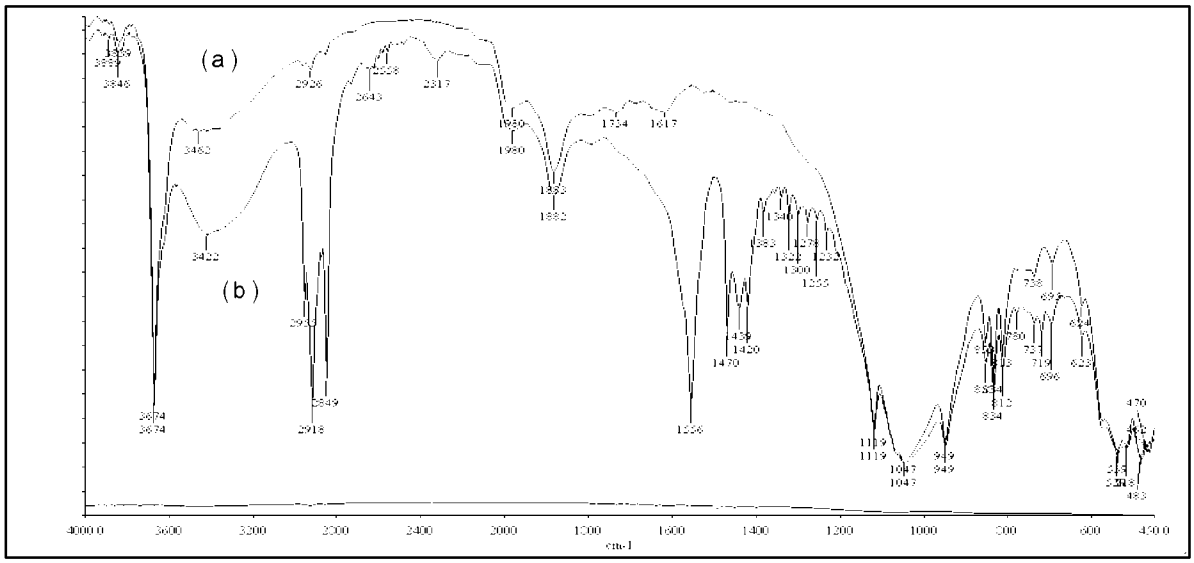

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Figure 2/4

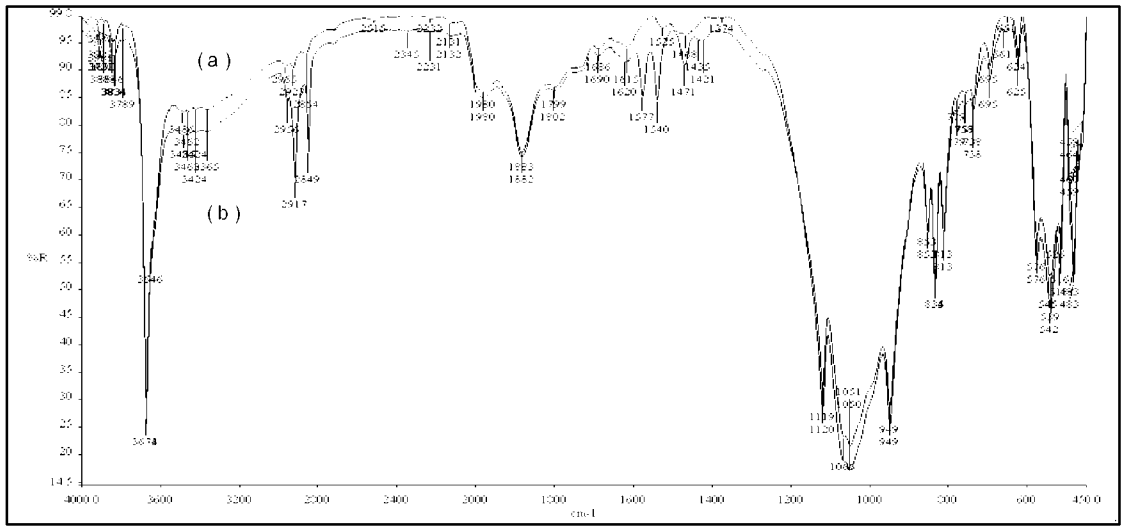

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Figure 3/4

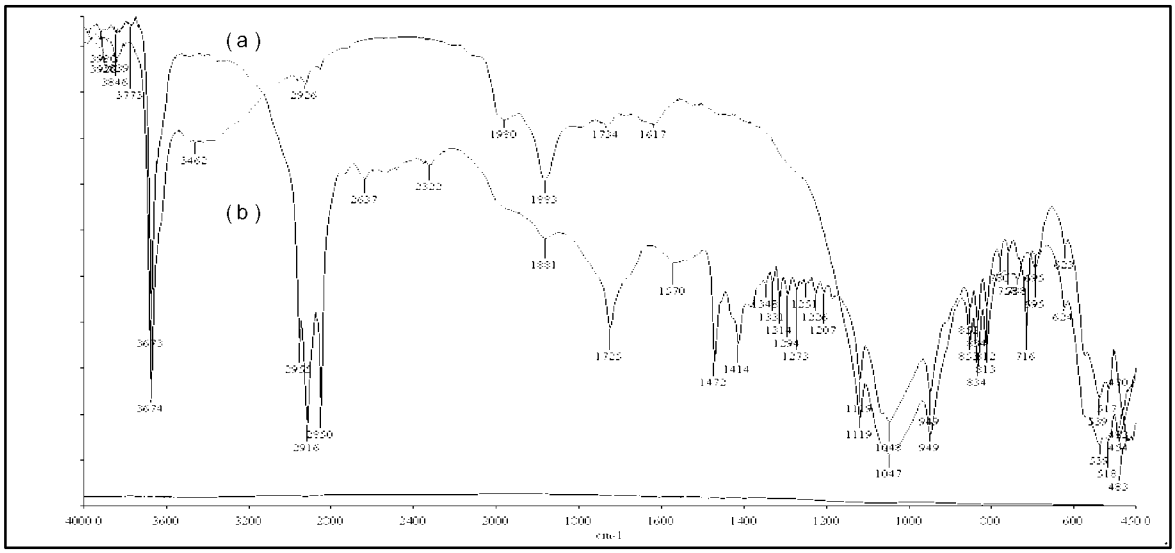
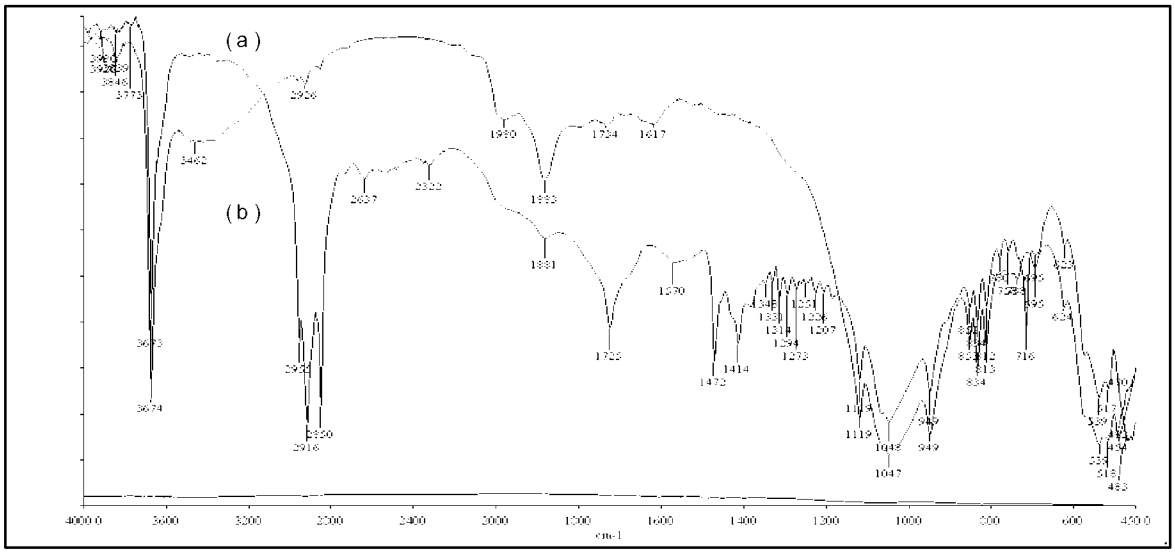

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Figure 4/4


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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/066500

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09C1/42 C01B33/44

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)
C09C C01B

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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	US 4 857 308 A (FUKASAWA JUNICHI [JP] ET AL) 15 August 1989 (1989-08-15) column 1, line 65 - column 3, line 67 examples 1-10 tables 1-3,5	1-4,8 5-7,9-10
X	US 3 211 565 A (BUNDY WAYNE M) 12 October 1965 (1965-10-12) cited in the application column 2, line 3 - column 3, line 50 claims 1-5	1-4
Y	FR 93 672 E (SHELL INT RESEARCH [NL]) 2 May 1969 (1969-05-02) page 1, column 1 - page 3, column 1	1-10

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
24 March 2010	30/03/2010

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Marino, Emanuela

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2009/066500

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	US 3 450 666 A (NEASE JOHN C) 17 June 1969 (1969-06-17) column 2, line 15 - column 6, line 28 examples 1-4	1-10
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A	US 4 715 986 A (GRUENING BURGHARD [DE] ET AL) 29 December 1987 (1987-12-29) cited in the application column 4, line 10 - column 10, line 21 examples 1-7	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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