Abstract: The invention relates to a particle stabilised high or medium dispersed phase emulsion comprising a dispersed phase which constitutes 30% or more of the total volume of the emulsion, a continuous phase and hydrophobized organic particles, methods for producing said emulsion and porous polymer foams produced therefrom.
HYDROPHOBIZED ORGANIC PARTICLE STABILIZED EMULSIONS

The present invention relates to hydrophobized renewable organic nano-particle stabilized emulsion templates, uses thereof and polymeric foams produced from the said emulsions.

An emulsion is a heterogeneous system consisting of two liquids, referred to as phases, which are immiscible or have limited miscibility. In an emulsion, one phase (the dispersed phase) is dispersed as droplets within the other phase (the continuous phase). Usually, one phase comprises water or an aqueous solution and the other phase comprises an oil, although non-aqueous emulsions comprising two immiscible organic phases can be produced. Emulsions can be classified as oil-in-water emulsions (o/w) in which oil constitutes the dispersed phase or water-in-oil emulsions (w/o) in which water (or an aqueous solution) constitutes the dispersed phase. Emulsions containing multiple phases are also possible. Generally, in order to achieve metastable dispersion of one phase within another, the addition of an emulsifier to the emulsion is required. Conventional emulsifiers, such as surfactants, have an amphiphilic molecular structure and stabilise an emulsion by positioning themselves at the phase interface, thereby acting to prevent droplet coalescence. It is also possible to stabilize an emulsion by the addition of a particulate solid. Particle-stabilized emulsions, known as Pickering or Ramsden emulsions, are extremely stable due to the adsorption of particles (which are usually not amphiphilic) at the interface between the continuous and dispersed phases, providing a barrier to prevent droplet coalescence and phase separation. Stability of an emulsion is determined by the extent to which the particles are wetted by the two immiscible phases, particle size, concentration, and mutual interaction between the particles.

Emulsions have uses in many fields, including the food, pharmaceutical and cosmetics industries. One application is in the preparation of polymer (and polymer matrix composite) foams. Emulsion templating using high dispersed phase emulsions (HIPEs) is an effective route to prepare polymer foams known as polyHIPEs. Typically, polyHIPEs are prepared by a process, which involves providing a w/o
HIPE in which the organic continuous phase comprises polymerizable monomers and crosslinkers and initiating polymerization of the continuous monomer phase. The dispersed phase droplets act as a template about which polymerization occurs. After polymerization, the dispersed phase is removed, leaving voids in place of the dispersed phase droplets and thus providing a highly porous foam structure. The pore structure of the polymer foam replicates the dispersed phase structure of the emulsion at the gel point. PolyHIPEs may also be produced from o/w emulsion or non-aqueous templates.

Research efforts are being focused on the development of environmentally friendly renewable nanocomposites in the desire to seek alternatives to petroleum-based composites. The present application provides renewable (truly green) nanocomposite polymer foams which are synthesized from Pickering-emulsion templates.

The first aspect of the invention therefore provides a particle stabilized high or medium dispersed phase emulsion comprising a dispersed phase which constitutes 30% or more of the total volume of the emulsion, a continuous phase and hydrophobized organic particles.

For the purposes of the present invention, the dispersed phase is any phase which is not miscible with the continuous phase (as defined below). The dispersed phase is preferably a hydrophilic dispersed phase, more preferably an aqueous dispersed phase (such as an aqueous solution or water). The dispersed phase constitutes more than 30% of the total volume of the emulsion, such as from 30% to 95%, preferably from 50 to 92%, more preferably 75% to 92%. The dispersed phase may be provided as a percentage of the total volume of the emulsion of 75% to 90%, 80 to 90% or 80 to 85%. The dispersed phase may be provided as a percentage of the total volume of the emulsion of 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90%, 92% or 95%. It will be appreciated that emulsion with a dispersed phase volume of greater than 74.4% will consist of deformed spheres as this is the limit of close sphere packing.
The continuous phase is preferably one or more of functionalized natural oils, thermostet resins derived from vegetable oils, such as soybean, linseed, cashew, palm, nut, coconut and sunflower, reactive low molecular weight resins based on functionalized poly(ε-hydroxyester) oligomers, (e.g. polylactide functionalized by methacrylic anhydride, or end-capped with dimethacrylate or diacrylate groups which can be polymerized). It will be appreciated that where the continuous phase is an oil-like monomer, the continuous phase is hydrophobic and practically immiscible with the dispersed phase. In the case of highly viscous monomers or functionalized oils a suitable hydrophobic solvent may be added to improve flow properties during processing. Suitable solvents include toluene, benzene, chloroform, dichloromethane and cyclohexane.

In addition, the continuous phase may comprise a blend of synthetic monomers such as styrene, di-vinyl benzene and polyethylene glycol (diacrylated or dimethacrylated), the said blend can be tailored to obtain required mechanical properties. For the purposes of this invention, the synthetic monomers can be any monomers capable of polymerization or cross-linking. Cross-linkers with renewable credentials such as squalene or keratin may also be incorporated in the continuous phase.

For the purposes of this invention, the particles are derived from organic (i.e. carbon based material). The particles of the present invention are particularly derived from a renewable source. The particles are therefore derived from an organism such as a plant, animal or a micro-organism such as a bacteria, fungus, amoeba or virus. It will be appreciated that the particles can be derived from an agriculture resource such as a plant.

The particles are preferably cellulose derived particles. The particle can be derived from any origin of cellulose for example of plant, bacterial, animal, fungal or amoebic. The particles are preferably derived from nano-cellulose, which can be derived from: bacteria, the banana plant (obtained through steam explosion); parenchymal walls; cotton; animal sources such as Tunicata. The renewable particle may also be derived from chitin, for example, chitosan. It will be appreciated that
cellulose derived particles are particularly preferred for the present invention as cellulose is a cheap, renewable source of a particulate/fibrilar/whisker like stabilizer. Cellulose derived from bacteria inherently has aspects in the nano-size range and has high mechanical properties, with stiffness exceeding those of glass fibres and aramid fibres. Furthermore, cellulose particles possess many hydroxyl groups for facile functionalization (hydrophobization), such that the wettability or 3-phase contact angle between the particles and the continuous and disperse phases can be tuned; thereby enabling cellulose to act as a Pickering emulsion stabilizer.

Additionally or alternatively, the cellulose (nano)particles can be hydrophobized with bi-functional chlorosilanes, such as chlorodimethylvinylsilane, dimethylchlorosilylpropylmethacrylate or chloromethylphenylvinylsilane.

Cellulose can be rendered hydrophobic by organic acid esterification, with organic acids (saturated or ideally unsaturated) of varying carbon chain length, including but not limited to acetic acid (C2), butyric acid (C4), hexanoic acid (C6), lauric acid (C12), oleic acid (Cl 8) and linoleic acid (Cl 8). Where the organic acids are unsaturated, the carbon-carbon double bonds can form cross-linkages to crosslink with the polymer matrix and/or to crosslink the particles. The cellulose (nano)particles may also be functionalized by various means known to persons skilled in the art, with other reactive groups, such as dimethacrylates or methacrylates and cross-linked into the polymer matrix. The hydroxyl groups can be functionalized using similar procedures for end-capping polyethylene glycol functionalization, for example by reacting PEG with methacryloyl chloride or acryloyl chloride in the presence of triethylamine. Other grafting techniques may include reversible addition-fragmentation chain transfer (RAFT) for example of polystyrene to cellulose; or by grafting using plasma treatments.

In a preferred embodiment of this invention, the particles have an average diameter of up to 900nm. Preferably, the particles have an average diameter of up to 500 nm. More preferably, the particles have an average diameter of from 10nm to 100 nm, preferably 15 to 50nm, more preferably 20 to 30 nm. The length of the particles is in
the region of 1µm to 100µm, such as 10 to 90µm, preferably 20 to 80µm, more preferably 30 to 70µm, or 40 to 60µm or 40 to 50µm.

For the purposes of this invention, the emulsion may comprise a surfactant. The surfactant is preferably from renewable resources, and includes lecithin or natural fatty alcohols derived from coconut and other triglycerides. Preferred natural surfactants are those having a hydrophilic-lipophilic balance (HLB) value between 4 and 8, that is 4, 5, 6, 7 or 8, ideally 7, suitable for stabilizing w/o emulsions.

The emulsion may further comprise one or more of additional functionalized particles, wherein said additional functionalised particles are titania, silica or cellulose, non-stabilizing particles, wherein the non-stabilising particles have a particle size of less than 1mm, or biodegradable particles. For the purposes of this invention, the term non-stabilizing particles indicates that the particles do not stabilize at the three phase interface. The non-stabilizing particles act to increase the viscosity and therefore the stability of the emulsion, reducing propensity towards coalescence. In addition, the non-stabilising particles act as reinforcement or a third phase within in the walls of the resultant foams (such particles may be crosslinked into the polymer matrix). Finally, in the case of a degradable polymer, particles provide a means to induce interconnectivity between pores on their degradation.

The emulsion may be an o/w emulsion or a w/o emulsion, preferably a w/o emulsion.

The second aspect of the invention provides a porous polymer foam produced by polymerization of the continuous phase of a stabilized medium or high dispersed phase emulsion comprising a dispersed phase, a continuous phase comprising at least one type of polymerizable monomer and hydrophobized organic particles.

In a preferred feature of the second aspect there is provided a porous polymer foam comprising bi-modal pores produced by the polymerization of the continuous phase of a stabilised medium or high dispersed phase emulsion comprising a dispersed phase, a continuous phase comprising at least one type of polymerizable monomer and organic
hydrophobized particles of at least two differing sizes wherein preferably said organic hydrophobized particles comprise (larger) fles or fibrils of cellulose and hydrolyzed (smaller) fibrils of cellulose, (which may be termed cellulose nano-whiskers). The particles preferably have a section/diameter of from 20 to 200 nm, such as 50 to 150 nm, preferably 75 to 100 nm. Where particles are provided of two differing sizes the larger particles preferably have a length of from 10 to 100 \( \mu \text{m} \), such as 10 to 90 \( \mu \text{m} \), preferably 25 to 75 \( \mu \text{m} \), more preferably 50 to 60 \( \mu \text{m} \) and the smaller particles preferably have a length of from 200 nm to 1 \( \mu \text{m} \), such as 300 nm to 5 \( \mu \text{m} \), preferably 500 nm to 1 \( \mu \text{m} \), more preferably 700 nm to 800 nm.

For the purposes of this invention, the foam can be produced by polymerization of an emulsion according to the first aspect of the invention. Thus all preferred features of the emulsion, in particular as far as they relate to the continuous phase, the dispersed phase and the particles also apply to the foam of the second aspect of the invention.

It will be appreciated that if the cellulose is not hydrophobized sufficiently to disperse in the organic media, then stable o/w emulsions are formed. Polymerization of the organic phase of these emulsions will result in the formation of spheres; a mixture of hydrophobized and non-hydrophobized cellulose may be used to viscosity and improve the stability of the emulsion.

The third aspect of the invention relates to a method of producing a stabilized medium or high dispersed phase emulsion comprising a dispersed phase, a continuous phase and hydrophobized organic particles, wherein the dispersed phase constitutes 30% or more of the total volume of the emulsion, the method comprising suspending hydrophobized organic particles within the continuous phase, within the dispersed phase or within both the continuous phase and the dispersed phase and combining the dispersed phase with the continuous phase to form a stabilized emulsion. For the purposes of this invention, the particles can be suspended in either the continuous or the dispersed phase or both. The emulsion can be formed by adding either of the continuous or dispersed phases to each other, in the proportion 0-90% by volume, preferably 30 to 95% by volume of the dispersed phase. The composition can be
emulsified using either agitation such as vigorous hand-shaking, homogenization, blending, sonication, pumping through a colloid mill or any other form of emulsification.

The fourth aspect of the invention relates to method of producing a porous polymer foam wherein the method comprises providing a medium dispersed phase emulsion as defined in the first aspect of the invention or as produced by the process of the third aspect of the invention wherein the continuous phase comprises a polymerizable monomer and wherein the continuous phase and/or the dispersed phase comprises an initiator, and initiating polymerization of the continuous phase. The initiator can be incorporated in either the continuous, dispersed or both phases. Preferred thermal initiators are cumene hydroperoxide, azobisisobutyronitrile, potassium persulphate, although many initiators could be used by persons skilled in the art; the principle requisite is that the initiator has a thermal decomposition temperature below the boiling point of the lower boiling point of either phase. UV initiators may be used solely or in combination with thermal initiators. In this case, emulsions may be exposed to UV irradiation to trigger polymerization, and once the sample has gelled it may be transferred to an oven for residual thermal curing. Suitable liquid UV initiators may be selected from the classes of oc-hydroxyketones, phenylglyoxylates, oc-aminoketones or iodonium salts, and preferably the oc-hydroxyketone: 2-hydroxy-2-methyl-1-phenyl-1-propanone (such as Darocur 1173, from Ciba).

The fifth aspect of the invention relates to a method for the hydrophobization of a particle comprising grafting of poly(oc-hydroxyesters), such as polylactide, polyglycolide, polycaprolactone or their co-polymers to the surface of the particle. Ring-opening polymerization of the poly(oc-hydroxyesters) may be performed in the presence of cellulose, whereby the hydroxyl groups on the cellulose act as initiation sites for the ring-opening polymerization. Grafting can also be performed via redox graft polymerization, whereby an initiator such as cerium ammonium is added and acts as an oxidant for the glucose ring of cellulose, creating a free radical, which can propagate diisomethacrylate linkage of the monomer; for example short chain length polycaprolactone methacrylate.
A sixth aspect of the invention relates to the use of hydrophobized organic particles to stabilize an emulsion, which can be destroyed and then reformed. The hydrophobized organic particles therefore provide temporary stabilization of the emulsion for a desired duration.

It will be appreciated that the emulsion can be destroyed and then reformed by varying the dispersed phase volume, the particle concentration and/or the pH of the dispersed phase. In addition or alternatively, the hydrophobized organic particles can be used to stabilise an o/w emulsion which can be destroyed and reformed as a w/o emulsion. In addition or alternatively, the hydrophobized organic particles can be used to stabilise a w/o emulsion which can be destroyed and reformed as an o/w emulsion. Again, the inversion of the emulsion from an o/w to a w/o emulsion and vice-versa can be carried out by varying the dispersed phase volume, the particle concentration and/or the pH of the dispersed phase. In a preferred feature of the sixth aspect of the invention, the hydrophobized organic particle is a hydrophobically modified bacterial cellulose particle.

It will be appreciated that the reversibility of the emulsion can be tuned by functionalizing the cellulose through different degrees of surface substitution of the hydroxyl groups for hydrophobic groups and by varying the length of those hydrophobic groups.

It will be appreciated that preferred features of the invention apply to all other aspects mutatis mutandis.

The invention may be put into practice in various ways and a number of specific embodiments will be described by way of example to illustrate the invention with reference to the accompanying drawings in which:

Figure 1 shows polyPickering (MIPE) foam, stabilized by hydrophobized bacterial cellulose. The diameter of the sample was 25 mm;
Figure 2 shows polyPickering (MIPE) foam, hydrophobized bacterial cellulose can be seen lining the pores (arrowed);

Figure 3 shows a pore wall at high magnification showing hydrophobized bacterial cellulose (arrowed) lining the pore wall in the AESO foam;

Figure 4 shows hollow spheres. The diameter of the sample shown in the background image was 25 mm;

Figure 5 shows organic acid hydrophobized bacterial cellulose/photopolymerized acrylated epoxidized soybean oil nano-composite foam (23 mm in diameter);

Figure 6 shows organic acid hydrophobized bacterial cellulose shown to line the pore wall of the photopolymerized acrylated epoxidized soybean oil nano-composite foam (shown in Fig. 5.);

Figure 7 shows low magnification SEM image of the foam morphology of a polyPickering MIPE based on AEOS stabilised by titania particles;

Figure 8 shows a high magnification SEM image showing the titania particles at the pore wall surfaces;

Figure 9 shows (A) a picture of a 50 vol.-% emulsion solely stabilised by 0.5 wt.-% hydrophobized bacterial cellulose particles. A w/o emulsion was formed. (B) a picture of a fractured section of the resultant polymerized foam;

Figure 10 shows SEM images at low (A) and high (B) magnification of a polyMIPE synthesised from a 50 vol.-% MIPE stabilised solely by 0.5 wt.-% hydrophobized bacterial cellulose particles;

Figure 11 shows a low magnification SEM image showing the interconnected pore
structure resulting from the fused sphere (polymerized AEOS) network; and

Figure 12 shows a high magnification SEM image showing the fused sphere (polymerized AEOS) network that was stabilised by lecithin and hydrophobized bacterial cellulose.

The present application will now be illustrated by reference to one or more of the following non-limiting examples:

EXAMPLES

Materials
Bacterial cellulose was extracted from nata-de-coco, a commercially available product, CHAOKOH coconut gel in syrup (Thep. Padung Porn Coconut Co. Ltd, Bangkok, Thailand). Soybean oil, acrylated epoxidized soybean oil (AESO), chloro(dimethyl)isopropylsilane (CDMIPS) (97%), imidazole (99%), toluene (99.8%), cumene hydroperoxide solution (-80% in cumene), toluene (99.8%), methanol (99.8%), acetone (99.8%), tetrahydrofuran (99.9%) and 17-toluenesulfonyl chloride (99%), hexanoic acid (Aldrich, 99.5%) and lauric acid (Aldrich 98%) were purchased from Sigma-Aldrich (Poole, UK). Pyridine (99.7%), acetic acid (glacial, 100%) were obtained from VWR, UK. All reagents were used without further purification.

Example 1
Preparation of hydrophobic cellulose nano-fibrils via silylation
Bacterial cellulose was extracted from nata-de-coco, by first rinsing the food product three times with deionized water (dH2O), the product was then sieved, homogenized and blended using a variable speed laboratory blender operated at maximum speed (Waring Laboratory, Essex, UK). The bacterial cellulose was then purified by boiling a mixture having a concentration of 0.6 w/v% in 0.1M NaOH at 80 °C for 2 h to remove any remaining microorganisms and soluble polysaccharides. Bacterial cellulose was successively centrifuged, homogenized and rinsed to neutral pH. The cellulose was hydrophobized by adapting a protocol described in a) L. Ladouce et al.
US Pat., 6 703 497 Bl, 2004; (b) Gousse et al. Polymer, 2002, 43, 2645-2651; (c) M. Andresen et al. Cellulose, 2006, 13, 665-677, which was slightly modified to suit our application. Briefly, bacterial cellulose fibrils in aqueous suspension (0.3%, w/v) were solvent exchanged into acetone, through methanol to dry toluene. CDMIPS was added at a molar ratio of 4:1 with respect to the repeating glucose units of the bacterial cellulose. Imidazole was added equimolar to CDMIPS to drive the reaction and trap the HCl released. During the silylation procedure, the CDMIPS reacts with the hydroxyl groups of the cellulose resulting in hydrophobization of its surface. The reaction mixture was agitated using an orbital shaker (600 rpm) for 16 h prior to centrifugation (15 000 g) and decantation. Afterwards, a mix of methanol and THF (20:80, v/v) was added to dissolve the imidizolium chloride byproduct and any disilylethers that may have formed, followed by centrifugation and decantation to obtain a modified cellulose plug. Dispersions of hydrophobized bacterial cellulose in AESO were obtained after rinsing twice with THF and successive centrifugation and re-dispersion operations to exchange the THF with toluene, and exchange of toluene with AESO.

Preparation of water-in- AESO emulsions and macroporous polyAESO synthesized using silylated bacterial cellulose

Between 10-15 ml of AESO was added into Falcon™ tubes, containing 0.5-5 wt.% silylated bacterial cellulose with respect to the AESO phase. The mixtures were homogenized in an ice bath to prevent premature polymerization of the AESO at 20 000 rpm (using a Polytron PTI 0-35 GT batch homogenizer, Kinematica, Switzerland with a 9 mm rotor) for 1 min to disperse the cellulose nano-fibrils prior to drop-wise addition of the aqueous phase, which contained 0.3 M CaCV2H₂O. Homogenization was continued for a further minute after addition of the aqueous phase. Samples of the emulsions were then taken and dripped into water to determine the emulsion type. The emulsion stability index, which is the time dependent emulsion volume relative to the total volume of the water and oil phases, was assessed over a 3-day period. A summary of selected emulsion compositions, their character and stability is given in Table 1. Emulsions containing aqueous phase levels > 70 vol.% (Samples F and G, Table 1) underwent catastrophic phase inversion from w/o to o/w emulsions, this type
of inversion has been reported to occur for other Pickering emulsions at this volume fraction (0.7) as this is near the limit of sphere close packing. Samples F and G (Table 1), creamed into an o/w phase at the top, with a water phase at the bottom; increasing the cellulose loading increased the creamed volume and stability. Emulsions that undergo catastrophic phase inversion can be multiple emulsions (w/o/w for example). Whilst the density of AESO is 1.04 g cm$^{-3}$ the creaming observed may be due to the entrapment of air, along side the formation of a multiple emulsion and due to the hydrophobic cellulose nano-fibrils favoring an air interface over a water interface, as has been observed during their centrifugation. A slight decrease in emulsion volume (< 2.5 vol.%) occurred in samples A-E (Table 1) during the first few hours and can be attributed to the ejection of little continuous phase; a separate oil phase was observed below the emulsion. It was not possible to prepare stable emulsions with > 4 wt.% hydrophobized bacterial cellulose loadings relative to the organic phase (with < 40 vol.% organic phase) due to flocking of cellulose fibrils and an inability to introduce enough shear during homogenization to disperse the fibrils effectively. To polymerize the emulsion template, 3 wt.% of the initiator cumene hydroperoxide (relative to the organic phase) was added to the AESO immediately prior to the preparation of the emulsion (the aqueous phase addition is described above). The Falcon™ tubes were then capped and placed in an oven at 80 °C for 24 h. The polymerized samples were then removed from the tubes and dried in vacuo at 80 °C for a further 24 h. The polymerization of the continuous phase of emulsions A-E (Table 1), containing 50 and 60 vol.% aqueous disperse phase, resulted in closed celled polymer foams (Fig. 1-3). The silylated bacterial cellulose nano-fibrils can clearly be seen (arrowed) lining the pore walls in Fig. 2 and 3, proving their adsorption at the former w/o interface. The smallest pores exhibiting these cellulose nano-flbril linings were > 7 mm in diameter (Fig. 2), indicating a lower limit on the size of the stabilized emulsified drops; the majority of pores were in the range 10-300 μm diameter, with a mean of 80 μm. However, some larger pores several millimetres in diameter were also present. Polymerization of emulsions having aqueous phase levels > 70 vol.% resulted in the formation of a porous material consisting of fused solid spheres. Interestingly when 70 vol.% aqueous phase emulsions stabilized by 3 wt.% of hydrophobized cellulose were polymerized, fused hollow spheres were produced (Fig. 4; SEM of the sectioned
sample inset). In this case a water-in-oil-in-water emulsion is likely to have formed, leading to the development of hollow spheres after drying. The foam produced from the polymerized continuous phase of emulsion formulation B (polyMIFE B, Table 1), which had a dispersed aqueous phase of 50 vol.% exhibited a porosity of 76 ± 1% which is due to the presence of air being beaten in during homogenization and its stabilization by the hydrophobic particles (causing some of the larger pores), and some ejection of the continuous phase.

Example 2
Preparation of hydrophobic cellulose nano-fibrils via organic acid esterification
Bacterial cellulose was extracted as previously described in Example 1 and solvent exchanged from water through methanol into pyridine at a concentration of 0.3% w/v. After each solvent exchange the mixture was homogenised at 20 000 rpm for 1 min to disperse the nano-fibrils, then centrifuged at 15 000 g prior to redispersion in the required solvent. Three solvent exchanges were performed for each solvent during the exchange. The cellulose was adjusted to a concentration of 0.5% w/v with respect to pyridine in a 3-neck round bottom flask and p-toluenesulfonyl chloride added at a ratio of 1:4 by weight with respect to the pyridine. Acetic acid, chosen as the organic acid (although other organic acids can be applied here, such hexanoic, lauric, oleic and linoleic acids as examples), was added equimolar with respect to the p-toluenesulfonyl chloride. Batches of 2 g equivalent dry weight of bacterial cellulose were modified using this route. The mixture was magnetically stirred and the reaction allowed to progress at 50 °C for 2 h under nitrogen. The reaction was subsequently quenched using 1.5 l of ethanol and the mixture then solvent exchanged from pyridine/ethanol through ethanol to water as previously described using successive centrifugation and homogenization steps. This was performed until the colour of the supernatant did not change.

Production of water-in-AESO emulsions and foams using acetic acid modified bacterial cellulose
Water-in-AESO emulsions were prepared via an organic phase exchange method,
described below. This method was used because the AESO phase was initially too viscous to prepare the emulsions. 20 ml water containing 0.5 wt.% acetic acid esterified bacterial cellulose were added into a 50 ml capacity Falcon™ tube and an equal volume of soybean oil (with a density of 0.9 g cm⁻³) was added. The mixture was homogenized at 20 000 rpm for 1 min to disperse the cellulose nano-fibrils throughout the system. The mixture was then left overnight in the capped tube to allow the modified nano-fibrils to swell and migrate to the water-oil interface. Afterwards, the sample was shaken by hand for a period of 30 s, resulting in the formation of a water-in-oil emulsion. The emulsion was allowed to sediment to a stable volume; water droplets were observed to sediment to the bottom of the Falcon™ tube, reaching a stable level at circa 30 ml after several hours. The ejected oil phase was then removed using pipette from the top of the tube and an equal mass of soybean oil replaced by AESO, which was added at 80 °C to allow the otherwise viscous monomer to flow. The sample was then re-shaken by hand to reform the stable emulsion. This process of soybean oil removal and AESO addition was repeated (twice) until 18 ± 2 ml of the original soybean oil was replaced by AESO. Finally, 4 wt.% of a UV-photoinitiator (Darocure 1173, Giba, Basel, Switzerland) was added with respect to the monomer phase. The sample was then re-shaken to improve homogeneity of the emulsion. The sample was then capped and left in an oven at 80 °C to allow the water droplets to sediment until reaching a stable emulsion volume (30 ± 0.5 ml) and any further excess ejected phase was removed. The sample was then exposed to UV radiation using a 100 W mercury lamp (SB-IOOP flood lamp, Spectronics, NY, USA) with a wavelength > 280 nm to photopolymerize the AESO phase; the Falcon™ tube containing the sample was rotated on a stage in front of the lamp at 20 rpm to enable more homogeneous polymerization. The polymerized sample was then removed from the tubes and dried in vacuo at 80 °C for 24 h. The resultant foam is shown (sectioned) in Fig. 3a; the heterogeneously esterified bacterial cellulose nano-fibrils can be seen lining the pore walls in the SEM (Fig. 6), akin to the silylated nano-fibril example (Example 1 and shown in Fig. 3). The porosity of the sample shown in Fig. 5 was 69 ± 1%, consistent with the dispersed aqueous phase volume present prior to polymerization.
Example 3
Poly-Pickering foams made from water-in-functionalized soybean oil emulsions stabilized solely by hydrophobized titania nano particles.

Functionalized titania particles, rendered hydrophobic by treatment in oleic acid are sufficiently hydrophobic to adsorb at the interface of w/o emulsions (International patent application number PCT/GB2008/002537). For the first time, water-in-acrylated epoxidized soybean oil emulsions have also been stabilized by addition of 1 wt.% of titania particles with respect to the organic phase. The mixture of 15 ml AEOS oil and particles were homogenized at 20 000 rpm for 1 min to disperse the particles. The initiator, cumene hyperoxide (3 wt.% relative to the organic phase) was added immediately prior to the aqueous phase addition. The aqueous phase, containing 0.3M CaCl₂ . 2H₂O was added drop-wise under further homogenization. The tube containing the emulsion was placed in an ice bath during homogenization to prevent premature polymerization. Samples were then capped and placed in a vacuum oven at 80 °C for 24 h; samples were then removed from the tubes, dried in vacuo for 12 h and post-cnred at 90 °C for 12 h. The pore structure of the resulting foam is shown at low magnification (Fig. 7) and at high magnification (Fig. 8); the hydrophobized titania particles are visible at the pore wall surfaces.

Example 4:
A macroporous polymer made via Pickering emulsion templating made from water-in-styrene emulsions, stabilized by hydrophobized bacterial cellulose

Hydrophobized bacterial cellulose dispersed in suspension of toluene was centrifuged and then re-dispersed in purified styrene by homogenization at 20 000 rpm and subsequent ultrasonication for 5-10 min using an ultrasound bath. This step was repeated twice. The cellulose plug was finally re-dispersed at a concentration of 0.5 wt.-% (dry equivalent of hydrophobized bacterial cellulose) into a styrene/divinyl benzene mixture (50:50 by vol.). The initiator (2 mol% with respect to the monomers) abisisobutyronitrile (AIBN) was dissolved in the oil phase. In this example, 20 ml of monomer containing the required concentration of modified cellulose was added to a
50 ml polypropylene tube and homogenized at 15 000 rpm and dH₂O added drop-wise at an approximate rate of 3 ml per minute until the monomer/water volumes were equal. The tube containing the stable (w/o) medium dispersed phase emulsion (MIPE) was capped and transferred into an oven for polymerization for 24 h at 70 °C to produce a poly-Pickering foam (Fig. 9). The foam was purified in water overnight and dried at 70°C for 24h prior to microscopic analysis; the foam was brittle, principally due to the choice of monomers. The microstructure of the resultant poly-Pickering foam is shown in Fig. 10. There was negligible shrinkage of the foam, as noted during extraction from the polypropylene tube. The pore size was determined from image analysis of scanning electron micrograph images to be between 200-550 µm with a median pore size of 350 ± 90 µm; smaller pores were evident in the walls of the matrix of sizes < 20 µm.

Example 5:

A macroporous polymer made via Pickering emulsion templating made from functionalized soybean oil resin/water emulsion templates, stabilized using a combination of hydrophobized bacterial cellulose, hydrophobic silica nanoparticles and a natural surfactant, lecithin.

Water-in-acrylated epoxidized soybean oil emulsions (with 50 vol.% aqueous phase) have also been stabilized by addition, relative to the organic phase, of 20 wt.% lecithin, a natural surfactant; 1 wt.% hydrophobized bacterial cellulose and 1 wt.% hydrophobized silica nano-particles (R202, of particle size ~10 nm, Degussa, Germany). A mixture of ~2 ml AEOS, lecithin and particles together was homogenized at 20 000 rpm for 1 min. The initiator, cumene hydroxide (3 wt.% relative to the organic phase) was added immediately prior to the aqueous phase addition. The aqueous phase, containing 0.3M CaG₂O₄.H₂O was added drop-wise under further homogenization. The curing methodology described in Example 1 was applied to polymerize the AEOS phase. The resultant foam (from the emulsion stabilized using lecithin and particles) has a pore structure formed of a network of fused spheres shown at low magnification (Fig. 11) and high magnification (Fig. 12),
indicating that the emulsions were oil-in-water; the spheres fused together during curing to produce the interconnected foam structure.

**Example 6**

Cellulose nano-particles hydrophobized with organic acids act as emulsifiers which permit emulsions to be rapidly destroyed but reformed (reversible emulsions) and display a pH dependency; changing pH allows the emulsions to be phase inverted from w/o to o/w

Cellulose was hydrophobized by organic acids of different chain length, nominally, acetic acid (C2), hexanoic acid (C6) and lauric acid (C12) as described in Example 2. Water-in-toluene emulsions were initially formed by adding a 50:50 by volume mixture of these phases to 50ml Falcon™ tubes containing 1 wt.% of hydrophobized cellulose (relative to the organic phase). Emulsions were shaken by hand at 4Hz for a period of 1 minute and the emulsion stability subsequently recorded after a period of 3 h, provided the emulsion was stable, after some sedimentation and ejection of the oil phase, some of the toluene was removed from the emulsions. The removal of toluene acted to increase the effective dispersed phase (aqueous) volumes. The samples were subsequently re-shaken after altering the dispersed phase volume and the point (dispersed phase volume) at which the emulsions were destroyed was recorded. These emulsions could be reformed by mere addition of some of the organic phase (toluene in this example). The pH of the aqueous phase was reduced or increased by addition of hydrochloric acid or sodium hydroxide and the effect of pH on emulsion type and stability assessed. Changing the pH to increasingly lower values resulted in the emulsions phase inverting from w/o to o/w emulsions; this effect could be reversed on raising the pH. The cellulose particles provide the ability to destroy and recreate emulsions, as well as reversibly phase inverting the emulsions. The maximum dispersed phase that could be achieved for water-in-toluene emulsions for acetic acid modified bacterial cellulose (BC), hexanoic acid modified BC and lauric acid modified BC was 71 vol.%, 82% and 77% by volume, respectively, relative to the total volume. The viscosity of w/o emulsions stabilized by hexanoic acid modified BC increases as the pH was reduced to 1; on changing the pH to 14 the emulsion is
destroyed. Whereas whilst the same viscosity increasing effect is observed for emulsions stabilized by lauric acid modified BC the emulsion is not destroyed at pH 14. In the case of acetic acid modified BC the emulsion is destroyed from a w/o emulsion at pH 14 and then at pH 1 reforms to an o/w emulsion. It is therefore possible to use this mechanism as a means to encapsulate active ingredients.

Applicable to all examples using cellulose as the renewable particulate stabilizer: Characterization of the hydrophobized bacterial cellulose deemed suitable as water/oil emulsion particulate stabilizers

Films of unmodified bacterial cellulose (as control) were formed by taking some centrifuged sample (circa 1 g equivalent dry weight), rolling and pressing this in between release film to remove the water. The films were near fully dried in a hot press (George E. Moore and Sons, Birmingham, UK) and then pressed at 100 °C and 50 kN for 5 min, then further dried in a vacuum oven over night. Films of the modified bacterial cellulose (silylated, as in Example 1, and modified by organic acids (acetic acid, hexanoic and lauric acid) as in Example 2) were made by dispersing the nano-fibrils in chloroform and then filtering this through PTFE membranes; the resultant films that formed on top of the membrane were then pressed. The degree of hydrophobization was assessed by advancing and receding sessile drop contact angle measurement. The wettability of cellulose films was determined by contact angle analysis using a Drop Shape Analyser (DSA 10 MK2, Krüss, Germany). Advancing and receding contact angles were measured by increasing the volume of water droplets placed on the cellulose films in the range 2 ml-20 ml at a rate of 6.32 ml min⁻¹ and then decreasing the drop volume at the same rate, using a motorized syringe. At least six independent determinations at different sites for each sample were made. Zeta (ζ)-potential measurements (EKA, Anton Paar KG, Graz, Austria) in the streaming mode on films of the unmodified and modified bacterial cellulose, following the method previously described in Safinía et al. Macromol. Biosci., 2007, 7, 315-327. The (ζ)-potential and contact angle analyses are given in Table 2. It is apparent that contact angles of water in air, measured on the cellulose surface with angles over 70 ° and 140 ° are capable of stabilizing water-in-oil emulsions. The real
three-phase contact angle between bacterial cellulose (unmodified and modified by silylation, Example 1), water-in-air and acrylated expoxidized soybean oil (AESO) resin-in water was measured on films cast on glass slides of, ~1g of cellulose was cast from their centrifuged plugs and dried overnight in a vacuum oven. AESO resin-in-water contact angles were obtained by the sessile drop method (at 80°C, which was the curing temperature applied in the presence of the initiator) to better represent the real three-phase contact angle in the emulsion. AESO resin-in-water contact angles (measured through water) were 134° ± 10 and 40° ± 9, on hydrophobized and unmodified bacterial cellulose films, respectively. Contact angles of > 90° characterize hydrophobic particles and allow them to be adsorbed at the interface, stabilizing w/o emulsions; the converse is true if this angle is < 90°. The silylated bacterial cellulose is preferentially wet by the oil phase than the water phase and is able to stabilise w/o emulsions. A particle (idealised spherical) is most strongly held at the interface when the real three-phase contact angle is 90°. The modification by organic acids to the cellulose was further characterized using Fourier infra-red attenuated total reflectance spectroscopy (ATR-FTIR) (Spectrum 100, PerÅη Elmer, Bucks UK). Carbonyl bonds not present for the unmodified cellulose appeared at their characteristic wavenumber of 1750 cm⁻¹, denoting successful esterification and therefore the grafting of the hydrophobic acid.

The dynamic vapour sorption of unmodified and organic acid hydrophobized bacterial cellulose was assessed with water and toluene separately to determine swelling behaviour. Results shown in Table 3 show that the modified celluloses swell in toluene more than water, this is likely to be the mechanism for their stronger adsorption at the interface between water/oils, thereby stabilizing water-in-oil emulsions; whereas, the unmodified cellulose swells to a larger extent in water and is predisposed to stabilize oil-in-water emulsions.
Table 1. Composition of the emulsion templates stabilized by silylated bacterial cellulose and their stability as a function of time.

<table>
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<tr>
<th>Sample ID</th>
<th>Organic phase[^a] [vol.%]</th>
<th>Modified cellulose [wt.%][^b]</th>
<th>Emulsion Character</th>
<th>Emulsion stability index [%][^c]</th>
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<tr>
<td>A</td>
<td>50</td>
<td>0.5</td>
<td>w/o</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>50</td>
<td>1</td>
<td>w/o</td>
<td>100</td>
</tr>
<tr>
<td>C</td>
<td>50</td>
<td>2</td>
<td>w/o</td>
<td>100</td>
</tr>
<tr>
<td>D</td>
<td>40</td>
<td>0.5</td>
<td>w/o</td>
<td>100</td>
</tr>
<tr>
<td>E</td>
<td>40</td>
<td>2</td>
<td>w/o</td>
<td>97.5</td>
</tr>
<tr>
<td>F</td>
<td>30</td>
<td>1</td>
<td>o/w</td>
<td>57.6</td>
</tr>
<tr>
<td>G</td>
<td>30</td>
<td>2</td>
<td>o/w</td>
<td>68.4</td>
</tr>
</tbody>
</table>

[^a]: Volume of the organic phase (AESO) relative to the total volume of the emulsion.
[^b]: wt.% of hydrophobized bacterial cellulose relative to the organic phase volume.
[^c]: Volume of emulsified phase relative to the total volumes of monomer and aqueous phases.

Table 2. Summarising the wettability (contact angles and Zeta-potential) of unmodified and hydrophobized bacterial cellulose. *Receding contact angle could not be obtained due to wicking.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ζ-Potential (plateau value) [mV]</th>
<th>Iso-electric point [pH value]</th>
<th>Advancing contact angle [°]</th>
<th>Receding contact angle [°]</th>
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<tbody>
<tr>
<td>Unmodified BC</td>
<td>-7.1 ± 0.5</td>
<td>3.6 ± 0.1</td>
<td>11 ± 3</td>
<td>*</td>
</tr>
<tr>
<td>Silylated BC</td>
<td>-24.0 ± 1.0</td>
<td>3.8 ± 0.1</td>
<td>105 ± 2</td>
<td>73 ± 2</td>
</tr>
<tr>
<td>Acetic acid esterified</td>
<td>-20.8 ± 0.7</td>
<td>3.8 ± 0.1</td>
<td>75 ± 3</td>
<td>35 ± 6</td>
</tr>
<tr>
<td>Hexanoic acid esterified BC</td>
<td><strong>-21.0± 0.8</strong></td>
<td>3.9 ± 0.1</td>
<td>92 ± 2</td>
<td>45 ± 2</td>
</tr>
<tr>
<td>Laurie acid esterified BC</td>
<td><strong>-20.9 ± 0.7</strong></td>
<td>3.8 ± 0.1</td>
<td>133 ± 9</td>
<td>80 ± 11</td>
</tr>
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</table>
Table 3. Dynamic vapour sorption of unmodified and hydrophobized bacterial cellulose.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water uptake at 90% RH (wt.%)</th>
<th>Toluene uptake at 90% PP (wt.%)</th>
</tr>
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<tbody>
<tr>
<td>Neat Bacterial Cellulose (BC)</td>
<td>17.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Acetic acid modified BC</td>
<td>6.8</td>
<td>15.2</td>
</tr>
<tr>
<td>Hexanoic acid modified BC</td>
<td>6.2</td>
<td>29.1</td>
</tr>
<tr>
<td>Laurie acid modified BC</td>
<td>7.5</td>
<td>28.4</td>
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</table>
Claims

1. A particle stabilised high or medium dispersed phase emulsion comprising a dispersed phase which constitutes 30% or more of the total volume of the emulsion, a continuous phase and hydrophobized organic particles.

2. An emulsion as claimed in claim 1 wherein the hydrophobized organic particles are derived from a renewable source.

3. An emulsion as claimed in claim 1 or claim 2 wherein the particles are cellulose derived particles.

4. An emulsion as claimed in claim 3 wherein said cellulose is nano-cellulose.

5. An emulsion as claimed in claim 1 or claim 2 wherein the particle is derived from chitin.

6. An emulsion as claimed in any one of claims 1 to 5 wherein said dispersed phase is an aqueous dispersed phase.

7. An emulsion as claimed in any one of claims 1 to 6 wherein said continuous phase is one or more of functionalised soybean oil, a thermoset resin derived from vegetable oil, a reactive oil or a low molecular weight resin.

8. An emulsion as claimed in any one of claims 1 to 7 wherein said continuous phase is a monomer phase comprising styrene, di-vinyl benzene and/or functionalized polyethylene glycol monomer, renewable monomers or a crosslinker.

9. An emulsion as claimed in any one of claims 3, 4 or 6 to 8 wherein the cellulose particles or the cellulose (nano)particles are hydrophobized with bifunctional chlorosilanes, such as chlorodimethylvinylsilane, dimethylchlorosilylpropylmethacrylate or chloromethylphenylvinylsilane.
10. An emulsion as claimed in any one of claims 3, 4 or 6 to 8 wherein the cellulose particles are hydrophobized by esterification with an organic acid.

11. An emulsion as claimed in any one of claims 4 or 6 to 10 wherein the cellulose (nano)particles are endcapped with reactive groups and cross-linked into the polymer.

12. An emulsion as claimed in any one of claims 1 to 11 additionally comprising a surfactant.

13. An emulsion as claimed in claim 12 wherein said surfactant is lecithin or a natural fatty alcohol.

14. An emulsion as claimed in any one of claims 1 to 13 additionally comprising additional functionalised particles.

15. An emulsion as claimed in claim 14 wherein said additional functionalised particles are titania, silica or cellulose.

16. An emulsion as claimed in any one of claims 1 to 15 further comprising non-stabilising particles.

17. An emulsion as claimed in claim 16 wherein the non-stabilising particles have a particle size of less than 1μm.

18. An emulsion as claimed in any one of claims 1 to 17 further comprising biodegradable particles.

19. A porous polymer foam produced by polymerization of the continuous phase of a stabilized medium or high dispersed phase emulsion comprising a dispersed phase, a continuous phase comprising at least one type of polymerizable monomer and hydrophobized organic particles.
20. A porous polymer foam comprising bi-modal pores produced by the polymerization of the continuous phase of a stabilised medium or high dispersed phase emulsion comprising an dispersed phase, a continuous phase comprising at least one type of polymerizable monomer and hydrophobized organic particles of at least two differing sizes.

21. A foam as claimed in claim 20 wherein said hydrophobized particles comprise tlocs or fibrils of cellulose and hydrolysed fibrils of cellulose.

22. The foam as claimed in any one of claims 19 to 21, wherein the foam is produced by polymerization of an emulsion according to any of claims 1 to 18.

23. A method of producing a stabilised medium or high dispersed phase emulsion comprising a dispersed phase, a continuous phase and hydrophobized organic particles, wherein the dispersed phase constitutes 30% or more of the total volume of the emulsion, the method comprising suspending hydrophobized particles within the dispersed phase, within the continuous phase or within both the dispersed phase and the continuous phase and combining the dispersed phase with the continuous phase to form a stabilised emulsion.

24. A method as claimed in claim 23 wherein the emulsion is formed by agitation, homogenization, blending, sonication or pumping through a colloid mill.

25. A method of producing a porous polymer foam wherein the method comprises providing a medium dispersed phase emulsion as defined in any of claims 1 to 18 or as produced by the process of claim 23 or 24, wherein the continuous phase comprises a polymerizable monomer and wherein the continuous phase and/or the dispersed phase comprises an initiator, and initiating polymerization of the continuous phase.

26. A method for the hydrophobisation of a particle comprising grafting of a poly (α-hydroxyester) to the surface of the particle.
27. A method as claimed in claim 26 wherein the poly (α-hydroxyester) is a polylactide, a polyglycolide, a polycaprolactone or a co-polymer thereof.

28. The use of hydrophobized organic particles to stabilize an emulsion, which is subsequently destroyed and then reformed by modification of the dispersed phase volume, particle concentration and/or pH.

29. The use as claimed in claim 28 wherein the initial emulsion is a o/w emulsion and the reformed emulsion is a w/o emulsion or wherein the initial emulsion is a w/o emulsion and the reformed emulsion is a o/w emulsion.
Figure 8
### A. CLASSIFICATION OF SUBJECT MATTER

INV. C08J9/28 C08J7/04

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)

C08L C08J A61L BOIJ

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<td>X</td>
<td>US 5 958 495 A (KLINKSIEK BERND [DE]) 28 September 1999 (1999-09-28) abstract</td>
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Further documents are listed in the continuation of Box C

See patent family annex

| 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 |
| A | document member of the same patent family |

Date of the actual completion of the international search: 26 January 2010

Date of mailing of the international search report: 08/02/2010

Name and mailing address of the ISA/Authorized officer: European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel (+31-70) 340-20,0 Fax (+31-70) 340-3016

Authorised officer: olde Scheper, Bernd
<table>
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<td>X</td>
<td>WO 2007/068127 A (ETH ZURICH [CH]; GAUCKLER LUDWIG J [CH]; STUDART ANDRE R [CH]; TERVOOR) 21 June 2007 (2007-06-21) claims 1-38; figures 1-5</td>
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Continuation of Box II.2

Claims Nos.: 28-29

1 Independent claim 28 relates to the use of hydrophobized organic particles. Said use is defined as "to stabilize an emulsion". Nevertheless, said claim 28, which relates to a physical entity (product) seeks to define the invention by reference to features relating to the entity's use. In the present case the claim not only defines the entity itself but also specifies its relationship to a second entity which is not part of the claimed entity ("......which is subsequently destroyed and then reformed by modification of the dispersed phase volume, particle concentration and/or pH"); see PCT/GL/ISPE/1, 5.37. The scope of the claim can therefore not be established (Art. 6 PCT).

2 Claim 29 refers back to claim 28 and is therefore considered to be too unclear as well (Art. 6 PCT).

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.
INTERNATIONAL SEARCH REPORT

**Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [x] Claims Nos because they relate to subject matter not required to be searched by this Authority, namely

2. [x] because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically see FURTHER INFORMATION sheet PCT/ISA/210

3. [x] Claims Nos because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6 4(a)

**Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. [ ] As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos

4. [ ] No required additional search fees were timely paid by the applicant Consequently, this international search report is restricted to the invention first mentioned in the claims, it is covered by claims Nos

Remark on Protest

- [ ] The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee
- [ ] The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation
- [ ] No protest accompanied the payment of additional search fees

Form PCT/ISA/21 0 (continuation of first sheet (2)) (April 2005)
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