

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property

Organization

International Bureau

(43) International Publication Date

01 February 2024 (01.02.2024)



(10) International Publication Number

WO 2024/022672 A1

(51) International Patent Classification:

B01J 20/10 (2006.01) B01J 20/26 (2006.01)

B01J 20/12 (2006.01) B01J 20/28 (2006.01)

B01J 20/14 (2006.01) B01J 20/30 (2006.01)

B01J 20/24 (2006.01)

Published:

- with international search report (Art. 21(3))
- in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE

(21) International Application Number:

PCT/EP2023/066158

(22) International Filing Date:

15 June 2023 (15.06.2023)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

22386052.9 29 July 2022 (29.07.2022) EP

(71) Applicant: **IMERTECH SAS** [FR/FR]; 43, Quai de Grenelle, 75015 Paris (FR).

(72) Inventors: **RILEY, Andy**; 53 Penkernick Way, St Columb Major, Cornwall TR9 6BQ (GB). **CASARIN, Simon**; 3 rue de Saragosse, Appt A16, 31200 Toulouse (FR). **LABOULFIE, Fabien**; 37 rue René Aversenq, 31130 Balma (FR). **IPSILANTI, Eleni**; Pavlou Bakogianni 69, 15238 Halandri (GR).

(74) Agent: **HASELTINE LAKE KEMPNER LLP**; One Portwall Square, Portwall Lane, Bristol BS1 6BH (GB).

(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, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, 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, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, 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, ME, 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).

(54) Title: GRANULATE OF AT LEAST ONE OF EXPANDED MILLED PERLITE, DIATOMACEOUS EARTH AND SEPIOLITE AS AN ABSORBENT

(57) Abstract: A granulate comprising a binder and at least one of expanded milled perlite particles, diatomaceous earth particles, and sepiolite particles; wherein the particles are bound together by the binder forming pores between the particles; and the granulate has a D₅₀ from about 150 to about 2000 microns.

WO 2024/022672 A1

GRANULATE OF AT LEAST ONE OF EXPANDED MILLED PERLITE,
DIATOMACEOUS EARTH AND SEPIOLITE AS AN ABSORBENT

TECHNICAL FIELD

5

The present disclosure concerns a granulate comprising a binder and at least one of expanded milled perlite particles, diatomaceous earth particles, and sepiolite particles, methods for preparing granulate materials, absorbent materials comprising granulate materials, animal feed compositions comprising granulate materials and methods for
10 treating fluid spills using granulate materials.

BACKGROUND

Perlite is a naturally-occurring amorphous volcanic glass which has a relatively-high
15 water content. When heated rapidly, the water turns to steam and expands the glass to form a foamed structure. The lightweight expanded perlite foamed structures are milled and classified to suit a wide variety of applications.

Expanded milled perlite is commonly used as a lightweight absorbent material in
20 applications which require absorption of liquids of interest. Expanded milled perlite is already used as a carrier in animal feed to absorb liquid nutrients. Additionally, expanded perlite is an ideal medium for cleaning fluid spills.

Diatomaceous earth products are obtained from diatomaceous earth (also called "DE"
25 or "diatomite"), which is generally known as a sediment enriched in biogenic silica (silica produced or brought about by living organisms) in the form of siliceous skeletons (frustules) of diatoms. Diatoms are a diverse array of microscopic, single-celled, golden-brown algae generally of the class Bacillariophyceae that possess an ornate siliceous skeleton of varied and intricate structures comprising two valves that, in the living diatom,
30 fit together much like a pill box. Diatomaceous earth may form from the remains of water-borne diatoms and, therefore, diatomaceous earth deposits may be found close to either current or former bodies of water. Those deposits are generally divided into two categories based upon source: freshwater and saltwater.

35 Sepiolite is a fibrous hydrated magnesium silicate that is opaque and white, grey or cream in colour. This light, porous clay is said to resemble sea foam. Sepiolite, like milled

perlite, is known to have good adsorption properties and is an abundantly available material.

It would be desirable to produce a granulate product which comprises a binder and at least one of expanded milled perlite particles, diatomaceous earth particles, and sepiolite particles, which has improved absorption capacity, flowability that remains constant as the liquid incorporation is increased and reduced dust levels when compared to typically used expanded perlite.

10 SUMMARY

According to a first aspect, there is provided a granulate comprising a binder and at least one of expanded milled perlite particles, diatomaceous earth particles, and sepiolite particles, wherein:

- 15 i) the expanded milled perlite particles have a D_{50} from about 5 to about 40 microns;
- ii) the diatomaceous earth particles have a D_{50} from about 5 to about 40 microns;
- iii) the sepiolite particles have a D_{50} from about 5 to about 100 microns;
- 20 iv) the granulate has a D_{50} from about 150 to about 2000 microns; and

wherein the particles are bound together by the binder forming pores between the particles.

According to a second aspect, there is provided an absorbent material comprising a granulate according to the first aspect.

According to a third aspect, there is provided a method for treating fluid spills comprising applying the absorbent material according to the second aspect to the fluid spill so that the fluid is absorbed by the absorbent material.

30

According to a fourth aspect, there is provided an animal feed composition comprising the granulate according to the first aspect.

According to a fifth aspect, there is provided a method of preparing the granulate according to the first aspect comprising spray drying the milled expanded perlite particles with a binder and performing a curing step.

35

The skilled person will appreciate that, except where mutually exclusive, a feature described in relation to any one of the above aspects may be applied *mutatis mutandis* to any other aspect. Furthermore, except where mutually exclusive, any feature
5 described herein may be applied to any aspect and/or combined with any other feature described herein.

FIGURES

10 Embodiments will now be described by way of example only, with reference to the Figures, in which:

Figure 1 is a graph showing the impact of absorption on the flowability of powder samples prepared according to the present invention compared with comparative
15 examples.

Figure 2 includes SEM images showing various milled expanded perlite granulates formed according to the present invention.

20 DETAILED DESCRIPTION OF THE INVENTION

It has been surprisingly found that granulating at least one of expanded milled perlite, diatomaceous earth, and sepiolite using a binder results in a product with high absorption rate, constant flowability and minimal dust levels.

25

Expanded milled perlite particles

Perlite typically contains the following components: silicon dioxide, aluminium oxide, sodium oxide, potassium oxide, iron oxide, magnesium oxide, calcium oxide, water and
30 small amounts of other metallic elements.

The perlite particles of the present invention are in the form of expanded perlite. Typically, expanded perlite includes one or more cells, or parts of cells, in which a cell is a void space partially or entirely surrounded by walls of glass, usually formed from
35 expansion of gases when the glass is in the softened state. Processes for expanding perlite may include heating perlite in air to a temperature of least about 700 °C, typically

between 800 °C and 1100 °C, in an expansion furnace. Exemplary processes for producing expanded perlite are described in US 2006/0075930, the entire contents of which is hereby incorporated by reference. Expanded perlite typically has a bulk volume up to 20 times that of the unexpanded material.

5

In accordance with the present invention, the perlite is milled after it has been expanded in the expansion furnace.

10

Unless otherwise specified, the particle size properties referred to herein for the expanded milled perlite particles are as measured by the method employed in the art of laser light scattering, using a CILAS 1064L particle size analyser, as supplied by CILAS (or by other methods which give essentially the same result). In the laser light scattering technique, the size of particles in powders, suspensions and emulsions may be measured using the diffraction of a laser beam, based on an application of Fraunhofer and Mie theory. Such a machine provides measurements and a plot of the cumulative percentage by volume of particles having a size, referred to in the art as the 'equivalent spherical diameter' (e.s.d), less than given e.s.d values. The mean particle size d_{50} is the value determined in this way of the particle e.s.d at which there are 50% by volume of the particles which have an equivalent spherical diameter less than that d_{50} value.

20

According to the present invention, the expanded milled perlite particles have a d_{50} from about 5 to about 40 microns, such as from about 10 to about 35 microns, or from about 15 to about 30 microns, or from about 20 to about 25 microns.

25

In certain embodiments, the expanded milled perlite particles have a bulk density of from about 0.05 g/cm³ to about 0.20 g/cm³, such as from about 0.06 g/cm³ to about 0.19 g/cm³, such as from about 0.07 g/cm³ to about 0.18 g/cm³, such as from about 0.08 g/cm³ to about 0.17 g/cm³, such as from about 0.09 g/cm³ to about 0.16 g/cm³, such as such as from about 0.10 g/cm³ to about 0.15 g/cm³, such as from about 0.11 g/cm³ to about 0.14 g/cm³, such as from about 0.12 g/cm³ to about 0.13 g/cm³.

30

Diatomaceous earth particles

35

Unless otherwise specified, the particle size properties referred to herein for the diatomaceous earth particles are as measured by the method employed in the art of laser light scattering, using a CILAS 1064L particle size analyser, as supplied by CILAS

(or by other methods which give essentially the same result). In the laser light scattering technique, the size of particles in powders, suspensions and emulsions may be measured using the diffraction of a laser beam, based on an application of Fraunhofer and Mie theory. Such a machine provides measurements and a plot of the cumulative percentage by volume of particles having a size, referred to in the art as the 'equivalent spherical diameter' (e.s.d), less than given e.s.d values. The mean particle size d_{50} is the value determined in this way of the particle e.s.d at which there are 50% by volume of the particles which have an equivalent spherical diameter less than that d_{50} value.

- 10 According to the present invention, the diatomaceous earth particles have a d_{50} from about 5 to about 40 microns, such as from about 10 to about 35 microns, or from about 15 to about 30 microns, or from about 20 to about 25 microns.

- 15 In certain embodiments, the diatomaceous earth particles have a bulk density of from about 0.05 g/cm³ to about 0.20 g/cm³, such as from about 0.06 g/cm³ to about 0.19 g/cm³, such as from about 0.07 g/cm³ to about 0.18 g/cm³, such as from about 0.08 g/cm³ to about 0.17 g/cm³, such as from about 0.09 g/cm³ to about 0.16 g/cm³, such as from about 0.10 g/cm³ to about 0.15 g/cm³, such as from about 0.11 g/cm³ to about 0.14 g/cm³, such as from about 0.12 g/cm³ to about 0.13 g/cm³.

20

Sepiolite particles

Sepiolite is a naturally occurring clay mineral. It is a hydrous magnesium silicate which is lightweight, non-swelling and porous.

25

- The particle size properties referred to herein for the sepiolite particles are as measured by the method employed in the art of laser light scattering, using a CILAS 1064L particle size analyser, as supplied by CILAS (or by other methods which give essentially the same result). In the laser light scattering technique, the size of particles in powders, suspensions and emulsions may be measured using the diffraction of a laser beam, based on an application of Fraunhofer and Mie theory. Such a machine provides measurements and a plot of the cumulative percentage by volume of particles having a size, referred to in the art as the 'equivalent spherical diameter' (e.s.d), less than given e.s.d values. The mean particle size d_{50} is the value determined in this way of the particle e.s.d at which there are 50% by volume of the particles which have an equivalent spherical diameter less than that d_{50} value.
- 30
- 35

According to the present invention, the sepiolite particles have a d_{50} from about 5 to about 100 microns, such as from about 10 to about 90 microns, or from about 20 to about 80 microns, or from about 30 to about 70 microns, or from about 40 to about 60 microns,
5 from about 10 to about 50 microns, or from about 20 to 40 microns.

In certain embodiments, the sepiolite particles have a bulk density of from about 0.05 g/cm³ to about 0.30 g/cm³, such as from about 0.06 g/cm³ to about 0.19 g/cm³, such as from about 0.07 g/cm³ to about 0.18 g/cm³, such as from about 0.08 g/cm³ to about 0.17 g/cm³, such as from about 0.09 g/cm³ to about 0.16 g/cm³, such as such as from about 0.10 g/cm³ to about 0.15 g/cm³, such as from about 0.11 g/cm³ to about 0.14 g/cm³, such as from about 0.12 g/cm³ to about 0.13 g/cm³.

Granulate

15 According to the present invention at least one of the expanded milled perlite particles, the diatomaceous earth particles, and the sepiolite particles are bound together using a binder to form a granulate. Granulation is the act or process in which primary powder particles are adhered to form larger, multiparticle entities called granules or granulates.

20 In certain embodiments, the granulate comprises or consists of or consists essentially of expanded milled perlite particles, and a binder. In certain embodiments, the granulate comprises or consists of or consists essentially of diatomaceous earth particles, and a binder. In certain embodiments, the granulate comprises or consists of or consists essentially of sepiolite particles, and a binder. In certain embodiments, the granulate comprises or consists of or consists essentially of a blend of expanded milled perlite particles and diatomaceous earth particles, and a binder. In certain embodiments, the granulate comprises or consists of or consists essentially of a blend of expanded milled perlite particles and sepiolite particles, and a binder. In certain embodiments, the
25 granulate comprises or consists of or consists essentially of a blend of diatomaceous earth particles and sepiolite particles, and a binder. In certain embodiments, the granulate comprises or consists of or consists essentially of a blend of expanded milled perlite particles, diatomaceous earth particles and sepiolite particles, and a binder.

35 At least one of the expanded milled perlite particles, diatomaceous earth particles, and sepiolite particles are bound together by the binder forming pores or otherwise known as

interstitial void spaces between the particles. In some embodiments, the pores have a measurable pore size, which is explained in the experimental section below. In certain embodiments, the median pore size is from about 1 g/cm³ to about 6 g/cm³, or about 1.1 g/cm³, or about 1.2 g/cm³, or about 1.3 g/cm³, or about 1.4 g/cm³, or about 1.5 g/cm³, or
5 about 1.6 g/cm³, or about 1.7 g/cm³, or about 1.8 g/cm³, or about 1.9 g/m³, or about 2.0 g/m³.

According to the present invention, the granulate has a d₅₀, by laser diffraction method (as described above) of from about 150 to about 2000 microns, for example, of from
10 about 200 microns to about 1900 microns, or from about 300 microns to about 1800 microns, or from about 400 microns to about 1700 microns or from about 500 microns to about 1600 microns, or from about 600 microns to about 1500 microns, or from about 700 microns to about 1400 microns, or from about 800 microns to about 1300 microns, or from about 900 microns to about 1200 microns, or from about 1000 microns to about
15 1100 microns, or from about 200 microns to about 600 microns, such as from about 350 microns to about 550 microns, or from about 400 microns to about 500 microns, or from about 600 microns to about 1900 microns, such as from about 700 microns to about 1800 microns, or from about 800 microns to about 1600 microns, or from about 900 microns to about 1500 microns, or from about 1000 microns to about 1400 microns, or
20 from about 1100 microns to about 1300 microns. The granulate may have a d₅₀, by laser of from about 200 microns to about 1000 microns, or from about 300 microns to about 900 microns, or from about 400 microns to about 800 microns, or from about 500 microns to about 700 microns.

25 In certain embodiments, the granulate has a bulk density of from about 0.1 g/cm³ to about 0.50 g/cm³, such as from about 0.15 g/cm³ to about 0.45 g/cm³, such as from about 0.20 g/cm³ to about 0.40 g/cm³, such as from about 0.20 g/cm³ to about 0.35 g/cm³, such as from about 0.25 g/cm³ to about 0.30 g/cm³.

30 The granulate of the present invention may have a measurable BET surface area. BET specific surface area refers to the area of the surface of the particles of the granulate particulate with respect to unit mass, determined according to the BET method by the quantity of nitrogen adsorbed on the surface of said particles so as to form a monomolecular layer completely covering said surface (measurement according to the
35 BET method, AFNOR standard X11-621 and 622 or ISO 9277). Details of the BET

specific surface area measurement method used in the preparation of the present application are set out in the Examples.

- The granulate may have a BET specific surface area no less than about 1.5 m²/g, for example, no less than about 1.6 m²/g, or no less than about 1.7 m²/g, or no less than about 1.8 m²/g, or no less than about 1.9 m²/g, or no less than about 2.0 m²/g, or no less than about 2.5 m²/g, or no less than about 3.0 m²/g, or no less than about 5.0 m²/g, or no less than about 10 m²/g (e.g. 10.0 m²/g), or no less than about 20 m²/g (e.g. 11.0 m²/g). The granulate may have a BET specific surface area no greater than about 50 m²/g (e.g. 50.0 m²/g), for example, no greater than about 40 m²/g (e.g. 40.0 m²/g), or no greater than about 30 m²/g, (e.g. 30.0 m²/g) or no greater than about 20 m²/g (e.g. 20.0 m²/g), or no greater than about 15 m²/g (e.g. 15.0 m²/g), or no greater than about 12 m²/g (e.g. 12.0 m²/g), or no greater than about 11 m²/g (e.g. 11.0 m²/g), or no greater than about 10 m²/g (e.g. 10.0 m²/g), or no greater than about 8.0 m²/g, or no greater than about 7.0 m²/g, or no greater than about 6.0 m²/g. The granulate may have a BET specific surface area may be from about 1.5 m²/g to about 50 m²/g (e.g., 50.0 m²/g), for example, from about 2 m²/g to about 40 m²/g (e.g. 40.0 m²/g), or from about 5 m²/g to about 30 m²/g (e.g. 30.0 m²/g), or from about 10 m²/g to about 20 m²/g (e.g. 20.0 m²/g).
- In certain embodiments, the granulate has an angle of repose up to about 38°, as measured by the angle of repose (funnel method) using the EFT-01 Powder Flow Tester; the granulate has an absorption capacity of at least 150%, as measured using the Westinghouse method described herein in the experimental section and utilizing dioctyladipate as the absorbate; and a dust content less than 10, as measured by the Dust analyzer DustmonRD 100.

- The angle of repose of a granular material is the steepest angle of descent or dip relative to the horizontal plane to which a material can be piled without slumping. The morphology of the material affects the angle of repose. When bulk granular materials are poured onto a horizontal surface, a conical pile will form. The internal angle between the surface of the pile and the horizontal surface is known as the angle of repose and is related to the density, surface area and shapes of the particles, and the coefficient of friction of the material. Material with a low angle of repose forms flatter piles than material with a high angle of repose. Thus, smooth rounded sand grains cannot be piled as steeply as rough interlocking sands. The method for calculating the angle of repose is described in more detail below in the experimental section.

In certain embodiments the angle of repose (of the dry product) is up to about 38°, such as up to 37°, such as up to 36°, such as up to 35°, such as up to 34°, such as up to 33°, such as up to 32°, such as up to 31°, such as up to 30°.

5

In certain embodiments the granulate has an advantageously low dust content (measured using the Dust Analyzer Dustmon RD 100 (available from Retsch®)) of less than 10, such as less than 9, or 8. The method for calculating the dust content value is explained in more detail in the experimental section.

10

Expanded milled perlite, diatomaceous earth and sepiolite are already known for their ability to hold water and for a strong water absorption capacity. This absorption capacity is increased further by granulation of at least one of the expanded milled perlite particles, the diatomaceous earth particles, and the sepiolite particles, with a binder.

15

In certain embodiments, the granulate of the present invention has an absorption capacity of at least 150% (calculated as $100 \times (\text{weight of the absorbate} / \text{weight of the composition})$) as measured using the Westinghouse method as described herein in the experimental section. In certain embodiments, the granulate has an absorption capacity of at least 200%, such as at least 250%, such as at least 300%, such as at least 350%, such as at least 400%, such as at least 450%, such as at least 500%.

20

Binder

According to the present invention at least one of the expanded milled perlite particles, the diatomaceous earth particles, and sepiolite particles are bound together using a binder to form a granulate.

25

In certain embodiments, the binder is a polymer, bentonite or lignosulphonate.

30

In certain embodiments, the binder is a polymer.

In certain embodiments, the binder consists of a single type of polymer, or in certain embodiments the binder comprises one or more polymers.

35

In certain embodiments, the polymer is selected from one or more of a water-soluble synthetic polymer, a natural water-soluble polymer and a polyol. In certain embodiments, the polymer is a combinations of these types of polymers.

- 5 In certain embodiments the binder comprises or consists of a water-soluble synthetic polymer selected from, for example, polyvinyl alcohol (PVA), polyethylene glycol, urea formaldehyde, polyacrylamide, microcrystalline cellulose, polyacrylates, acrylic/maleic copolymers and polyvinylpyrrolidone.
- 10 In certain embodiments, the binder comprises or consists of natural water-soluble polymers, for example, xanthan gum, sodium alginate, potassium alginate, lignosulfonate, locust bean gum, pectin, dextran, carrageenan, agar, xanthan gum, guar gum, Arabic gum (acacia), cellulose ethers such as methyl cellulose and ethyl cellulose, starch or starch-based derivatives.

15

- In certain embodiments, the binder comprises or consists of a polyol. By the term "polyol" we mean an organic compound containing multiple hydroxyl groups. The polyol may be a low molecular weight polyol such as glycerol or pentaerythritol. Alternatively, the polyol may be a sugar alcohol which a class of low molecular weight polyols which are obtained
- 20 by the hydrogenation of sugars, for example, erythritol, hydrogenated starch hydrolysates, isomalt, lactitol, maltitol, mannitol, sorbitol and xylitol. Derivatives of polyols are also intended to be included in this definition, for example, sorbitan monolaurate which is a mixture of esters formed from the fatty acid lauric acid and polyols derived from sorbitol.

25

- In certain embodiments, the binder is selected from polyvinyl alcohol, sodium alginate, potassium alginate, lignosulphonate, urea-formaldehyde, agar, carrageenan, guar gum, cassia gum, xantham gum, cellulose, arabic gum (acacia), microcrystalline cellulose, methyl cellulose, ethyl cellulose, sorbitan monolaurate, starch or starch-based
- 30 derivatives, bentonite and combinations thereof.

- In certain embodiments, the binder comprises or consists of polyvinyl alcohol, preferably having a molecular weight greater than about 90,000 g/mol, or greater than about 100,000 g/mol, or greater than about 120,000 g/mol, or greater than about 150,000
- 35 g/mol.

In certain embodiments, the binder is a cross-linked binder which is a reaction product of a polymer and a cross-linking agent. Cross-linking is the formation of chemical links between polymer chains to form a three-dimensional network of connected molecules.

- 5 The polymer may be selected from the list of polymers described above. Cross-linking agents are well-known in the art and may be selected depending on the type of polymer.

In certain embodiments, the cross-linking agent is an acid selected from one or more of the following:

10

- (i) dicarboxylic acids, including oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid. Suberic acid, azelaic acid, sebacic acid, malic acid, tartaric acid, tartronic acid, aspartic acid, glutamic acid, fumaric acid, itaconic acid, maleic acid, traumatic acid, camphoric acid, phthalic acid and its derivatives that contain at least one boron or chlorine atom, tetrahydrophthalic acid and its derivatives that contain at least one chlorine atom, isophthalic acid, terephthalic acid, mesaconic acid and citraconic acid,

15

- (ii) tricarboxylic acids, including citric acid, tricarballylic acid, 1,2,4-butanetricarboxylic acid, aconitic acid, hemimellitic acid, trimellitic acid and trimesic acid;

20

- (iii) tetracarboxylic acids, including 1,2,3,4-butanetetracarboxylic acid and pyromellitic acid;

- (iv) polycarboxylic acids such as EDTA;

25

- (v) unsaturated carboxylic acids including eth)acrylic acid, crotonic acid, isocrotonic acid, maleic acid, cinnamic acid, 2-methylmaleic acid, fumaric acid, itaconic acid, 2-methylitaconic acid, α,β -methyleneglutaric acid and monoesters of unsaturated dicarboxylic acids, and the vinyl monomer is styrene optionally substituted with alkyl, hydroxyl or sulfonyl groups, or with a halogen atom, (meth)acrylonitrile, (meth)acrylamide optionally substituted with C₁-C₁₀ alkyl groups, alkyl (meth)acrylates, glycidyl (meth)acrylate, butadiene and a vinyl ester

30

- (vi) inorganic acids such as boric acid and phosphoric acid.

35

In certain embodiments, the cross-linking agent is selected from the following list: primary amines (for example N-hydroxysuccinimide esters), carbonyls (such as acrylic resins), inorganic acids (such as phosphoric acid), lewis acids (for example, boric acid or aluminium chloride) and carboxylic acids.

5

In certain embodiments, the cross-linking agent is a carboxylic acid selected from a dicarboxylic acid, tricarboxylic acid, tetracarboxylic acid, polycarboxylic acid and unsaturated carboxylic acid. In certain embodiments, the carboxylic acid is a polycarboxylic acid such as citric acid or succinic acid. In certain embodiments, the

10 carboxylic acid is an unsaturated carboxylic acid such as acrylic acid, methacrylic acid and maleic acid.

In certain embodiments the binder is a reaction product of polyvinyl alcohol and citric acid. Carboxylic acids are a preferred type of cross-linker because of their low toxicity

15 and cost. Polyvinyl alcohol is also known for being nontoxic and biodegradable.

In certain embodiments, the binder is present in an amount of from about 0.1 wt.% to about 40 wt.% of the total wt.% of the granulate, or from about 1 to wt.% to about 35 wt. % of the total wt. % of the granulate, or from about 5 to wt.% to about 30 wt. % of the

20 total wt. % of the granulate, or from about 10 to wt.% to about 25 wt. % of the total wt. % of the granulate, or from about 15 to wt.% to about 20 wt. % of the total wt. % of the granulate, or from or from about 1 to wt.% to about 5 wt. % of the total wt. % of the granulate.

25 In certain embodiments, the binder consists of a polymer, such that 100% by weight of the binder is polymer. In certain embodiments, in addition to the polymer component, the binder comprises a cross-linking agent, and the weight ratio of the polymer component to cross-linking agent is from 1:1 to 3:1; or 1:1 to 3.5:1 or 1:1 to 1:4. In accordance with an embodiment, the polymer component is polyvinyl alcohol and the

30 cross-linking agent is carboxylic acid; and the weight ratio of the polyvinyl alcohol to carboxylic acid is from 1:1 to 3:1; or 1:1 to 3.5:1 or 1:1 to 1:4.

Method of preparing granulates

35 In certain embodiments, the particles comprising at least one of the expanded milled perlite particles, the diatomaceous earth particles, and the sepiolite particles are mixed

together. The binder is first dispersed in water and is sprayed onto the particles comprising at least one of the expanded milled perlite particles, the diatomaceous earth particles, and the sepiolite particles so that the particles agglomerate and form granulates. Following on from the spraying step, a curing step is performed at a temperature from 80 °C to 120 °C. The curing step is typically performed for a length of time such that the granulate has dried and the binder has cured. After the curing step is performed, the moisture content of the granulate is below about 5 wt% of the granulate, such as less than about 3 wt%, or less than about 2 wt%. The curing step is performed for a length of time that the moisture content reaches the desired level as stated above, and may take up to 12 hours, or up to 8 hours or up to 4 hours.

Absorbent material

According to the present invention, there is provided an absorbent material comprising the granulate as already described herein. In certain embodiments, the binder is a cross-linked binder which is a reaction product of a polymer and cross-linking agent. This type of binder is particularly strong for applications where the granulate is performing as an absorbent material and where extra hydrophobicity is required (for example, when using for oil absorption).

The present inventors have found that the absorbent material is particularly useful in methods for treating fluid spills due to the improved absorption capacity of the granulate. By the term "fluid spills" this means the unwanted release of a fluid into an environment such as oil spills (for example, spill from an oil tanker or a leak at petrol station), aqueous spills (for example, soft drinks, acid solutions and basic solutions), chemical spills (for example, organic and inorganic solvents), food spills (for example soups or sauces) and bodily fluid spills (for example, blood, urine and vomit).

In some embodiments, the absorbent material may be used in enclosed containers for the disposal of liquid toxic waste substances.

In certain embodiments, the absorbent material absorbs the fluid spill up to 100 % of the weight of the granulate, such as up to 95 %, or up to 90 % or up to 85 %, or up to 80 %, or up to 75 % or up to 70 % of the weight of the granulate.

Animal feed composition

In accordance with the present invention there is provided an animal feed composition comprising the granulate as described herein. In certain embodiments, the animal feed composition comprises at least one nutrient. By the term "nutrient" we mean the basic substances which animals require for maintenance, growth, reproduction and good health which include carbohydrates, proteins, fats, minerals, vitamins and water. The main source of carbohydrates in animal feed are grains such as oats, wheat, barley, corn, sorghum, forages and hay. Proteins can be of plant or animal origin such as amino acids, oil cake meals, fish meals and meat scraps. Common sources of fat include fish oils, seed-derived oils such as flaxseed oil, sunflower, canola oil and vegetable derived oils such as corn and soybean. Minerals may include elements important for sustaining healthy and productive animal growth such as sodium, calcium, phosphorus, sulphur, potassium, magnesium, manganese, iron, copper, cobalt, iodine, zinc, molybdenum and selenium. Vitamins can either be water-soluble or fat-soluble and are broadly classified as vitamin A, B, C, D, E and K.

The above list is not intended to be limiting and the skilled person is aware of the nutrients available and will be able to select and blend nutrient ingredients to provide the required nutritional diet for the animal and will depend on the species of animal.

In certain embodiments, the granulate binder for the animal feed composition is selected from polyvinyl alcohol, bentonite, sodium alginate, potassium alginate, lignosulphonate, urea-formaldehyde condensation polymer, agar, carrageenan, guar gum, cassia gum, xanthan gum, cellulose, arabic gum (acacia), microcrystalline cellulose, methyl cellulose, ethyl cellulose, sorbitan monolaurate, starch or starch-based derivatives and combinations thereof, preferably wherein the binder is polyvinyl alcohol.

In certain embodiments, the animal feed consists of the granulate alone and does not comprise any additional nutrients or ingredients. The animal feed composition is therefore provided such that the granulate absorbs and carries a liquid of interest for the desired animal feed. The liquid of interest may be water, or may be any liquid nutritional animal feed. The skilled person is aware of suitable liquid nutritional animal feeds, and may select the liquid of interest depending on the animal to which it is to be fed.

In certain embodiments, the granulate absorbs the liquid of interest up to 100 % of the weight of the granulate, such as up to 95 %, or up to 90 % or up to 85 %, or up to 80 %, or up to 75 % or up to 70 % of the weight of the granulate.

- 5 In certain embodiments, the binder is present in an amount of from about 0.1 wt.% to about 40 wt.% of the total wt.% of the animal feed composition, or from about 1 to wt.% to about 35 wt. % of the total wt. % of the animal feed composition, or from about 5 to wt.% to about 30 wt. % of the total wt. % of the animal feed composition, or from about 10 to wt.% to about 25 wt. % of the total wt. % of the animal feed composition, or from about 15 to wt.% to about 20 wt. % of the total wt. % of the animal feed composition, or from or from about 1 to wt.% to about 5 wt. % of the total wt. % of the animal feed composition.
- 10

15 EXAMPLES

Example 1

- The following particles were used in the testing under this example (granulated as described below or in ungranulated form):
- 20

expanded milled perlite (EMP available from Imerys)

Diatomaceous earth

Binders used: polyvinyl alcohol; bentonite and lignosulfonate

- 25 500 g of the particles (either expanded milled perlite or diatomaceous earth) was placed in a mixer (Eireich mixer). 25 g of binder was dissolved in 700g water. The final % by weight of the binder was 5% by weight of the total granulate. The binder composition was then sprayed using a simple commercial sprayer on to the particles.

30

35

Table 1

5

Parameters	EMP	Granulated EMP + 5% PVA (200- 600 µm)	Granulated EMP + 5% PVA (600-1700 µm)	Granulated EMP + 5% Bentonite (200— 600 µm)	Granulated EMP + 5% Ligno- sulfonate (200–600 µm)	Granulated EMP + 5% Ligno- sulfonate (600-2500 µm)	Expanded Perlite	DE	Granulated DE (200-600 µm)
PSD laser (d50 - µm)	20	350	880	439	503	1206	280	10	320
Absorption capacity %	307	451	203	297	83	107	170	343	435
Dust (Dustmon)	116.3	7.5	18.5	26.4	x	x	2.8	57.9	43.7
Density (g/cm ³)	0.12	0.24	0.22	0.21	0.446	0.545	0.37	0.16	0.10
SSA (B.E.T. , m ² /g)	3.5	2	2.4	4.8	2.5	2.6	0.7	24	34
Porosity (mercury, g/cm ³)	1.42	1.638	1.033	x	x	x	1.183	1.282	1.01
Angle of repose ° for the dry product	No flow	35	35	35.2	x	35.8	32	No Flow	30
Cohesive index (granudrum , 10 rpm)	73.4	4.2	4.1	27.7	x	x	2.11	69	2.7

PSD laser

The Particle Size Distribution (PSD) was determined using a Mastersizer 2000 from
10 Malvern instruments.

D_{50} is the value of the mean particle size (d_{50}) measured by laser diffraction (standard NFX-11-666 or ISO 13320-1) and " d_{50}^{sed} " is the value of the median diameter obtained by sedimentation using a sedigraph (standard Afnor-X-11-683 or ISO 13317-3), as described above and in the Examples. Reference may be made to the article by G. Baudet and J. P. Rona, Ind. Min. Mines et Carr. Les techn. June, July 1990, pp 55-61, which shows that the lamellarity index is correlated to the mean ratio of the largest dimension of a particle to its smallest dimension.

Absorption capacity

10

The Westinghouse method was used to calculate the absorption capacity (based on NV V19-002). To carry out this method, the sample to be tested was introduced into a liquid via a sieving equipment. In this case, the liquid used was dioctyl adipate. The sample was then left to soak for 20 minutes, after this time the sample was removed and the excess liquid was removed. The weight of the product before and after being soaked was compared to calculate the absorption of the product.

15

Dust Analysis

The Dust Analyzer Dustmon RD 100 (available from Retsch®) characterizes the dustiness of powders and granulates.

20

DustMon RD 100 consists of a dosing control system (sample beaker with a valve and a tube, a sample collector, a light source and a detector). The sample is poured into the sample beaker. On starting the measurement, the valve opens and the sample drops down the tube into the sample collector. The dust generated in the sample collector will be measured by the detector and the resulting dust index will be displayed.

25

The results provide a measurements of maximum dust concentration in % (0-100 % of complete dust concentration).

30

Density

The bulk density of the samples was assessed by measuring the sample into a test tube and comparing the volume of the sample against the mass of the sample.

35

Specific Surface Area (SSA— B.E.T m²/g)

The BET specific surface area was determined using a method based on the standard NF X 11-621 titled "Détermination de l'aire massique (surface spécifique) des poudres par adsorption de gaz – Méthode B.E.T. – Mesure volumétrique par adsorption d'azote à basse température" (Determination of mass area (specific surface) of powders by gas adsorption – BET Methods – Volumetric measurement by nitrogen adsorption at low temperature).

10 The method made use of a Micromeritics measurement apparatus (available from Micromeritics Instrument Corp., USA) including a vacuum pump, a VacPrep 061 degassing section, a Tristar 3000S measurement section and sample holders, a Mettler AG204 scale with a precision of 0.1 mg, Dewar flasks, nitrogen adsorbant gas and helium carrier gas.

15

The sample was weighed (to 0.1 mg accuracy) near the empty sample holder and its mass M_0 was recorded in g. The previously homogenised powder sample was then introduced, using a funnel, into the sample holder. Sufficient space (dead volume) was left between the sample and the top of the sample holder to enable free circulation of gas. The sample holder was placed into one of the degassing stations and degassed at 250°C under a primary vacuum of 10 Pa for about 20 minutes. After degassing, a sufficient volume of nitrogen was added to the sample holder to avoid introducing air during transfer of the sample holder from the degassing station to the measurement station.

25

The sample holder was then attached to the measurement station and a Dewar flask containing liquid nitrogen was placed around the sample holder. The BET measurement was commenced using the device control software. The device then carried out the following operations automatically:

30

- Vacuum removal of the nitrogen introduced for the transfer of the sample holder;
- Leak test;
- Adding helium carrier gas;
- Measuring the dead volume at ambient temperature;
- 35 - Measuring the cold dead volume using liquid nitrogen;
- Helium vacuum removal;

- Leak test;
- Adding nitrogen at 950 mm Hg and measuring the saturation pressure; and
- Acquisition of analysis values.

5 The instrument's data acquisition and processing software plotted the transformed BET line from 5 measured adsorption points. The Dewar flask and then the sample holder were removed. The apparatus was allowed to return to ambient temperature and then the sample was again weighed (to an accuracy of 0.1 mg) near the sample holder and the weight was recorded as M_2 in g. The mass of the test portion of the sample, M , was
10 calculated (in g) according to:

$$M = M_2 - M_0$$

The value M was then introduced into the software calculation program which
15 automatically calculated the BET specific surface area of the sample in m^2/g .

Porosity

Porosity is the percentage of interstitial void space in a particulate. It is calculated using
20 the following formula:

$$\Phi = V_v/V_T$$

Where Φ is the porosity, V_v is the void volume and V_T is the total volume.

The porosity was measured using mercury porosimetry which characterizes porosity by forcing mercury into pores. The standard test for mercury porosimetry is set out in ASTM
25 D4404-18.

Angle of repose

The angle of repose was measured using a Manual Powder Flow Tester (EFT-01) using
30 ISO 8398:1989. The angle of repose is calculated as follows:

$$\Theta = \tan^{-1} h/r$$

Where Θ is the angle of repose, h is the height in cm of the conical pile and r is the radius in cm.

5

The complementary measurement to the angle of repose is the dynamical angle of repose (or flowing angle) which is measured using a Granudrum. The GranuDrum instrument (available from GRANUTOOLS™) is an automated powder flowability measurement technique predicated on the rotating drum principle. The drum is a horizontal cylindrical with transparent sidewalls and it is half-filled with the powder sample.

The drum rotates about its axis at an angular velocity varying from 2 to 70 rpm. In this case the angular velocity was measured at 10 rpm and a CCD camera captures a number of snapshots. For the measured rotating speed, the dynamic cohesive index is measured from the interface fluctuations, and the flowing angle, also called “dynamic angle of repose” in the literature, is calculated from the average interface position. A low value of the flowing angle corresponds to excellent flowability.

20 Flowability

Figure 1 shows the impact of absorption on a powder’s flowability. Powder flow, also known as flowability, is defined as the relative movement of a bulk of particles among neighbouring particles or along the container wall surface. In other words, powder flowability refers to the ability of a powder to flow in a desired manner in a specific piece of equipment.

Figure 1 measures the % liquid DOA against the repose angle to assess the impact of flowability. The following samples from Table 1 were tested:

30

Granulated EMP + 5 wt% PVA, granulate particle size 200 – 600 μm

Granulated EMP + 5 wt% PVA, granulate particle size 600 – 1700 μm

Granulated EMP + 5 wt% bentonite, granulate particle size 200 – 600 μm

Granulated DE, granulate particle size 200 – 600 μm

35 Granulated EMP + 5 wt% lignosulfonate, granulate particle size 600 – 2500 μm

Expanded perlite (not milled)

The data in Table 1 and Figure 1 shows that when the granulate is formed using PVA as the binder in accordance with the present invention, the powder samples achieved excellent absorption capacity (between 90 and 100%) and excellent flowability results.

5

The other inventive samples (3 to 5) showed lower absorption in some cases, but improved flowability over the non-granulated counterparts. Sample 6 showed no flowability at all.

- 10 lignosulphonate is shown capable of binding the EMP as well with good angle of repose for course, even though absorption is lower

SEM images were taken for the following samples from Table 1; and are presented in Figure 2:

15

- a) Expanded Milled Perlite
- b) Granulated EMP + PVA (200-600 μm)
- c) Granulated EMP + Lignosulfonate (200-600 μm)
- d) Granulated EMP + bentonite (200-600 μm)

- 20 The equipment used was an SEM FEI Quanta 200 microscope. The SEM images all show proper granulation of the primary EMP particles using the various binders.

Example 2

25

Table 2

Trial #	7		29	30
binder	Poval 8-88	Bentonite CT	Kuraray Excevl AQ-4104	Evostick Exterior PVA
binder type	polyvinyl alcohol, 88% hydrolysed	mineral	polyvinyl alcohol fully hydrolysed & formulated for water resistance	PVA adhesive formulated for external use
binder %	5	5	5	5
Oil Absorption Westinghouse %	274	337	583	378
Water Absorption Westinghouse %	disintegrated - no result recorded	disintegrated - no result recorded	541	417

Westinghouse absorption tests were performed on various granulates prepared using expanded granulated perlite (200 – 600 µm) and with the components as set out in Table 2 above. The Westinghouse method is as described above.

CLAIMS

1. A granulate comprising a binder and at least one of expanded milled perlite particles, diatomaceous earth particles, and sepiolite particles, wherein:
 - i) the expanded milled perlite particles have a D50 from about 5 to about 40 microns;
 - ii) the diatomaceous earth particles have a D50 from about 5 to about 40 microns;
 - iii) the sepiolite particles have a D50 from about 5 to about 100 microns;
 - iv) the granulate has a D50 from about 150 to about 2000 microns; andwherein the particles are bound together by the binder forming pores between the particles.
2. The granulate according to claim 1, having:
 - an angle of repose up to about 38°, as measured by the angle of repose (funnel method) using the EFT-01 Powder Flow Tester;
 - an absorption capacity of at least 150%, as measured using the Westinghouse method described herein and utilizing dioctyladipate as the absorbate; and a dust content less than 10, as measured by the Dust analyzer DustmonRD 100.
3. The granulate according to claims 1 or 2, wherein either or both of the expanded milled perlite particles and the diatomaceous earth particles have a D₅₀ from about 10 to about 30 microns.
4. The granulate according to claims 1 to 3, wherein the sepiolite particles have a D₅₀ from about 10 to about 50 microns.
5. The granulate according to any of claims 1 to 4, wherein the granulate has a D₅₀ from about 200 to about 600 microns, or from about 600 to about 1700 microns.
6. The granulate according to any of claims 1 to 5, wherein the binder is either:
 - (i) a polymer; or
 - (ii) a cross-linked binder which is a reaction product of a polymer and a cross-linking agent; or

- (iii) bentonite; or
- (iv) lignosulphonate.

5 7. The granulate according to claim 6, wherein the polymer is selected from one or more of a water-soluble synthetic polymer, a natural water-soluble polymer and a polyol.

8. The granulate according to claim 6 or 7, wherein the cross-linking agent is an acid selected from one or more of the following:

10

- (i) dicarboxylic acids, including oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, malic acid, tartaric acid, tartronic acid, aspartic acid, glutamic acid, fumaric acid, itaconic acid, maleic acid, traumatic acid, camphoric acid, phthalic acid and its derivatives that contain at least one boron or chlorine atom, tetrahydrophthalic acid and its derivatives that contain at least one chlorine atom, isophthalic acid, terephthalic acid, mesaconic acid and citraconic acid,

15

- (ii) tricarboxylic acids, including citric acid, tricarballylic acid, 1,2,4-butanetricarboxylic acid, aconitic acid, hemimellitic acid, trimellitic acid and trimesic acid;

20

- (iii) tetracarboxylic acids, including 1,2,3,4-butanetetracarboxylic acid and pyromellitic acid;

- (iv) polycarboxylic acids such as EDTA;

25

- (v) unsaturated carboxylic acids including eth)acrylic acid, crotonic acid, isocrotonic acid, maleic acid, cinnamic acid, 2-methylmaleic acid, fumaric acid, itaconic acid, 2-methylitaconic acid, α,β -methyleneglutaric acid and monoesters of unsaturated dicarboxylic acids, and the vinyl monomer is styrene optionally substituted with alkyl, hydroxyl or sulfonyl groups, or with a halogen atom, (meth)acrylonitrile, (meth)acrylamide optionally substituted with C₁-C₁₀ alkyl groups, alkyl (meth)acrylates, glycidyl (meth)acrylate, butadiene and a vinyl ester

30

- (vi) inorganic acids such as boric acid and phosphoric acid.

35

9. The granulate according to claim 6, wherein the binder comprises:

- (i) polyvinyl alcohol; or
- (ii) a reaction product of polyvinyl alcohol and a carboxylic acid, preferably wherein the carboxylic acid is citric acid.

- 5 10. An absorbent material comprising the granulate according to any of claims 1 to 9, wherein the binder is a cross-linked binder which is a reaction product of a polymer and a cross-linking agent.
- 10 11. A method for treating fluid spills comprising applying the absorbent material as defined in claim 10 to the fluid spill so that the fluid is absorbed by the absorbent material.
12. An animal feed composition comprising the granulate according to any of claims 1 to 9.
- 15 13. The animal feed composition according to claim 12, wherein the composition further comprises at least one nutrient.
14. The animal feed composition according to claim 12 or claim 13, wherein the
20 binder is selected from polyvinyl alcohol, bentonite, sodium alginate, potassium alginate, lignosulphonate, urea-formaldehyde, agar, carrageenan, guar gum, cassia gum, xanthan gum, cellulose, arabic gum (acacia), microcrystalline cellulose, methyl cellulose, ethyl cellulose, sorbitan monolaurate, starch or starch-based derivatives and combinations thereof,
25 preferably wherein the binder is polyvinyl alcohol.
15. A method of preparing the granulate according to any of claims 1 to 9, comprising spray drying the milled expanded perlite particles with the binder and performing a curing step.
- 30 16. The granulate according to any of claims 1 to 5, wherein the binder comprises starch or starch-based derivatives and combinations thereof.
17. The animal feed composition according to claim 14, wherein the binder
35 comprises starch or starch-based derivatives and combinations thereof.

FIGURE 1

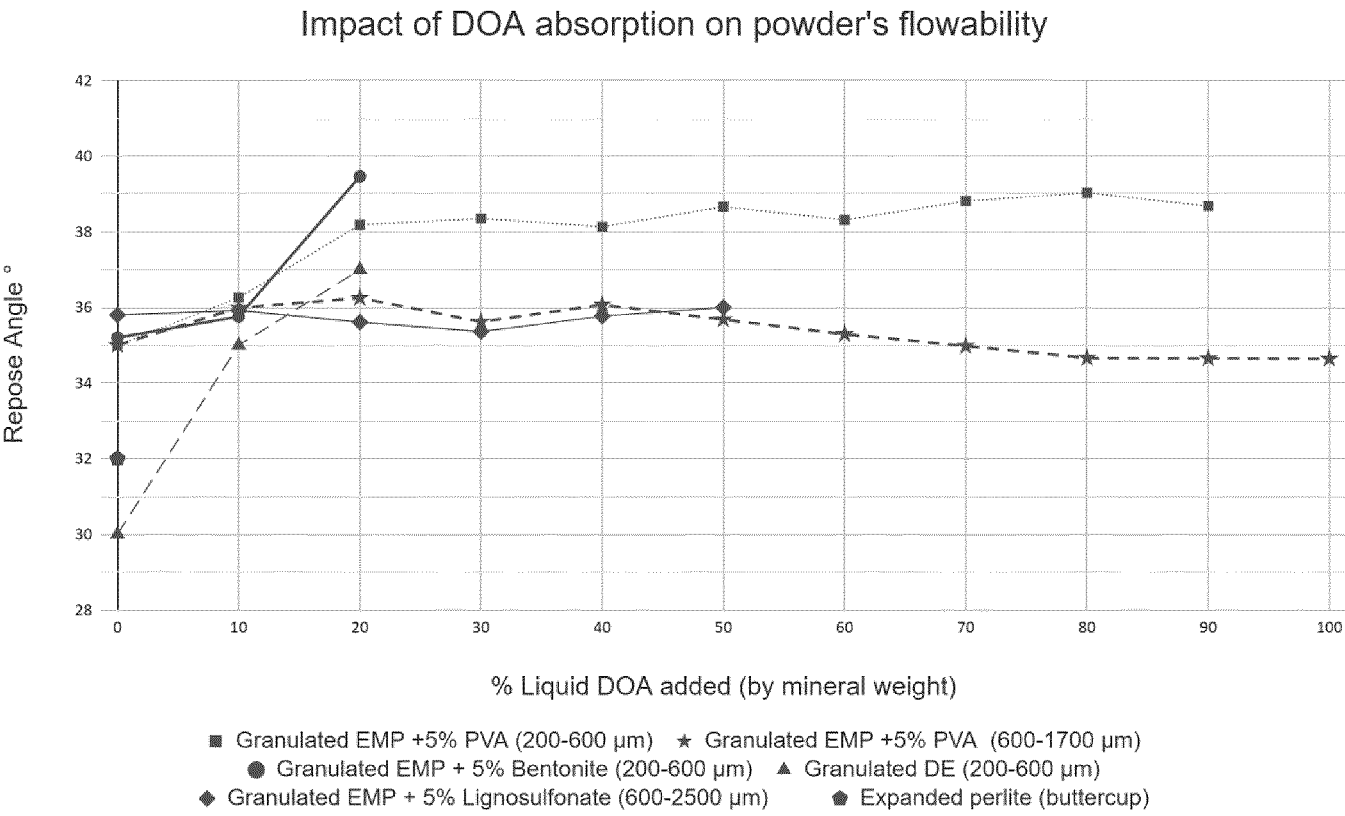
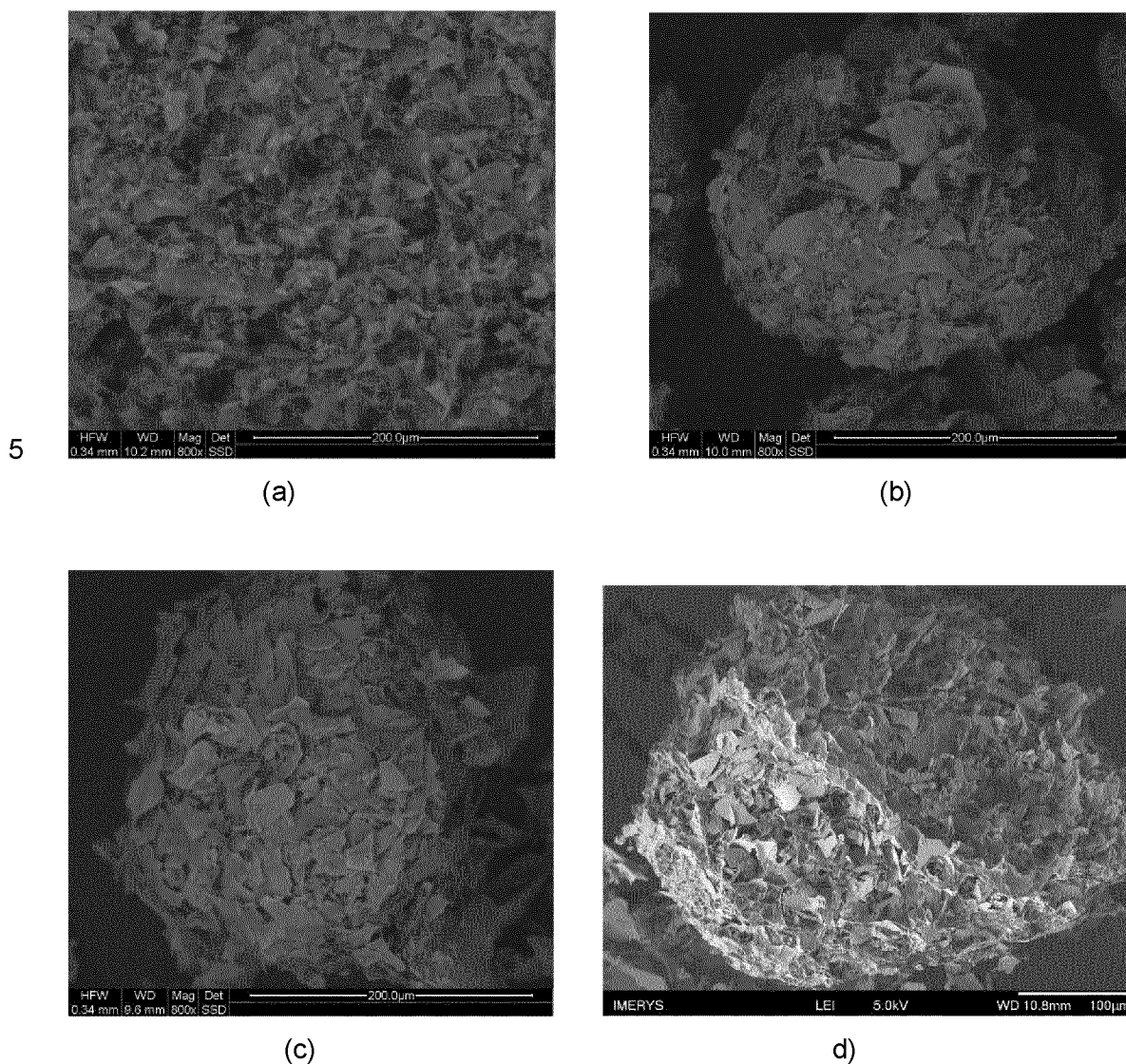


FIGURE 2



- 10
- (a) Expanded Milled Perlite
 - (b) Granules of Expanded Milled Perlite + PVA (200-600 μm)
 - (c) Granules of Expanded Milled Perlite + Lignosulfonate (200-600 μm)
 - (d) Granules of Expanded Milled Perlite + bentonite (200-600 μm)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/066158

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	B01J20/10	B01J20/12
	B01J20/28	B01J20/30
ADD.	B01J20/14	B01J20/24
		B01J20/26
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) B01J		
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		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 9 433 918 B2 (RILEY ANDREW [GB]; IMERYS MINERALS LTD [GB]) 6 September 2016 (2016-09-06) col. 4, lines 19-20; col. 6, line 14; col 6, lines 29-30; col. 6, line 56.; claims 1,13 -----	1-10,15, 16
X	US 2018/319670 A1 (RILEY ANDREW MARK [GB] ET AL) 8 November 2018 (2018-11-08) paragraph [0028] - paragraph [0029]; example 4; table 5 -----	11-14,17
A	US 2015/190778 A1 (WANG BO [US]) 9 July 2015 (2015-07-09) paragraph [0088] - paragraph [0089]; example 1 ----- -/-	1-15
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 19 September 2023		Date of mailing of the international search report 27/09/2023
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Mc Donnell, Shane

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2023/066158

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2018/187021 A1 (WANG BO [US] ET AL) 5 July 2018 (2018-07-05) claim 1; table 6 -----	1-15
A	US 2020/131456 A1 (DALE DOUGLAS A [US]) 30 April 2020 (2020-04-30) paragraph [0154] -----	1-15
A	US 2019/270067 A1 (WANG BO [US]) 5 September 2019 (2019-09-05) table 7 -----	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2023/066158

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
US 9433918	B2	06-09-2016	GB	2493187 A		30-01-2013
			US	2014371061 A1		18-12-2014
			WO	2013014450 A1		31-01-2013

US 2018319670	A1	08-11-2018	EP	3374079 A1		19-09-2018
			US	2018319670 A1		08-11-2018
			US	2020283301 A1		10-09-2020
			WO	2017081031 A1		18-05-2017

US 2015190778	A1	09-07-2015	CN	104718021 A		17-06-2015
			EP	2874740 A1		27-05-2015
			ES	2764788 T3		04-06-2020
			US	2015190778 A1		09-07-2015
			US	2017361303 A1		21-12-2017
			US	2019039044 A1		07-02-2019
			WO	2014004349 A1		03-01-2014

US 2018187021	A1	05-07-2018	EP	3116946 A1		18-01-2017
			US	2018187021 A1		05-07-2018
			WO	2015138901 A1		17-09-2015

US 2020131456	A1	30-04-2020	BR	112019027976 A2		07-07-2020
			CA	3067837 A1		03-01-2019
			CN	110809624 A		18-02-2020
			EP	3645696 A1		06-05-2020
			JP	2020527339 A		10-09-2020
			US	2020131456 A1		30-04-2020
			WO	2019006077 A1		03-01-2019

US 2019270067	A1	05-09-2019	EP	3532194 A1		04-09-2019
			US	2019270067 A1		05-09-2019
			WO	2018081688 A1		03-05-2018
