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(54) Title: METHOD FOR PREPARATION OF MICROCAPSULES FROM HEMICELLULOSE

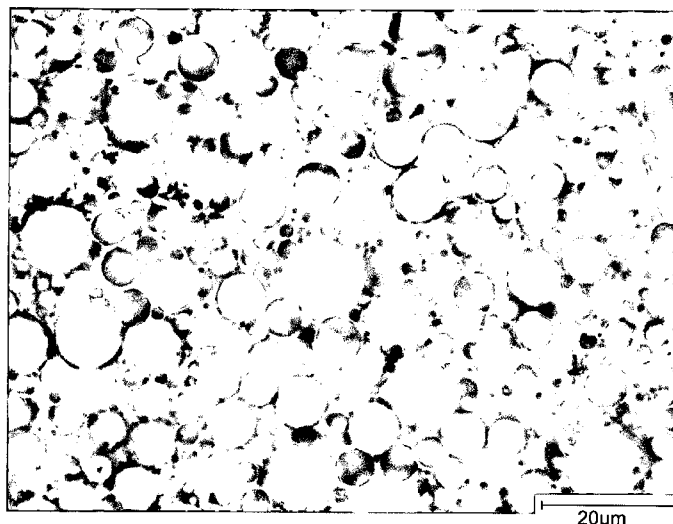


Fig. 1

(57) Abstract: A method for preparation of microcapsules from hemicellulosic substance comprises - dispersing hemicellulosic substance together with a gaseous medium in a liquid medium comprising water, organic solvent and surfactant so that microbubbles are formed in the liquid medium with the hemicellulosic substance gathered at interface of the microbubbles, and - forming the microcapsules from the dispersed hemicellulosic substance gathered at the interface of the microbubbles and the liquid medium.



Method for preparation of microcapsules from hemicellulose

Field of the invention

- 5 The present invention relates to a method for preparation of microcapsules from hemicellulose. The invention also relates to a microcapsule product, to a paper or cardboard product, and to the use of microcapsules.

Background of the invention

10

Polymer-based microcapsules are used in many applications because of their chemical or physical properties. In medical applications the microcapsules can be used for controlled or targeted delivery of various active agents to an organism. In pulp and paper industry the microcapsules are interesting as replacement of inorganic minerals, which are used as fillers or as coating pigments. Inorganic particles cause problems in recycling of fibre, in paper burning and in composting. The inorganic material also increases the weight of the paper and cardboard products.

Use of synthetic organic pigments has also been proposed. Even though they have good optical properties, which are based on their ability to scatter visible light, their disadvantage is that alone they are not suitable as coating or filler pigments for paper or cardboard. On one hand, they are very expensive compared with mineral pigments and on the other hand they cause retention problems when used as fillers in paper manufacture. Instead, they are usually used in admixture with mineral pigments. Pigments which are based on synthetic polymers are not ideal for recycling or composting either.

Natural polymer raw material can be formed into microcapsules by suitable encapsulation technique. The microcapsules made of a naturally occurring polymer is potential material for applications where biocompatibility and/or biodegradability is required, such as medical applications. They also have suitable optical properties for use in paper and cardboard products. For applications in pulp and paper industry, these microspheres have the advantage of being bulky, thus providing desired properties with less material. They must also be available from raw material that is abundant, because the cost is an important factor in mass production of paper or cardboard.

The publication US 6562459 discloses the preparation of spherical microparticles from water-insoluble starch (branched polyglucans) by dissolving the starch in DMSO and

precipitating the microparticles in water. The microparticles have average diameter most preferably from 1 μm to 5 μm . The microparticles are closed, that is, no encapsulation techniques are used. The proposed use of these microparticles is in pharmaceuticals, cosmetics, food technology, polymer technology and diagnostic tests.

5 Publication US 2007163737 discloses microcapsules made of starch or starch derivatives. The process includes preparation of microporous foam by dispersing air into an aqueous solution of starch or starch derivative and stabilizing the microbubbles of the foam with a surface-active agent and cross-linking agent, thus yielding microcapsules in dispersion. Starch was dissolved in water in a concentration of 10%
10 or 15%, and a smaller volume of solvent or oil not soluble to water, as well as ethanol or isopropanol was added. Surface active agents and a cross-linker were also added to the mixture. The mixture was stirred vigorously with a dispergator to make the foam. By this method, microbubbles with average particle diameter as small as 1.2 μm could be obtained. Stable foam with microbubbles could be obtained also using a mixture of
15 starch solution with a starch dispersion, adding surface active agents and a cross-linker to the mixture, and forming and stabilizing the microbubbles in water phase alone by stirring the mixture with a dispergator, without the use of solvents.

According to the publication, the obtained microcapsules can be used as paper
20 pigments and as fillers, making possible to produce paper or cardboard that is completely free of mineral particles and has good optical properties. The microcapsules have good opacity properties owing to their light scattering ability.

Further, publication WO 2010090594 shows a method for the preparation of polymer
25 shells, preferably composed of cellulose or hemicellulose. According to the method, a suitable cellulose component is dissolved in a first, non-polar solvent, air is mixed in the solution, and thereafter the shells are precipitated by contacting the solution with a second polar solvent, usually water. On page 7 line 10 the shell is said to relate any structure with dimensions between 0.1 μm and 10 mm, substantially encasing any
30 space. However, in the practice shells made of cellulose have diameter above 2 mm in all cases. The preparation of these shells requires two solvent steps, where the cellulose or hemicellulose is dissolved in the first step to the solvent used. The proposed uses of the polymer shell are drug delivery vehicles and means for chromatographic separation.

Summary of the invention

Embodiments of the present invention provide a method by which it is possible to make microcapsules from hemicellulose in a single-step formation process. The process
5 does not require subsequent solvent steps and can use hemicellulose, an abundant naturally occurring renewable polymer, or its derivative as raw material.

The starting material of the microcapsules is a hemicellulosic substance, which can be native hemicellulose and/or its derivative. The hemicellulosic substance is dispersed in
10 a liquid medium together with gas so that microbubbles are formed where the dispersed hemicellulosic substance concentrates around bubbles, at the interface between the liquid phase and gas. The liquid medium comprises water in admixture with an organic solvent or solvent mixture, and a surfactant. The organic solvent or solvent mixture can be soluble or insoluble in water. The organic solvent or solvent
15 mixture is required to enhance the mass transfer of the hemicellulosic substance inside the liquid medium to the surface of the bubble (interface gas/liquid). The surfactant is required for the creation of microbubbles in the liquid medium. So that stable microbubbles can be created, a frother is also to be used.

Structurally, the liquid medium exists at this intermediate process step in the form of a
20 foam with a three phase system: a continuous liquid phase comprising at least water and an organic solvent or solvent mixture, gaseous medium dispersed in the continuous liquid phase, as well as hemicellulosic substance dispersed at the interface of the liquid phase and the dispersed gaseous medium.

25 In an embodiment, also crosslinking agent is included in the liquid medium to consolidate the microcapsules. The crosslinking agent binds the molecules of the hemicellulosic substance together chemically. The cross-linking agent is preferably used, if the microcapsules are to be separated from the liquid and dried to obtain a solid microcapsule product.

30

The gaseous medium creating the microbubbles in the liquid medium is preferably air and the air is dispersed in the liquid medium to create these microbubbles preferably by intensive mixing of the liquid medium where all other constituents have been added. The intensive mixing is carried out at sufficiently high rpm values of the agitator, which
35 causes high peripheral speeds of the agitator blades and consequently high shear forces that are decisive for the formation of microbubbles of sufficiently small scale. In agitating the liquid medium, high nominal speed (rpm) and tpi speed over 5 m/s is preferred.

The method according to the invention allows a single-step, continuous process where all necessary reactions and interactions to form solid microcapsules can be performed in one volume of liquid medium where the necessary raw materials and ingredients, including the gaseous medium, can be added and from where the microcapsules can be optionally separated or concentrated, depending on the end use of the microcapsules. The process can be performed continuously in a continuously stirred tank reactor (CTSR), to which the raw materials and ingredients can be supplied and from which the products can be withdrawn after a suitable residence time required for the formation of the microbubbles.

The purpose of the invention is also to provide novel microcapsules that can be used in various applications, for example in paper and cardboard manufacture, plastics industry and pharmaceutical industry. These microcapsules, which have never been reported before, have a shell made of hemicellulose or its derivative and volume median particle size of 0.5 μm to 10 μm .

The hemicellulose microcapsules prepared in accordance with the invention can be used in paper and cardboard manufacture as surface sizing agent, coating pigment, paper filler and, if the paper or cardboard is to be used for example in cardboard or packaging industry, as barrier chemical. The microcapsules with suitably adjusted adherent characteristics can be used as adhesive in many applications, for example in plastics industry and in packaging industry. In medicine and pharmaceutical industry, the hemicellulose microcapsules can be used as drug delivery carriers in which the active agent can be incorporated in various ways.

Brief description of the drawings

The invention will be described in the following with reference to the accompanying drawings where

Fig. 1 is a light-microscope image of hemicellulose (GGM) microcapsules prepared in accordance with the invention.

Detailed description of the invention

In the present disclosure, the following terms are to be interpreted in the following way.

Hemicellulosic substance is any polymer that contains monosaccharide units that are typical for hemicellulose. These monosaccharide units may be modified so that they differ from the native form of hemicellulose. Thus, hemicellulosic substance includes hemicelluloses and derivatives of hemicellulose. A hemicellulosic substance may also
5 be a mixture of two or more chemically different hemicelluloses or hemicellulose derivatives, where all components may be hemicelluloses or hemicellulose derivatives or at least one component may be a hemicellulose and at least one component may be a hemicellulose derivative.

10 Hemicellulose is any polymer of natural origin conventionally classified as hemicellulose according to its polymeric structure and its monosaccharide units.

Hemicellulose derivative is any above-mentioned hemicellulose where the polymer is modified chemically at its monosaccharide units. Most commonly modification means
15 adding functional groups to the carbon skeleton of the hemicellulose by a chemical reaction. The reaction can take place by any mechanism, such as substitution or addition.

Microcapsules are particles where the volume of an individual particle enclosed by its
20 outer surface is larger than a volume normally taken up of the solid material of the particle, that is, the mass divided by the volume is smaller than the density of the solid material, indicating that there is void or voids inside the particle. These capsules have a distinctive outer solid shell that surrounds the void or voids.

25 Liquid medium is material which is in liquid state and which can comprise two or more different liquid substances that are totally miscible forming one continuous liquid phase, or immiscible to the extent that they form two or more liquid phases. The liquid medium can comprise dissolved or dispersed solid and/or gaseous substances.

30 A dispersion is a system in which particles are dispersed in a continuous phase of a different composition or state.

Microbubbles are bubbles of submillimeter size that exist as gas-in-liquid dispersion. Collectively the microbubbles can be called a foam.

35

For the sake of conciseness, the term "hemicellulose microcapsules" refers to microcapsules as defined above where the major constituent is hemicellulosic substance as defined above, which can be a hemicellulose or a hemicellulose

derivative, or a mixture of different hemicelluloses, different hemicellulose derivatives, or at least one hemicellulose and one hemicellulose derivative in any proportion.

5 The size of the hemicellulose microcapsule is the diameter of the microcapsule which is spherical or near-spherical. In microcapsules deviating from spherical shape the size is the equivalent spherical diameter (e.s.d.), that is, diameter of a sphere of equivalent volume.

In the method, the following constituents are used in the liquid medium:

10

Water is used in the liquid medium in admixture with an organic solvent or mixture of organic solvents. The organic solvent is preferably a hydrocarbon solvent based on a petroleum distillate or a lower monovalent alcohol of 1 to 4 carbon atoms. The petroleum distillate based hydrocarbon solvents include special gasoline (hydrotreated
15 light petroleum distillate having boiling point about 80 - 110°C) and a solvent commonly known as "white spirit" (mineral spirit). 4 carbon atoms. The monovalent alcohols of 1 to 4 carbon atoms include ethanol, methanol, iso-propanol, n-propanol and butanols. Any mixture of the above-mentioned solvents can be used.

20 The proportion of water and the organic solvent or solvent mixture is preferably approximately 50/50 (w/w), but the proportion can vary within wide limits. The proportion can be for example from 30/70 to 70/30.

The hemicellulosic substance can be any natural hemicellulose or any derivative of a
25 natural hemicellulose. Particularly preferred are xylan which is major hemicellulose component in hardwood, for example birch, and galactoglucomannan (GGM), which is principal hemicellulose in softwood (coniferous wood). The concept of galactoglucomannan also includes the substance with a low galactose content that is sometimes referred to as glucomannan.

30

In galactoglucomannan, hydroxyl groups in the monosaccharide units are partly substituted by *O*-acetyl groups, for which reason a designation "*O*-acetyl-galactoglucomannan" is often used.

35 Other hemicelluloses include softwood arabinoglucuronoxylan, which may be referred to as xylan for short, but has also L-arabinose units attached to the polymer backbone and has no acetyl groups, unlike native hardwood xylan.

The above-mentioned hemicelluloses are preferred, because they are available in large amounts from plant sources, especially wood, and can be recovered as by-products from processes of pulp and paper industry. It is to be understood that the native hemicellulose may also have undergone some changes during the pulp manufacturing process, especially by the effect of chemical treatment, and the isolated hemicellulose that is to be used as the raw material is not necessarily in its native form.

The hemicellulose derivative can be for example a derivative of any of the above-mentioned hemicelluloses. Examples are xylan esters, for example acetylated xylan, hydroxypropylated xylan and benzylated hemicelluloses, for example benzyl ether of xylan and benzyl ether of galactoglucomannan.

The surfactant can be any surface-active agent that can reduce the surface tension of water at the liquid-gas interface. The surfactant is added to the liquid medium in an amount to reach the critical micelle formation concentration (cmc). The surfactant can be chosen from anionic, cationic, amphoteric or non-ionic surface-active agents. One example of a group of cationic surface active agents that can be used are quaternary amines. Sodium lauryl sulfate is an example of anionic surface active agents.

The frother (known also as foaming agent) is an agent that stabilizes the foam. Methyl isobutyl carbinol (MIBC) is one example of a frother that can be used. Polypropylene glycol ether is an example of another frother that can be used.

The cross-linking agent can be any cross-linking agent that can create chemical bonds between molecules of the hemicellulosic substance and that make the dispersed particles of the hemicellulosic substance gathered at the interface of liquid and air to a permanent structure, that is, to permanent microcapsules. Glyoxal is one suitable cross-linking agent.

Depending on the use of the microcapsules, other substances may be present, for example substances that form a functional constituent in the microcapsules. One example is a pharmaceutical agent that is to be delivered in the microcapsules to a target where it can perform its function, especially a human body. The microcapsules, being constituted of biodegradable and biocompatible material, are suitable to be administered to a living organism for the purpose of local delivery (by injection or implantation for example) to a restricted area of a living organism and/or for the purpose of sustained delivery of a pharmaceutical agent to the living organism. The pharmaceutical agent can be included in the same liquid phase where the

microcapsules are formed so that it will become a constituent of the microcapsules, for example in the core or in the shell where it is mixed with hemicellulose.

5 In view of the use of the microcapsules in paper and cardboard manufacture, additional substances may be included in the microcapsules, for example coloring agents which influence the optical properties.

10 A liquid medium is formed of the above-mentioned materials by mixing them in suitable proportions before the microbubbles are formed in the liquid composition. Also other substances which may have some process aid function or are to be integrated permanently in the microspheres may also be included in the composition at this stage. Hemicellulose is used in the liquid medium preferably in a ~~amount~~ concentration of 1 to 30 wt-%, preferably 5 to 15 wt-%.

15 Cross-linking agent can be used in the amount of 0.1 to 5 wt-%, preferably in an amount of 1 to 4 wt-% of dry hemicellulose. The amount of the cross-linking agent is dependent on the amount of the hemicellulose present and the desired degree of crosslinking.

20 The liquid medium is subjected to intensive mixing. The mixing is performed by an agitator that has typically mixing blades or the like mixing elements that shear the liquid medium and create shearing forces. The mixing by the agitator can be started already during the addition of various substances. The intensive mixing creates foam in the form of microbubbles by dispersing ambient air into the liquid medium. By suitable
25 choice of the mixing parameters, the size of the microbubbles and consequently the size of the microcapsules can be adjusted to a desired range. During the intensive mixing, the temperature of the liquid medium may rise above ambient temperature, above 50°C, approximately to 70 °C. The rise of the temperature is dependent on the duration of the intensive mixing. The intensive mixing to create the microbubbles is
30 allowed to proceed for a time of 2 to 30 min.

When microbubbles are formed, the walls of the bubbles will become consolidated by the effect of the dispersed particles of the hemicellulosic substance that migrate to these walls and are preferably crosslinked by the cross-linking agent.

35

The microcapsules formed have a typical core-shell-structure, where the core is gas (for example air) and the shell is solid hemicellulosic substance. The wall thickness of the shell is dependent on the amount and size of the microbubbles, the amount of the

hemicellulosic substance used in the liquid medium, the organic solvent used, pH and surfactant. The void volume (core) of the microcapsules is preferably more than 50 % of the total volume of the microcapsules, more preferably more than 60 %. The light-scattering properties of the microcapsules are optimal when the void volume is
5 between 70 and 80 %. However, the optimal light-scattering is also size-dependent and if microcapsules are manufactured for light-scattering properties, small sizes are preferred.

After the microcapsules have been formed, they can be separated from the liquid
10 medium and dried. The organic solvent can be separated from the liquid medium and recycled.

More or less water can also be left in the microcapsules, depending on the end use. The microcapsules can be left in dispersion in water after the organic solvent has been
15 removed for example by evaporation or distillation. The concentration of the microcapsules in the dispersion can be increased further by removing water.

The hemicellulosic substance used may contain water-soluble hemicellulose or hemicellulose derivative in addition to water-insoluble hemicellulose or hemicellulose
20 derivative. This water-soluble fraction of the hemicellulosic substance remains in the liquid phase or exists on the dried microcapsules.

In paper and pulp manufacture the hemicellulose microcapsules can be used because of their good optical properties as coating pigment and as filler for paper or cardboard.
25 It has been found that for example GGM has originally brown color, but a dried film made of the GGM microcapsules is white.

The mass of material used for achieving the optical properties (light scattering) is considerably smaller than with conventional pigments and fillers based on minerals and
30 plastics. Hemicellulose microcapsules in their original dispersion form can be used as surface sizing agent or other adhesive purposes, such as gluing plastic films. For example microcapsules made of GGM have been observed to glue polystyrene. Because the microcapsule dispersions have film-forming properties, they can be used to make coating films or barrier films, for example in the packaging industry. The
35 hemicellulosic substances do not leave ash when burning, and they make the paper and cardboard products in which they are included more easily recyclable.

If the hemicellulose microcapsules are to be used as a surface sizing agent, a suitable composition is obtained by removing the organic solvent from the mixture, leaving the microcapsules in dispersion in the aqueous phase. The concentration of the microcapsules may be increased to a suitable level by removing water. The dispersion
5 may be used as such for preparing the surface sizing composition.

The invention is explained further below by way of some examples which do not restrict the scope of the invention.

10 Example 1

To a vessel 83 g galactoglucomannan (GGM) having a concentration of 32 wt-% was added. GGM was diluted by using 150 ml water (21 °C). The suspension was agitated with Kinematica Polytron PT3000 –homogenisator at 10000 rpm. During the agitation
15 200 ml 80/110 "special gasoline" (petroleum distillate) was added. Further, 0,5 g quaternary amine (Armoflote 18) was added as surfactant, 2 ml 1 % MIBC (methyl isobutyl carbinol) was added as frother, and 1,7 ml 40 % glyoxal was added as cross-linking agent. After the addition of these chemicals the agitation speed was raised to 20 000 rpm and the liquid was agitated for 8 min. At the end of the agitation the
20 temperature was 70 °C.

A homogeneous one-phase dispersion containing microcapsules was obtained as product. The dispersion remained stable at least for one week. The volume median particle size of the microcapsules (d_{50}) was 3,8 µm measured with Coulter LS particle
25 size analyser. The solvent can be removed for example by distillation and recycled back to the manufacture.

Example 2

30 The hydroxypropylation of xylan was performed with 1,2-propylene oxide by using sodium hydroxide as catalyst. To a vessel 83 g hydroxypropylated xylan having a concentration of 33 wt-% was added. The hydroxypropylated xylan was diluted by using 150 ml water (21 °C). The suspension was agitated with Kinematica Polytron PT3000 –homogenisator at 10000 rpm. During the agitation 200 ml 80/110 "special
35 gasoline" (hydrocarbon solvent) was added. Further, 0,5 g quaternary amine (Armoflote 18) was added as surfactant, 2 ml 1 % MIBC (methyl isobutyl carbinol) was added as frother, and 1,7 ml 40 % glyoxal was added as cross-linking agent. After the

addition of these chemicals the agitation speed was raised to 20 000 rpm and the liquid was so agitated for 8 min. At the end of the agitation the temperature was 70 °C.

A homogeneous one-phase dispersion containing microcapsules was obtained as
5 product. The dispersion remained stable at least for one week.

Claims

1. Method for preparation of microcapsules from hemicellulosic substance, **characterized** in that the method comprises
- 5 - dispersing hemicellulosic substance together with a gaseous medium in a liquid medium comprising water, organic solvent and surfactant so that microbubbles are formed in the liquid medium with the hemicellulosic substance gathered at interface of the microbubbles, and
- 10 - forming the microcapsules from the dispersed hemicellulosic substance gathered at the interface of the microbubbles and the liquid medium.
2. The method according to claim 1, **characterized** in that the liquid medium further comprises a frother.
- 15 3. The method according to claim 1 or 2, **characterized** in that the liquid medium further comprises a cross-linking agent, and the hemicellulosic substance at the interface of the microbubbles and the liquid medium is cross-linked by the cross-linking agent.
- 20 4. The method according to claim 1, 2 or 3, **characterized** in that the volume median particle size of the microcapsules formed is 0.5 μm to 10 μm .
5. The method according to claim 1, 2 or 3, **characterized** in that the volume median particle size of the microcapsules formed is 1 μm to 5 μm .
- 25 6. The method according to any of the preceding claims, **characterized** in that the gaseous medium is dispersed in the liquid medium by mixing, especially by an agitator containing elements moving through the liquid medium and creating shearing forces in the liquid medium.
- 30 7. The method according to any of the preceding claims, **characterized** in that the hemicellulosic substance is
- hemicellulose,
 - hemicellulose derivative,
 - 35 - a mixture of different hemicelluloses,
 - a mixture of different hemicellulose derivatives, or
 - a mixture of at least one hemicellulose and one hemicellulose derivative.

8. The method according to claim 7, **characterized** in that the hemicellulosic substance is selected among xylan, galactoglucomannan or their derivatives or any of their mixtures.

5

9. The method according to any of the preceding claims, **characterized** in that the concentration of the hemicellulosic substance in the liquid medium is 1 to 30 wt-%, preferably 5 to 15 wt-%.

10 10. The method according to any of the preceding claims, **characterized** in that the hemicellulosic substance comprises a water-soluble fraction in addition to the water-insoluble fraction.

11 11. The method according to any of the preceding claims, **characterized** in that the microcapsules are separated from the liquid medium and dried.

12 12. The method according to any of the preceding claims 1 to 10, **characterized** in that the microcapsules are left in dispersion in the liquid medium, preferably in concentrated form.

20

13. A microcapsule product, **characterized** in that it comprises microcapsules having a shell of hemicellulosic substance and having volume median particle size of 0.5 μm to 10 μm , the product being in the form of isolated microcapsules or microcapsules in dispersion.

25

14. The microcapsule product according to claim 13, **characterized** in that the volume median particle size of the microcapsules is 1 μm to 5 μm .

15 15. The microcapsule product according to claim 13 or 14, **characterized** in that it has adhesive properties in the form of dispersion.

16 16. The microcapsule product according to claim 13 or 14, **characterized** in that it comprises active agent in the microcapsules, such as pharmaceutical agent.

17 17. A paper or cardboard product having a basic structure of cellulose-based fibers and comprising the microcapsule product according to any of the claims 13 to 15 in at least one of the following positions:
surface sizing,

18. The use of the microcapsules according to any of the claims 13 to 15 or the
5 microcapsules prepared according to any of the claims 1 to 12 in paper or cardboard
manufacture as surface sizing, as coating pigment, as filler or as barrier material.

19. The use of the microcapsules according to claim 15 or the microcapsules
prepared according to claim 12 as adhesive for plastics.
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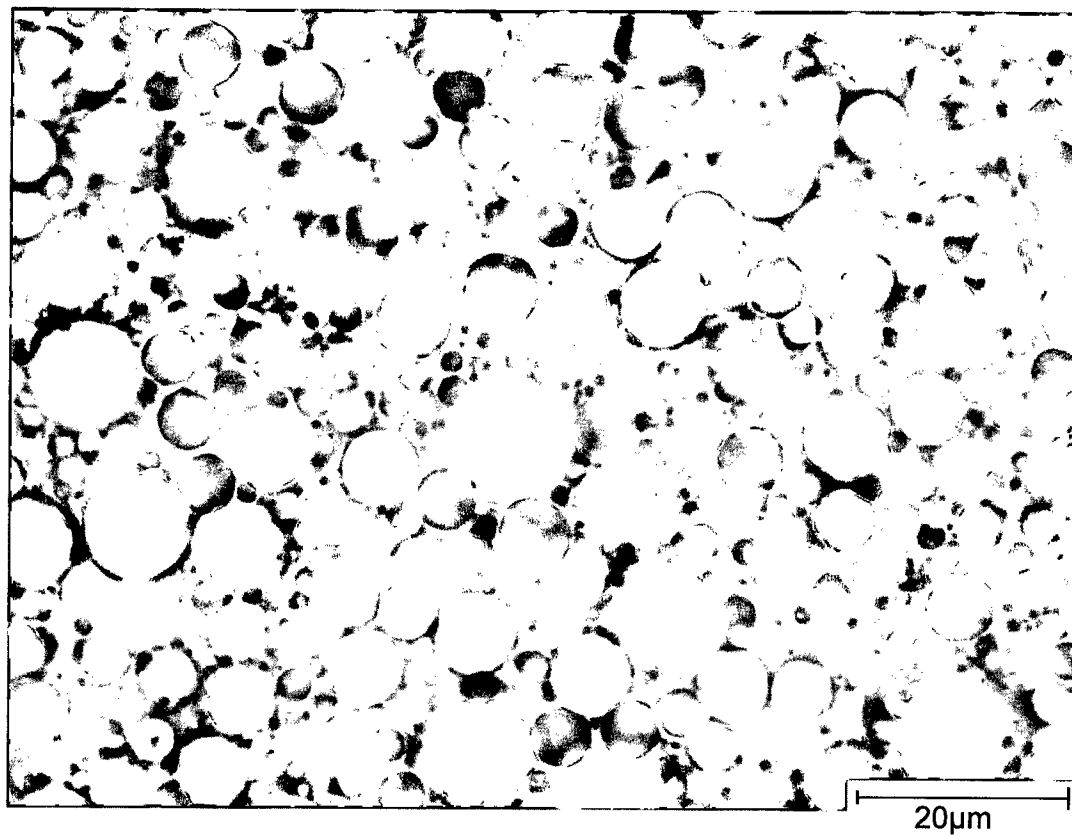


Fig. 1