



(51) International Patent Classification:

*A23D 7/005* (2006.01) *A61Q 19/00* (2006.01)  
*A23K 1/16* (2006.01) *A61K 8/02* (2006.01)  
*A23K 1/175* (2006.01) *A61K 8/06* (2006.01)  
*A61K 8/25* (2006.01) *C01B 33/18* (2006.01)  
*A61K 8/73* (2006.01) *C09C 1/30* (2006.01)

(21) International Application Number:

PCT/EP2016/052034

(22) International Filing Date:

1 February 2016 (01.02.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

15153442.7 2 February 2015 (02.02.2015) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: PICKERING EMULSIONS

(57) Abstract: The present invention relates to new emulsions, which are stabilized by solid particles, to their productions as well as to their use.



### **Pickering Emulsions**

The present invention relates to new emulsions, which are stabilized by solid particles, to their production as well as to their use. Furthermore the present invention also relates to the solid particles.

Emulsions, which are stabilized by solid particles, which absorb onto the interface between the two phases, are known as Pickering emulsions. Such emulsions were first described by S.U. Pickering in the early 20<sup>th</sup> century.

An example of a well-known Pickering emulsion is for example homogenized milk, wherein the casein particles are adsorbed at the surface of milk fat globules and act as a surfactant.

One major advantage of Pickering emulsions lies therein that there is no need of surfactants. Especially the surfactants with a short chain show some irritation issues when used.

Due to the importance of such Pickering emulsions, there is always a need for improved emulsions.

Furthermore the long-term stability of emulsions is an essential requirement in a wide number of applications in food and cosmetics industry. This stability is desirable for sensorial, textural and visual reasons and also to improve the shelf-life of the products. However, emulsions are inherently thermodynamically unstable and tend to undergo rapid coalescence and Ostwald ripening of droplets, due to the markedly high interfacial energy associated with the liquid-liquid interface. Moreover, new food-grade stabilizers are needed to respect the regulations and allow the stabilization of droplets of the order of microns.

Furthermore, some particles, which are used in Pickering emulsion are very limited in regard to their use in various applications. A big problem of particles used in Pickering

emulsions is the limitation of use in regard to the pH value of the application. This limits the use in broad manner.

From the prior art modified fumed silica particles are known. In fumed silica the particles aggregate in large fractal-like structures by both physical and chemical bonds. As a result these agglomerated particles have a very broad particle size distribution with average sizes well above 100 nm. Therefore when these modified particles are used in Pickering emulsions, the final emulsion oil droplet size is large and final applications are very limited.

The goal of the present invention was to provide Pickering emulsions with improved properties in view of stability as well more flexibility in its use in an application form (broader pH-value range, less limitation in terms of droplet size).

Surprisingly it was found that a Pickering emulsion with such improved properties is obtained, when the particles, which stabilize the emulsion, are hydrophilic, non-agglomerated silica nanoparticles having an average particle size ( $d_{50}$ ) of 5 nm to 100 nm, which are modified by at least one polysaccharide.

Therefore, the present invention relates to a Pickering emulsion (PE), comprising at least one oil, that is stabilized by hydrophilic, silica nanoparticles having an average particle size ( $d_{50}$ ) of 5 nm to 100 nm, which are modified by at least one polysaccharide.

Preferably the silica nanoparticles are non-agglomerated.

The term “non-agglomerated” in the sense of the present invention means that the particles are not forming agglomerates and therefore do have a very narrow particle size distribution of a few nanometers or tens of nanometers.

Therefore, the present invention relates to a Pickering emulsion (PE'), which is Pickering emulsion (PE), wherein the silica nanoparticles are non-agglomerated.

The hydrophilic, (non-agglomerated) silica nanoparticles ( $\text{SiO}_2$ ) do have an average particle size ( $d_{50}$ ) of about 5 – 100 nm (preferred around 15 - 80 nm, more preferably 15

– 50nm), when suspended in water. The particle size has been measured by using commonly known and used methods (such as dynamic light scattering). The particle size is measured by using an ALV CGS-3 compact goniometer (result output is mass weighted linearized mean radius).

Therefore, the present invention relates to a Pickering emulsion (PE''), which is Pickering emulsion (PE) or (PE'), wherein the silica nanoparticles have an average particle size ( $d_{50}$ ) of 5 – 100 nm (preferred 15 - 80 nm, more preferred 15 – 50 nm), when suspended in water.

Such hydrophilic, (non-agglomerated) silica nanoparticles are available commercially, for example under the Tradename Ludox TM 50® (from Grace).

The hydrophilic, (non-agglomerated) silica nanoparticles are modified mainly through electrostatic adsorption; no covalent bonds are involved in the modification. The so obtained modified particles are then used to prepare the Pickering emulsions.

The hydrophilic, (non-agglomerated) silica nanoparticles are modified by a polysaccharide (or a mixture of polysaccharides). Preferably it is a cationic polysaccharide, which is used to modify the hydrophilic silica nanoparticles.

A preferred polysaccharide is chitosan, more preferred it is a water dispersible chitosan.

Chitosan is a linear polysaccharide composed of randomly distributed  $\beta$ -(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It is obtained by treating shrimp shells and other crustacean shells with the alkali sodium hydroxide. The water dispersible chitosan is commercially available, is produced from the enzymolysis of chitosan by complex enzymes and has a low molecular weight, can be used from pH 3 and 7, and is for example modified with an amino acid like glutamine. Such water dispersible chitosan is available commercially, for example under the trade name Chitosan Oligosaccharide from Haide Bei with a molecular weight < 3kDa.

The hydrophilic, (non-agglomerated) silica nanoparticles are modified by adding the polysaccharide (or mixture of polysaccharides) to a (aqueous) suspension comprising

the hydrophilic silica nanoparticles. This is usually done under stirring. The polysaccharide (or mixture of polysaccharides) is usually added as an aqueous solution.

The hydrophilic, (non-agglomerated) silica nanoparticles are modified by at least 0.2 wt-% of polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

The hydrophilic, (non-agglomerated) silica nanoparticles can be modified by up to 10 wt-% of polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

Preferably the hydrophilic, (non-agglomerated) silica nanoparticles are modified by 0.2 wt-% - 10 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

More preferably the hydrophilic silica nanoparticles are modified by 1 wt-% - 5 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

Therefore, the present invention relates to a Pickering emulsion (PE1), which is a Pickering emulsion (PE), (PE') or (PE''), wherein the hydrophilic silica nanoparticles are modified by 0.2 wt-% - 10 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

Therefore, the present invention relates to a Pickering emulsion (PE1'), which is Pickering emulsion (PE), (PE') or (PE''), wherein the hydrophilic silica nanoparticles are modified by 1 wt-% - 5 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

Most preferred polysaccharide is chitosan. Especially a water dispersible chitosan having a low molecular weight, which is modified by an amino acid.

Therefore, the present invention relates to a Pickering emulsion (PE2), which is Pickering emulsion (PE), (PE'), (PE''), (PE1) or (PE1'), wherein the hydrophilic silica nanoparticles are modified by chitosan; (preferably by a water dispersible chitosan having a low molecular weight, which is modified by an amino acid).

The hydrophilic silica nanoparticles modified by at least one polysaccharide are not known from the prior art.

Therefore, the present invention also relates to hydrophilic silica nanoparticles (HSN) modified by at least one polysaccharide.

Preferably the hydrophilic silica nanoparticles are non-agglomerated.

The hydrophilic, (non-agglomerated) silica nanoparticles ( $\text{SiO}_2$ ) do have an average particle size ( $d_{50}$ ) of about 5 – 100 nm (preferred around 15 - 80 nm, more preferred 15 – 50 nm), when suspended in water. The particle size has been measured by using commonly known and used methods (such as dynamic light scattering). The particle size is measured by using an ALV CGS-3 compact goniometer system.

Therefore, the present invention also relates to hydrophilic silica nanoparticles (HSN1), which are hydrophilic silica nanoparticles (HSN), wherein the hydrophilic, (non-agglomerated) silica nanoparticles have an average particle size ( $d_{50}$ ) of 5 – 100 nm (preferred 5 - 80 nm, more preferred 15 – 50nm), when suspended in water.

Furthermore the present invention relates to hydrophilic (non-agglomerated) silica nanoparticles (HSN2) which are hydrophilic silica nanoparticles (HSN) or (HSN1), wherein the hydrophilic silica nanoparticles are modified by chitosan; (preferably by a water dispersible chitosan having a low molecular weight, which is modified by an amino acid).

Furthermore the present invention relates to modified hydrophilic (non-agglomerated) silica nanoparticles (HSN3), which are (non-agglomerated) silica nanoparticles (HSN), (HSN1) or (HSN2) modified by at least 0.2 wt-% of one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

Furthermore the present invention relates to modified silica nanoparticles (HSN3'), which are hydrophilic silica nanoparticles (HSN), (HSN1) or (HSN2) modified by up to 10 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

Furthermore the present invention relates to modified silica nanoparticles (HSN3''), which are hydrophilic silica nanoparticles (HSN), (HSN1) or (HSN2) modified by 0.2 wt-% - 10 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

Furthermore the present invention relates to modified silica nanoparticles (HSN3'''), which are hydrophilic silica nanoparticles (HSN), (HSN1) or (HSN2) modified by 1 wt-% - 5 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.

The modified particles according to the present invention have a positive zeta potential, which can be measured by using commonly known methods, such the electroacoustic colloidal vibration current technique (using a DT 300 from Dispersion Technology at T = 25°C). All zeta potentials in the present patent application are measured by this method and apparatus.

The zeta potential of the modified silica particles as disclosed to be close to 0mV. Preferably the modified particles have a zeta potential of between -15 and +15 mV, more preferably -7 and +7mV.

Therefore the present invention also relates to modified hydrophilic silica nanoparticles (HSN4), which are the modified hydrophilic silica nanoparticles (HSN), (HSN1), (HSN2), (HSN2), (HSN3'), (HSN3') or (HSN3''') having a zeta potential of between -15 and +15 mV, preferably between -7 and +7mV.

The Pickering emulsion is then produced by commonly known methods. Usually the oil (or the mixture of oils) is mixed with the aqueous phase containing the hydrophilic silica nanoparticles modified by at least one polysaccharide (or mixture of polysaccharides) and then emulsified by using a common emulsifier device (e.g. a commercially available high pressure homogenizer like Nano DeBEE from BEE International).

The amount of the oil(s) in the emulsion can vary. The Pickering emulsion is an oil-in-water emulsion. An oil-in-water emulsion is an emulsion, wherein the oil is the dispersed phase, and water is the dispersion medium.

The amount of the oil(s) which is present in the emulsion according to the present invention can vary. Usually the emulsion according to the present invention comprises 5 – 50 wt-%, based on the total weight of the Pickering emulsion, of at least one oil.

Preferably, the Pickering emulsion comprises 5 – 45 wt-%, more preferably 5 – 40 wt-% of at least one oil.

Therefore, the present invention relates to a Pickering emulsion (PE3), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1') or (PE2), wherein the Pickering emulsion comprises 5 – 50 wt-%, based on the total weight of the Pickering emulsion, of at least one oil.

Therefore, the present invention relates to a Pickering emulsion (PE3'), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1') or (PE2), wherein the Pickering emulsion comprises 5 – 45 wt-%, based on the total weight of the Pickering emulsion, preferably 5 – 40 wt-% of at least one oil.

The oils can be from any origin. They can be natural, modified or synthetic (or a mixture of such oils). If the oils are natural they can be plant or animal oils. Suitable oils are i.e. coconut oil, corn oil, cottonseed oil, olive oil, palm oil, peanut oil, rapeseed oil, canola oil, safflower oil, sesame oil, soybean oil, sunflower oil, hazelnut oil, almond oil, cashew oil, macadamia oil, mongongo nut oil, pracaxi oil, pecan oil, pine nut oil, pistachio oil, sacha Inchi (*Plukenetia volubilis*) oil, walnut oil, polyunsaturated fatty acids (such as triglyceride and/or ethyl ester, (for example arachidonic acid, eicosapentaenoic acid, docosahexaenoic acid and  $\gamma$ -linolenic acid and/or ethyl ester) and oily nutraceuticals (such as rosemary extract, oregano extract, hop extract, and other lipophilic plant extracts).

Also suitable are any oil soluble vitamins (vitamins, A, D, E, and K as well as derivatives of them).

Furthermore, the Pickering emulsions according to the present invention can also be used in the field of personal care applications, therefore the oil(s) can also be an oil (or a mixture of oils) usually used in such applications.

Cosmetic oils which are suitable for the use according to the present invention are all cosmetic oils conventionally used in topical cosmetic formulations. Such cosmetic oils are e.g. described in the International Cosmetic Ingredient Dictionary & Handbook by Personal Care Product Council (<http://www.personalcarecouncil.org/>), accessible by the online INFO BASE (<http://online.personalcarecouncil.org/jsp/Home.jsp>), without being limited thereto.

Particularly suitable cosmetic oils are for example selected from esters of saturated and/or unsaturated, branched and/or unbranched alkanecarboxylic acids having a chain length of 3 to 30 carbon atoms and saturated and / or unsaturated, branched and / or unbranched alcohols having a chain length of 3 to 30 carbon atoms, or from esters of aromatic carboxylic acids and saturated and/or unsaturated, branched and/or unbranched alcohols having a chain length of 3 to 30 C atoms. Such esters are advantageously chosen from the group consisting of isopropyl myristate, isopropyl palmitate, isopropyl oleate, n-butyl stearate, n-hexyl laurate, n-decyl oleate, isononyl isononanoate, 2-ethylhexyl palmitate, 2-hexyl decyl stearate, oleyl oleate, oleyl erucyloleate, erucyl erucate and synthetic, semi-synthetic and natural mixtures of such esters such as e.g. jojoba oil.

Further suitable cosmetic oils can advantageously be chosen from the group of branched and unbranched hydrocarbons such as paraffin oil, squalane and squalene, silicone oils such as cyclomethicone, phenyldimethicone, dimethicone, methicone and the like, dialkyl ethers such as dicaprylylether; the group of saturated or unsaturated, branched or unbranched alcohols, liquid fatty alcohol triglycerides or unsaturated, branched and/ or unbranched alkanecarboxylic acids having a chain length of 8-24, in particular 12-18 C-atoms. The liquid fatty alcohol triglycerides can advantageously be chosen from the group of synthetic, semi-synthetic and natural oils such as such as caprylic capric triglyceride, olive oil, sunflower oil, soy oil, peanut oil, almond oil, palm kernel oil, palm oil, rapeseed oil, coconut oil and the like more.

Further suitable cosmetic oils encompass natural organic oils derived from animal, vegetable, or mineral sources. Preferred natural organic oils according to the invention are modern cosmetic oils known to be safe for cosmetic purposes such as almond oil, apricot kernel oil, argan oil, avocado butter, avocado oil, cocoa butter (theobroma oil), camelina oil, canola oil, carrot seed oil, castor oil, citrus seed oil, coconut oil, corn oil, cottonseed oil, cucumber oil, egg oil, grapeseed oil, hemp seed oil, jojoba oil, lanolin oil, linseed oil, macadamia nut oil, meadowfoam seed oil, mineral oil, mink oil, olive oil, palm kernel oil, peach kernel oil, peanut oil, rapeseed oil, rose hip oil, safflower oil, sesame oil, shark liver oil, shea butter, soybean oil, sunflower seed oil, sweet almond oil, tallow (beef) oil, tallow (mutton) oil, turtle oil, vegetable oil, and wheat germ oil as well as mixtures thereof. Particularly preferred natural organic oils according to the present invention are plant derived oils and fats such as in particular almond oil, apricot kernel oil, argan oil, avocado butter, avocado oil, cocoa butter (theobroma oil), camelina oil, canola oil, carrot seed oil, castor oil, citrus seed oil, coconut oil, corn oil, cottonseed oil, cucumber oil, grapeseed oil, hemp seed oil, jojoba oil, lanolin oil, linseed oil, macadamia nut oil, meadowfoam seed oil, olive oil, palm kernel oil, peach kernel oil, peanut oil, rapeseed oil, safflower oil, sesame oil, soybean oil, sunflower seed oil, sweet almond oil, vegetable oil and wheat germ oil as well as mixtures thereof. The most preferred natural organic oils according to the present invention are argan oil and sweet almond oil (Prunus Amygdalus Dulcis Oil) as well as mixtures thereof.

Another class of particular suitable cosmetic oils encompass liquid organic UV-filters such as 2-ethylhexyl 2-cyano-3,3-diphenylacrylate (octocrylene, PARSOL<sup>®</sup> 340), ethylhexyl methoxycinnamate (PARSOL<sup>®</sup> MCX), isoamyl methoxycinnamate, polysilicone-15 (PARSOL<sup>®</sup> SLX); ethylhexyl salicylate (PARSOL<sup>®</sup> EHS, Neo Heliopan<sup>®</sup> OS), isooctyl salicylate and homomenthyl salicylate (homosalate, PARSOL<sup>®</sup> HMS, Neo Heliopan<sup>®</sup> HMS) without being limited thereto.

Particular suitable cosmetic oils are butylenglykoldicaprylat/-dicaprat, Butylene Glycol Dicaprylate/Dicaprate, octyldodecanol, caprylyl/ capric triglyceride, Caprylic/Capric Triglyceride, C<sub>12-15</sub>-Alkylbenzoat, C<sub>18-38</sub>-fatty acid triglyceride, dibutyladipate, cyclomethicone, 2-phenylethylbenzoate, isopropyl lauroyl sarkosinate, Diisobutyl Sebacate, Isopropyl Myristate, Isononyl Isononanoate, Cetearyl Isononanoate, Octyl dodecanol, Decyl Oleate, Hexyl Laurate, Dicaprylyl Carbonate, Diethylhexyl Carbonate,

Cocoglycerides, Isododecane, Squalane, Hydrogenated Polydecene, Paraffin Oil, Dimethicone, Dicaprylyl Ether, PPG-15 Stearyl Ether, Jojoba Seed Oil, (Macadamia Nut Oil), Ethylhexyl Salicylate, Homosalate, Ethylhexyl Methoxycinnamate, Polysilicone-15 as well as mixtures thereof.

Therefore, the present invention relates to a Pickering emulsion (PE4), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3) or (PE3'), wherein the at least one oil is natural, modified or synthetic (or a mixture).

Therefore, the present invention relates to a Pickering emulsion (PE4'), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3) or (PE3'), wherein at least one oil is chosen from the groups consisting of coconut oil, corn oil, cottonseed oil, olive oil, palm oil, peanut oil, rapeseed oil, canola oil, safflower oil, sesame oil, soybean oil, sunflower oil, hazelnut oil, almond oil, cashew oil, macadamia oil, mongongo nut oil, pracaxi oil, pecan oil, pine nut oil, pistachio oil, sachal Inchi (*Plukenetia volubilis*) oil, walnut oil, polyunsaturated fatty acids (such as triglyceride and/or ethyl ester, (for example arachidonic acid, eicosapentaenoic acid, docosahexaenoic acid and  $\gamma$ -linolenic acid and/or ethyl ester) and oily nutraceuticals (such as rosemary extract, oregano extract, hop extract, and other lipophilic plant extracts); as well as oil soluble vitamins (vitamins, A, D, E, and K as well as derivatives of them).

Therefore, the present invention relates to a Pickering emulsion (PE4''), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3) or (PE3'), wherein the oil is corn oil or vitamin E acetate.

The Pickering emulsion also comprises the modified silica nanoparticles (HSN), (HSN1), (HSN2), (HSN2'), (HSN3'), (HSN3'), (HSN3'') or (HSN4), in an amount of 0.1 – 20 wt-% (preferably 0.5 – 12 wt-%; more preferably 2.4 – 9.5wt-%), based on the total weight of the Pickering emulsion.

Therefore, the present invention relates to a Pickering emulsion (PE5), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3), (PE3'), (PE4), (PE4') or (PE4'') comprising 0.1 – 20 wt-% (preferably 0.5 – 12 wt-%; more preferably 2.4 – 9.5

wt-%), based on the total weight of the Pickering emulsion of the modified silica nanoparticles (HSN), (HSN1), (HSN2), (HSN2), (HSN3'), (HSN3'), (HSN3''') or (HSN4).

The Pickering emulsion also comprises water in an amount of 35 – 94.9 wt-% (preferably 43 – 94.5 wt-%; more preferably 45.5 – 92.6 wt-%), based on the total weight of the Pickering emulsion.

Therefore, the present invention relates to a Pickering emulsion (PE6), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3), (PE3'), (PE4), (PE4'), (PE4'') or (PE5) comprising 35 – 94.9 wt-% (preferably 43 – 94.5 wt-%; more preferably 45.5 – 92.6 wt-%), based on the total weight of the Pickering, of water.

It is also possible to add further auxiliary agents to the Pickering emulsions. These auxiliary agents can be used to modify the Pickering emulsion as such and/or modify the formulation, wherein the Pickering emulsion is finally used. Such further auxiliary agents can be antioxidants [such as ascorbic acid or salts thereof, (synthetic or natural) tocopherol (i.e. dl-alpha-tocopherol); butylated h-droxytoluene (BHT); butylated hydroxyanisole (BHA); propyl gallate; tert. butyl hydroxyquinoline and/or ascorbic acid esters of a fatty acid)], ethoxyquin, plasticizers, preservatives (such as sorbic acid and its salts), stabilizers, acids (such as citric acid, acetic acid as well as their salts), humectants (such as glycerol, sorbitol, polyethylene glycol) protective colloids, dyes, fragrances, fillers and pH-buffers.

These auxiliary agents are usually used up to an amount of 5wt-%, based on the total weight of the Pickering emulsion.

In Pickering emulsions according to the present invention the oil droplets usually have an average size ( $d_{50}$ ) of less than 5  $\mu\text{m}$ , usually less than 4  $\mu\text{m}$ , usually between 0.5 – 4  $\mu\text{m}$ .

The oil droplet size has been measured by using commonly known and used methods (such as laser diffraction). All the oil droplet sizes ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$  of the size distribution) are measured by using a Malvern Mastersizer 2000.

Therefore, the present invention relates to a Pickering emulsion (PE7), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3), (PE3'), (PE4), (PE4'), (PE4''), (PE5) or (PE6), wherein the oil droplets have an average size of less than 5  $\mu\text{m}$ , preferably less than 4  $\mu\text{m}$ , most preferably in the range of between 0.5 – 4  $\mu\text{m}$ .

Therefore, the present invention relates to a Pickering emulsion (PE7'), which is Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3), (PE3'), (PE4), (PE4'), (PE4''), (PE5) or (PE6), wherein the oil droplets have an average size of between 0.5 – 4  $\mu\text{m}$ .

The Pickering emulsions (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3), (PE3'), (PE4), (PE4'), (PE4''), (PE5), (PE6), (PE7) or (PE7') can be used in many fields of applications. Depending on the quality of the ingredients as well as the concentrations it can be used in food, feed, pharmaceutical and personal care products.

Therefore the present invention also relates to the use of at least one Pickering emulsion (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3), (PE3'), (PE4), (PE4'), (PE4''), (PE5), (PE6), (PE7) or (PE7') in food, feed, pharmaceutical and personal care products.

Therefore the present invention also relates to food, feed, pharmaceutical and personal care products comprising at least one Pickering emulsions (PE), (PE'), (PE''), (PE1), (PE1'), (PE2), (P3), (PE3'), (PE4), (PE4'), (PE4''), (PE5), (PE6), (PE7) or (PE7').

The concentration of the Pickering emulsion according to the present invention in these applications depends on the respective application and can be easily determined by a person skilled in the art.

The following Examples illustrate the invention further without limiting it. All percentages and parts, which are given, are related to the weight and the temperatures are given in  $^{\circ}\text{C}$ , when not otherwise stated.

## Examples

### **Example 1:** *Non-agglomerated, hydrophilic silica particle size*

Dynamic light scattering measurements were done to determine the size of the silica nanoparticles. We use an ALV/CGS-3 compact goniometer system (ALV-GmbH, Germany) at 25°C at a wavelength of 532 nm, a scattering angle of 90°, a refractive index (RI) of 1.332 and a viscosity of 0.885 cP for water (dispersant medium). A 1 wt% silica suspension was prepared from a Ludox TM50 solution and sonicated in an ultrasonic bath. The second order of the cumulant fit gives a radius of 14 nm, so the average particle diameter is 28 nm. The non-agglomerated state of the silica nanoparticles was also verified in scanning electron microscopy images (Zeiss Gemini 1530, Oberkochen).

### **Example 2:** *Preparation of the chitosan-modified silica particles*

#### a) 4.8 wt% chitosan-modified silica particles

A 20 wt% chitosan solution was prepared by dissolution of a water-dispersible chitosan grade with a  $M_w < 3$  kDa (Haide Bei) in double distilled water. An aqueous silica particle suspension (Ludox TM50, Sigma-Aldrich) was used for the chitosan modification. The hydrophilic silica particles as characterized in Example 1 were used. In order to prepare 100 g of an aqueous suspension of chitosan-modified silica particles, 17.4 g of Ludox TM50 (50 wt% silica particles in an aqueous suspension) were mixed in 80.425 g of double distilled water. The chitosan solution (2.175 g) was added drop by drop under magnetic stirring to the silica particle suspension. The prepared solution thus contained 8.7wt% silica, 0.435wt% chitosan and the balance water. The chitosan was allowed to adsorb on silica for 15 minutes. The successful chitosan modification of the silica particles was verified by measuring the zeta potential of the particles at  $T = 25^\circ\text{C}$  by the electroacoustic colloidal vibration current technique (DT 300 from Dispersion Technology) before and after modification, respectively. A 1M HCl solution was used for the titration of the samples with a decreasing pH ramp, so the corresponding zeta potential and electrical conductivity were measured simultaneously as a function of pH. The initial silica suspension had an isoelectric point (IEP) at about pH 1.55 and at pH >

IEP the zeta potential was negative at all pH. In contrast, the 4.8 wt% chitosan-modified silica particles had an IEP at about pH 6.7. At pH < IEP, the zeta potential had positive values (in the range 0 to +6.5 mV), thus demonstrating the successful chitosan modification of the silica particle surface.

b) 1 wt% chitosan-modified silica particles

The 1 wt% chitosan-modified silica particles were prepared as described in Example 2a but using the following quantities. 17.4 g of Ludox TM50 (50 wt% silica particles in an aqueous suspension) were mixed in 82.165 g of double distilled water. The chitosan solution (0.435 g) was added drop by drop under magnetic stirring to the silica particle suspension. The prepared solution thus contained 8.7 wt% silica, 0.087 wt% chitosan and the balance water. The zeta potential of the 1wt% chitosan-modified silica particles at pH 5.5 is -7.3mV.

c) 23 wt% chitosan-modified silica particles

The 23 wt% chitosan modified silica particles were prepared as described in Example 2a but using the following quantities. 17.4 g of Ludox TM50 (50 wt% silica particles in an aqueous suspension) were mixed in 69.55 g of double distilled water. The chitosan solution (13.05 g) was added drop by drop under magnetic stirring to the silica particle suspension. The prepared solution thus contained 8.7 wt% silica, 2.61 wt% chitosan and the balance water. The zeta potential of the 23wt% chitosan-modified silica particles at pH 5.5 is 28.8mV.

**Example 3:** *Preparation of a Pickering emulsion with 10 wt% of corn oil using the 1 wt% chitosan-modified silica particles*

The chitosan-modified silica particles prepared in Example 2b were used as Pickering particle stabilizers of an oil-in-water (O/W) emulsion. The chitosan-modified silica particle suspension from Example 2b was adjusted at pH 5.5 by adding HCl solution at 1M and mixed with corn oil. A pre-emulsification was performed with a T25 Ultra-Turrax (IKA) disperser at 10200 rpm for one minute. The O/W emulsion was then further processed with a high pressure homogenizer (Nano DeBEE from BEE international). A D5 nozzle

(diameter = 150  $\mu\text{m}$ ) was used and the emulsification was carried out with three passes at 20 000 psi followed by one final pass at 40 000 psi. The high pressure homogenizer was cooled by a water cooling system ( $T = 15^\circ\text{C}$ ). The composition of the product O/W emulsion is shown in Table 1.

**Table 1.** Composition of the corn oil O/W emulsion stabilized by the 1 wt% chitosan-modified silica particles.

| Material                 | Content, wt% |
|--------------------------|--------------|
| Corn oil                 | 10           |
| Water                    | 82.1         |
| Chitosan modified silica | 7.9          |

The oil droplet size in the O/W emulsion was measured by laser diffraction (Mastersizer 2000 with Hydro 2000S accessory, Malvern Instruments, using a refractive index (RI) for the modified silica = 1.5, an absorption of 0.005, and a RI for water = 1.33). The emulsion was stored in a fridge at 4  $^\circ\text{C}$  and the oil droplet size was re-measured after 3 weeks and 12 weeks. Table 2 shows the oil droplet size of the as-prepared emulsion as well as after storage. The emulsion thus had an average as-prepared oil droplet size of 1.6  $\mu\text{m}$  (median diameter  $d_{50}$ ) that stayed stable for at least three months at 4  $^\circ\text{C}$ .

**Table 2.** Oil droplet size ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ) of the corn oil emulsion as-prepared as well as after storage at 4 $^\circ\text{C}$ .

|             | $d_{10}$ , $\mu\text{m}$ | $d_{50}$ , $\mu\text{m}$ | $d_{90}$ , $\mu\text{m}$ |
|-------------|--------------------------|--------------------------|--------------------------|
| as-prepared | 0.9                      | 1.6                      | 2.7                      |
| 3 weeks     | 1.1                      | 1.8                      | 3.2                      |
| 12 weeks    | 1.1                      | 2.1                      | 5.3                      |

**Example 4:** *Preparation of a Pickering emulsion with 10 wt% of corn oil using the 4.8 wt% chitosan-modified silica particles*

The chitosan-modified silica particles prepared in Example 2a were used as Pickering particle stabilizers of an oil-in-water (O/W) emulsion. The chitosan-modified silica particle suspension from Example 2a was adjusted at pH 5.5 and mixed with corn oil. The Pickering O/W emulsion was prepared following the procedure described in Example 3. The composition of the product O/W emulsion is shown in Table 3 and the oil droplet size as-prepared as well as after storage in Table 4. The emulsion thus had an as-prepared average oil droplet size of 1.7  $\mu\text{m}$  ( $d_{50}$ ) that stayed stable for at least three months at 4 °C.

**Table 3.** Composition of the corn oil emulsion stabilized by the 4.8 wt% chitosan-modified silica particles.

| Material                 | Content, wt% |
|--------------------------|--------------|
| Corn oil                 | 10           |
| Water                    | 81.8         |
| Chitosan modified silica | 8.2          |

**Table 4.** Oil droplet size ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ) of the corn oil emulsion as-prepared as well as after storage at 4°C.

|             | $d_{10}$ , $\mu\text{m}$ | $d_{50}$ , $\mu\text{m}$ | $d_{90}$ , $\mu\text{m}$ |
|-------------|--------------------------|--------------------------|--------------------------|
| as-prepared | 1.0                      | 1.7                      | 2.7                      |
| 3 weeks     | 1.1                      | 1.8                      | 2.8                      |
| 12 weeks    | 1.2                      | 1.9                      | 3.3                      |

**Example 5:** *Preparation of a Pickering emulsion with 10 wt% of Vitamin E using the 4.8 wt% chitosan-modified silica particles*

The chitosan-modified silica particles prepared in Example 2a were used as Pickering particle stabilizers of an oil-in-water (O/W) emulsion. The chitosan-modified silica particle suspension from Example 2a was adjusted at pH 6.8 and mixed with Vitamin E acetate (d,l-alpha-Tocopheryl acetate, DSM Nutritional Products Ltd). The Pickering O/W emulsion was prepared following the procedure described in Example 3 except we used 30 paths instead of 4 paths through the high pressure homogenizer because of the high viscosity of Vitamin E acetate. The composition of the product O/W emulsion is shown in

Table 5 and the oil droplet size as-prepared as well as after storage in Table 6. The emulsion thus had an as-prepared average oil droplet size of 2.1  $\mu\text{m}$  ( $d_{50}$ ) that stayed stable for at least three months at 4 °C.

**Table 5.** Composition of the Vitamin E acetate O/W emulsion stabilized by the 4.8 wt% chitosan-modified silica particles.

| Material                 | Content, wt% |
|--------------------------|--------------|
| Vitamin E acetate        | 10           |
| Water                    | 81.8         |
| Chitosan modified silica | 8.2          |

**Table 6.** Oil droplet size ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ) of the Vitamin E acetate emulsion as-prepared as well as after storage at 4 °C.

|             | $d_{10}$ , $\mu\text{m}$ | $d_{50}$ , $\mu\text{m}$ | $d_{90}$ , $\mu\text{m}$ |
|-------------|--------------------------|--------------------------|--------------------------|
| as-prepared | 1.4                      | 2.1                      | 3.3                      |
| 3 weeks     | 1.4                      | 2.1                      | 3.3                      |
| 12 weeks    | 1.5                      | 2.2                      | 3.4                      |

**Example 6:** *Preparation of a non-stable Pickering emulsion with 10 wt% of corn oil using the 23 wt% chitosan-modified silica particles*

The chitosan-modified silica particles prepared in Example 2c were used as Pickering particle stabilizers of an oil-in-water (O/W) emulsion. The chitosan-modified silica particle suspension from Example 2c was adjusted at pH 5.5 and mixed with corn oil. The Pickering O/W emulsion was prepared following the procedure described in Example 3. The composition of the product O/W emulsion is shown in Table 7 and the oil droplet size as-prepared as well as after storage in Table 8. The emulsion thus had an as-prepared average oil droplet size of 1.5  $\mu\text{m}$  ( $d_{50}$ ) that did **NOT** stay stable over time ( $d_{90}$  increases significantly) even if it is stored at 4 °C.

**Table 7.** Composition of the corn oil O/W emulsion stabilized by the 23 wt% chitosan-modified silica particles.

| Material                 | Content, wt% |
|--------------------------|--------------|
| Corn oil                 | 10           |
| Water                    | 79.8         |
| Chitosan modified silica | 10.2         |

**Table 8.** Oil droplet size ( $d_{10}$ ,  $d_{50}$  and  $d_{90}$ ) of the corn oil emulsion as-prepared as well as after storage at 4°C.

|             | $d_{10}$ , $\mu\text{m}$ | $d_{50}$ , $\mu\text{m}$ | $d_{90}$ , $\mu\text{m}$ |
|-------------|--------------------------|--------------------------|--------------------------|
| as-prepared | 0.7                      | 1.5                      | 2.9                      |
| 3 weeks     | 0.8                      | 2.2                      | 8.6                      |
| 12 weeks    | 0.9                      | 2.4                      | 16.6                     |

### **Claims**

1. A Pickering emulsion, comprising at least one oil, that is stabilized by hydrophilic, silica nanoparticles having an average particle size ( $d_{50}$ ) of 5 nm to 100 nm, which are modified by at least one polysaccharide.
2. Pickering emulsion according to claim 1, wherein the hydrophilic silica nanoparticles are modified by 0.2 wt-% - 10 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.
3. Pickering emulsion according to claim 1, wherein the hydrophilic silica nanoparticles are modified by 1 wt-% - 5 wt-% of at least one polysaccharide (or mixture of polysaccharides), based on the total weight of the modified silica nanoparticles.
4. Pickering emulsion according to anyone of the preceding claims, wherein the at least one polysaccharide is chitosan.
5. Pickering emulsion according to anyone of the preceding claims, wherein the Pickering emulsion comprises 5 – 50wt-%, based on the total weight of the Pickering emulsion, (preferably 5 – 45 wt-% of at least one oil, more preferably 5 – 40 wt-% of at least one oil).
6. Pickering emulsion according to anyone of the preceding claims, wherein the oil is corn oil or vitamin E acetate.
7. Pickering emulsion according to anyone of the preceding claims comprising the modified hydrophilic silica nanoparticles in an amount of 0.1 – 20 wt-% (preferably 0.5 – 12 wt-%, more preferably 2.4 – 9.5 wt-%), based on the total weight of the Pickering emulsion.

8. Pickering emulsion according to anyone of the preceding claims comprising water in an amount of 35 – 94.9 wt-% (preferably 43 – 94.5 wt-% preferably 45.5 – 92.6 wt-%), based on the total weight of the Pickering emulsion.
9. Pickering emulsion according to anyone of the preceding claims, wherein the oil droplets have an average size of between 0.5 – 4 $\mu$ m.
10. Hydrophilic silica nanoparticles having an average particle size ( $d_{50}$ ) of 5 – 100 nm (preferred 5 - 80 nm, more preferred 15 – 50nm), which are modified by at least one polysaccharide.
11. Use of at least one Pickering emulsion according to anyone of claims 1 - 9 in food, feed, pharmaceutical and personal care products.
12. Food, feed, pharmaceutical and personal care products according to anyone of claims 1 - 9.

## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/052034

## A. CLASSIFICATION OF SUBJECT MATTER

INV. A23D7/005 A23K1/16 A23K1/175 A61K8/25 A61K8/73  
 A61Q19/00 A61K8/02 A61K8/06 C01B33/18 C09C1/3072  
 C09C1/3063

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)

A23D A23K A61K A61Q

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 practicable, 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.    |
|-----------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|
| X         | THOMAS S. SKELHON ET AL: "Quiescent water-in-oil Pickering emulsions as a route toward healthier fruit juice infused chocolate confectionary", JOURNAL OF MATERIALS CHEMISTRY, vol. 22, no. 36, 1 January 2012 (2012-01-01), page 19289, XP055081593, ISSN: 0959-9428, DOI: 10.1039/c2jm34233b page 19290 - page 19294<br>----- | 1-12                     |
| X<br>A    | WO 2014/118489 A1 (KRAFT FOODS R & D INC [US]) 7 August 2014 (2014-08-07) page 1, line 33 - page 2, line 5 page 11, line 25 - page 15, line 6; claims 1, 4-6, 11<br>-----<br>-/-                                                                                                                                                | 1,4,<br>10-12<br>2,3,5-9 |



Further documents are listed in the continuation of Box C.



See patent family annex.

## \* Special categories of cited documents :

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"&amp;" document member of the same patent family

Date of the actual completion of the international search

13 April 2016

Date of mailing of the international search report

21/04/2016

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/052034

| C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT |                                                                                                                                                                                                                                                                                                                                                                                                         |                       |
|------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------|
| Category*                                            | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                                      | Relevant to claim No. |
| A                                                    | <p>HAO LIU ET AL: "Facile Preparation of Core-Shell Nanocomposite Microgels", JOURNAL OF MACROMOLECULAR SCIENCE, PART B: PHYSICS, vol. 53, no. 1, 18 January 2014 (2014-01-18), pages 52-66, XP055204648, ISSN: 0022-2348, DOI: 10.1080/00222348.2013.789306 the whole document</p> <p>-----</p>                                                                                                        | 1,10                  |
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## INTERNATIONAL SEARCH REPORT

### Information on patent family members

International application No

PCT/EP2016/052034

| Patent document<br>cited in search report | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
|-------------------------------------------|---------------------|----------------------------|---------------------|
| WO 2014118489                             | A1                  | 07-08-2014                 | NONE                |
| -----                                     |                     |                            |                     |