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(54) Title: SPRAY-DRIED PARTICLE COMPRISING POLYUNSATURATED FATTY ACIDS

(57) Abstract: The present invention relates to spray-dried particles comprising PUFA oil and caseinate. Said particles comprise a relative large amount of caseinate and are free of sucrose. Surprisingly, a low amount of surface oil is measured when the particle's compounds are used in the specified weight ratios. The invention also relates to a method of producing spray-dried particles having a reduced amount of glucose and/or sucrose.

SPRAY-DRIED PARTICLE COMPRISING POLYUNSATURATED FATTY ACIDS

Technical field

The present invention relates to the encapsulation of oils containing polyunsaturated fatty acids (PUFA). It also relates to the constant strive for healthier teeth.

Background of the invention

Powders comprising polyunsaturated fatty acids (PUFA) are known in the art. Said powders are added to baby food or any other kind of food.

Polyunsaturated fatty acids (PUFA) are prone to oxidation, which leads to a fishy taste or smell. Oxidation can be avoided by encapsulation or microencapsulation. If (micro-)encapsulation is not successful, significant amounts of free surface oil are detected. As a result, such PUFA powders get relatively quickly an unacceptable fishy off-flavor.

Consumers that take PUFA supplements on a regular basis are particularly health conscious. They have adopted a healthy life style which includes doing sports, refraining from smoking and avoiding unhealthy food ingredients. A known unhealthy food ingredient is sugar. Hidden sugar has become a widely discussed topic.

WO 07/061804 A3 discloses a composition comprising at least one fatty acid and at least one sweet taste improving composition.

Example 1 of WO 2009/080702 discloses a PUFA product comprising 1700 g sucrose. The authors of WO 2009/080702 have tried to reduce the amount of sucrose. This, however, resulted in an unacceptable amount of free surface oil (cf. comparative example 2 of WO 2009/080702).

Sugar such as sucrose is bad for teeth health. Surprisingly, sugar is not directly the cause of tooth decay. What causes tooth decay is acid produced by bacteria being located in the mouth - and said bacteria consume sugar. Thus, sugar triggers the growth of bacteria which produce acid and said acid eventually damages teeth.

This applies to several types of sugar. However, acid is produced more quickly when sucrose is consumed (Stephan R., Intra-oral hydrogen-ion concentrations associated with dental caries activity. Journal of Dental Research. Vol. 23, No. 4. 1944). Whereas complex starches must be broken down into their component sugars before bacteria can digest them, sucrose can be metabolized straight away.

Thus, sucrose as used in WO 2009/080702 is particularly bad for teeth health.

S. A. Hogan et al. ("Microencapsulation and oxidative stability of spray-dried fish oil emulsions", Journal of Microencapsulation, vol. 20, no. 5, 1 January 2003, pages 675-688) disclose formulations which comprise a lot of carbohydrate. A formulation, wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1 is *not* disclosed.

Zhongxiang Fang et al. ("Effects of Type and Concentration of Proteins on the Recovery of Spray-dried Sucrose Powder", Drying technology, vol. 31, no. 13-14, 26 October 2013, pages 1643-1652) discuss the production of sugar-rich food. The use of selected caseinates for producing spray-dried particles which have a reduced glucose and/or sucrose content is *not* disclosed.

Example 1 of CN 101 125 133 A relates to a process for preparing microcapsules of unsaturated fatty acids. Said example does *not* disclose a method of producing spray-dried particles with a reduced amount of glucose and/or sucrose, said method comprising the step of spray-drying an emulsion which comprises oil and at least one caseinate, wherein the weight ratio oil:caseinate is from 1:1 to 3:1.

Summary of the invention

The problem to be solved by the present invention is the provision of PUFA powders having low surface oil despite of having a low content of sucrose, glucose and/or

fructose. Surface oil is defined as the amount of oil in percent of a powder weight which can be washed away with an appropriate solvent, i.e. an organic solvent, e.g. cyclohexane.

The problem is solved by providing a powder consisting essentially of spray-dried particles. The spray-dried particle of the invention comprises

- 20-40 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,

wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1.

This solution is surprising because claim 1 of prior art document EP2234502 B1 teaches to use an oil: caseinate weight ratio of as high as 6:1. It is also surprising that the amount of free surface oil is reduced when the weight ratio oil: (polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1.

The powder of the present invention is made of spray-dried particles. These particles are of relatively small sizes, viz. with average diameters (d50) in the range of about 50 to 500 microns, preferably of about 50 to 200 microns, more preferably of about 50 to 120 microns. The particle size can be measured by any method well-known in the art, e.g., by laser diffraction, using well-known, available equipment (e.g., MALVERN Mastersizer 2000). Said spray-dried particles comprise oil-droplets having a droplet size (Sauter Diameter D(3,2)) of less than 450 nm such as a droplet size (Sauter Diameter D(3,2)) from 100 nm to 300 nm.

The person skilled in the art understands that the spray-dried particle according to the invention contains a limited amount of glucose only. If high amounts of glucose were used, either the indicated weight ratios and/or the indicated amount of oil could not be reached.

A spray-dried particle comprising for example

- 40 weight-% of oil,
- 40 weight-% of caseinate and
- 10 weight-% of polymers, consisting of 10 or more glucose units

has an oil: caseinate ratio of 1:1 and an oil: (polymers, consisting of 10 or more glucose units) ratio of 4:1. Such a spray-dried particle cannot comprise more than 10 weight-% glucose because all weight-% must add up to 100 weight-%. The preferred spray-dried particle of the invention comprises less than 5 weight-% glucose.

The present invention also relates to a method of producing spray-dried particles with low surface oil and a reduced amount of glucose and/or sucrose, said method comprising the step of spray-drying of an emulsion which comprises or consists of

- water
- oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- at least one antioxidant
- less than 10 weight-% of at least one adjuvant

wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1.

The spray-dried particle according to the invention comprises a relative high amount of caseinate. Surprisingly, better results (e.g. increased yield) are achieved when caseinates having a low viscosity are being used.

Thus, the present invention also relates to the use of caseinate for producing spray-dried particles comprising oil and caseinate in a weight ratio from 1:1 to 3:1, wherein the viscosity of water containing 20 weight-% of said caseinate is less than 200 Pa·s, preferably less than 100 Pa·s (e.g. from 1 Pa·s to 90 Pa·s) and most preferably less

than 50 Pa·s when measured at 25°C at a shear stress of 10 Pa. Sodium caseinate is the preferred caseinate.

The present invention also relates to the use of caseinate for producing spray-dried particles having a reduced glucose and/or sucrose content, wherein the viscosity of water containing 20 weight-% of said caseinate (based on the total weight of water and said caseinate) is less than 200 Pa·s, preferably less than 100 Pa·s (e.g. from 1 Pa·s to 90 Pa·s) and most preferably less than 50 Pa·s when measured at 25°C at a shear stress of 10 Pa.

During spray-drying, hot air is used inside the spray tower. When self-heating compositions are being spray-dried, there is a certain risk of a fire incident inside the spray tower. It has been found that compositions comprising oil and caseinate tend to be self-heating. Surprisingly, self-heating can be reduced or avoided by reducing the amount of oil in the composition to be spray-dried. When doing so, it is beneficial to increase the amount of caseinate such that the weight ratio oil:caseinate is from 1:1 to 2:1.

Detailed description of the invention

The present invention relates to a spray-dried particle consisting essentially of

- oil comprising at least one type of polyunsaturated fatty acids,
- caseinate such as sodium caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- optionally residual water, and
- optionally at least one anti-oxidant.

Glucose is a monosaccharide consisting of 1 glucose unit. Thus, the expression "mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units" refers to the sum of

- glucose and

- “di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units”.

The spray-dried particle of the invention comprises 20-40 weight-% of an oil which comprises polyunsaturated fatty acids. In a preferred embodiment, the spray-dried particles of the invention comprise 20-30 weight-% of an oil which comprises polyunsaturated fatty acids.

Unless indicated differently, “weight-%” (abbreviation: “wt.-%”) always refers to the total weight of the spray-dried particle, not including any residual water/moisture (i.e. weight-% in dry matter).

Oil as used in the context of the present invention may comprise one type of polyunsaturated fatty acids only or multiple types of polyunsaturated fatty acids. In the context of the present invention, the term "PUFA" (polyunsaturated fatty acid) is used in its generally accepted meaning; it relates to fatty acids with at least 2 carbon-carbon double bonds (preferably 2 to 6, more preferably 4 or 5 or 6 carbon-carbon double bonds), preferably consisting of 16-24 carbon atoms (preferably 18-22 carbon atoms), and comprise n-3, n-6 and n-9 acids. Although the term PUFA defines free acids, it is generally understood to also mean their salts and these acids in the form of their naturally occurring esters, i.e. as glycerides (comprising mono-, di- and triglycerides) and in form of esters into which they are converted, e.g. by transesterification, such as ethyl esters. PUFAs of preferred interest in the context of the present invention are n-3 and n-6 PUFAs, especially EPA (eicosapenta-5,8,11 ,14,17-enoic acid) , DPA (docosapentaenoic acid), DHA (docosahexa-4,7,10,13,16,19-enoic acid), GLA (gamma-linolenic acid) and ARA (arachidonic acid), preferably of food-grade quality, as single compounds or in mixtures, preferably in the form of their esters, e.g., triglycerides, or ethyl esters, especially as components of oils obtained from marine animals, preferably from fish, from plants or by fermentation.

Well-known polyunsaturated fatty acids are docosahexaenoic acid (DHA), eicosapentaenoic acid (EPA) and arachidonic acid (ARA). The particle according to the invention comprises PUFA, preferably at least one type of omega-3 fatty acid.

Most preferably, the oil to be used in the context of the present invention comprises docosahexaenoic acid (DHA), eicosapentaenoic acid (EPA) and/or arachidonic acid (ARA). Suitable oils are commercially available at the company DSM®. Preferred brands are DHASCO® or ARASCO®, available at DSM®.

Oil as used in the context of the present invention comprises at least 30 weight-% of at least one type of polyunsaturated fatty acids (PUFA), preferably at least 35 weight-% of at least one type of polyunsaturated fatty acids, based on the total weight of the oil. When referring to the composition of the oil as used in the context of the present invention, weight-% are based on the total weight of said oil.

The spray-dried particle according to the invention also comprises at least one caseinate. In the context of the present invention, the term "caseinate" refers to a salt such as potassium caseinate and sodium caseinate. In term "at least one caseinate" means that the spray-dried particle comprises a suitable amount of one or multiple types of caseinate such as a suitable amount of sodium caseinate and/or potassium caseinate.

Preferably, the spray-dried particle according to the invention comprises oil which is microencapsulated by said caseinate. Microencapsulation is achieved by emulsifying the oil with caseinate before spray-drying.

The spray-dried particle according to the invention comprises a relatively large amount of at least one caseinate. When high viscosity caseinate is used, spray-drying might not be possible because the emulsion to be spray-dried may form a solid gel. Thus, to achieve a higher yield, a low viscosity caseinate is preferred. In a preferred embodiment of the invention, a caseinate (or a mixture of caseinates) is used wherein the viscosity of water containing 20 weight-% of said caseinate (or of said mixture of caseinates) is less than 200 Pa·s, preferably less than 100 Pa·s, more preferably less than 50 Pa·s and most preferably less than 20 Pa·s (e.g. from 1 to 19 Pa·s), when measured at 25°C at a shear stress of 10 Pa. Suitable caseinates are commercially available e.g. at the company TATUA®.

The spray-dried particle according to the invention comprises at least one type of caseinate and oil, wherein said oil comprises at least one type of polyunsaturated

fatty acids (PUFA). The weight ratio oil:caseinate is from 1:1 to 3:1, preferably from 1:1 to 2.5:1 and most preferably from 1:1 to 2:1. If the spray-dried particle according to the invention comprises more than one type of caseinate, the amount of all caseinates is added up to calculate the weight ratio oil:caseinate.

The present invention also relates to the use of caseinate for producing spray-dried particles comprising oil and caseinate in a weight ratio from 1:1 to 3:1, preferably from 1:1 to 2:1, wherein the viscosity of water containing 20 weight-% of said caseinate is less than 200 Pa·s, preferably less than 100 Pa·s, more preferably less than 50 Pa·s and most preferably less than 25 Pa·s when measured at 25°C at a shear stress of 10 Pa. In a preferred embodiment, the present invention also relates to the use of caseinate for producing spray-dried particles comprising oil and caseinate in a weight ratio from 1:1 to 2:1, wherein the viscosity of water containing 20 weight-% of said caseinate is less than 50 Pa·s when measured at 25°C at a shear stress of 10 Pa.

The spray-dried particle according to the invention comprises glucose. Multiple sources of glucose are known. Glucose is a monosaccharide and can be obtained e.g. by hydrolysis of carbohydrates such as milk sugar (lactose), cane sugar (sucrose), maltose, cellulose or glycogen, followed by separation/purification (if needed).

In addition to glucose, the spray-dried particle according to the invention comprises di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units. A well-known disaccharide consisting of 2 glucose units is maltose. Multiple sources of di-, tri- and small oligosaccharides consisting of 2 to 9 glucose units are known. They may be produced e.g. from starch by partial hydrolysis. Commercial products are available from various suppliers.

The spray-dried particle according to the invention further comprises polymers, consisting of 10 or more glucose units. Well-known polymers consisting of more than 10 glucose units are starch and cellulose. Cellulose, however, is to be avoided in the context of the present invention because cellulose is typically not water-soluble. The particle according to the invention is produced by spray-drying of an aqueous

emulsion and thus, any compound consisting of glucose units and not being water-soluble is not within the scope of the present invention.

In the context of the present invention, the terms “di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units” and “polymers, consisting of 10 or more glucose units” are limited to compounds that are water-soluble (i.e. suitable for preparing an emulsion that can be spray-dried). Such compounds are commercially available or can be produced by partial hydrolysis of e.g. starch.

Oils comprising polyunsaturated fatty acids (such as fish oil) are prone to oxidation. Upon oxidation, a fishy off-flavor and/or off-smell can be recognized. This is to be avoided and thus, such oils are (micro-)encapsulated. A well-known (micro-)encapsulant for fish oil are caseinates.

Even better storage stability is achieved when at least one antioxidant is added. Thus, the spray-dried particle according to the invention comprises preferably at least one antioxidant, preferably in an amount of 1-10 weight-%, more preferably in an amount of 1-3 weight-%. Preferred antioxidants are tocopherol, ascorbyl palmitate, rosemary extract and sodium ascorbate. A preferred spray-dried particle of the invention comprises 1-3 weight-% of sodium ascorbate.

Surprisingly, the amount of surface oil is lower when there is a certain amount of residual water in the spray-dried particle. In the context of the present invention, the term “residual water” refers to a water content of not more than 5 weight-%, based on the total weight of the spray-dried particle, including residual water. The spray-dried particle according to the invention preferably comprises not more than 5 weight-% of residual water and comprise more preferably 1 to 3 weight-% residual water, based on the total weight of the spray-dried particle, including residual water.

In the context of the present invention, the term “adjuvant” refers to a compound that is acceptable for a food product, for baby food, for a supplement and/or for an oral pharmaceutical product. The spray-dried particle according to the invention may but does not need to comprise any further adjuvants. However, it may comprise up to 10 weight-% of at least one adjuvant. Preferably, the spray-dried particle according to the invention comprises less than 2 weight-% of at least one adjuvant.

Surprisingly, the amount of surface oil is lower when the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1. In a preferred embodiment of the invention, the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 4:1, even more preferred from 1:1 to 3:1 and most preferred from 1:1 to 2:1.

Thus, a preferred embodiment of the invention relates to a spray-dried particle according to any of the preceding claims, comprising or consisting of

- 20-40 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- 1-10 weight-% of at least one antioxidant
- less than 10 weight-% of at least one adjuvant

wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1.

The person skilled in the art knows how to apply this technical teaching. More specifically, he knows that all weight-% must add up to 100 weight-%. Unless otherwise indicated, all weight-% are based on the total weight of the spray-dried particle, not including any residual water (i.e. weight-% in dry matter). The person skilled in the art refrains from combining weight ratios and/or weight-% in a manner that results in an embodiment which can obviously not be manufactured or which is otherwise obviously meaningless. The person skilled in the art uses common sense.

Another embodiment of the invention relates to a spray-dried particle comprising

- 20-40 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,

- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,

wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1.

An alternative embodiment of the invention relates to a spray-dried particle comprising

- 20-40 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,

wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 3:1.

Surprisingly, the amount of surface oil is lower when the weight ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is from 0.5:1 to 1:1 and is preferably from 0.6:1 to 0.9:1. When calculating the amount of “mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units”, the amount of glucose (=monosaccharide consisting of 1 glucose unit) is to be added to the amount of “di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units”.

Thus, a preferred embodiment of the invention relates to a spray-dried particle comprising

- 20-40 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose (= monosaccharide consisting of 1 glucose unit),
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units

- polymers, consisting of 10 or more glucose units,

wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1, and

wherein the weight ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is from 0.5:1 to 1:1 and is preferably from 0.6:1 to 0.9:1.

Examples 1 and 2 and the corresponding TABLES 1 and 2 illustrate how this technical teaching is to be applied.

An even more preferred embodiment of the invention relates to a spray-dried particle comprising

- 20-40 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose (= monosaccharide consisting of 1 glucose unit)
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,

wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 3:1, and

wherein the weight ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is from 0.5:1 to 1:1 and is preferably from 0.6:1 to 0.9:1.

Compositions comprising oil and caseinate tend to be self-heating. When a self-heating composition is spray-dried, there is an increased risk of a fire incident within the spray tower. Surprisingly, self-heating can be reduced or avoided by reducing the amount of oil in the composition to be spray-dried. Therefore, a preferred embodiment of the present invention relates to a spray-dried particle comprising 20-30 weight-% oil instead of 20-40 weight-% oil, said oil comprising comprises at least 20 weight-% polyunsaturated fatty acids (such as a mixture of DHA and EPA).

Thus, one embodiment of the invention relates to a spray-dried particle comprising

- 20-30 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,

wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 3:1.

The most preferred embodiment of the invention relates to a spray-dried particle comprising or preferably consisting of

- 20-30 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- 1-10 weight-% of at least one antioxidant
- less than 10 weight-% of at least one adjuvant
- residual water

wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 2:1, and

wherein the weight-% ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is from 0.6:1 to 0.9:1, and

wherein any compound consisting of glucose units is water-soluble, and

wherein the viscosity of water containing 20 weight-% of said caseinate is preferably less than 100 Pa·s when measured at 25°C at a shear stress of 10 Pa.

The spray-dried particle according to the invention has a low amount of surface oil such as less than 2 weight-%, preferably less than 1 weight-% and most preferably less than 0.5 weight-% surface oil. The person skilled in the art knows how to measure surface oil. A preferred method to measure surface oil is described in WO 2009/080702. However, instead of using petroleum ether, it is preferred to use cyclohexane.

Surprisingly, such low surface oil can be achieved despite of a reduced amount of glucose. The spray-dried particles as described herein comprise preferably less than less than 10 weight-%, preferably less than 5 weight-% glucose. Typically, the spray-dried particles according to the invention are free of sucrose, fructose and/or lactose. Most preferably, the spray-dried particle according to the invention does not contain any saccharide other than water-soluble saccharides consisting of at least 1 glucose unit.

Preferably, the spray-dried particle according to the present invention comprises oil droplets with a droplet size [Sauter Diameter D(3,2) as measured by laser diffraction (Malvern Mastersizer) when dispersing the spray-dried particles in water] of less than 450 nm, preferably of less than 300 nm. The person skilled in the art knows how to manufacture such particles.

The present invention also relates to a method of producing spray-dried particles comprising polyunsaturated fatty acids (i.e. a method of producing spray-dried particles as herein described), wherein an emulsion is spray-dried at a temperature of e.g. 80- 110°C. Thereby, the emulsion's composition is to be chosen in such manner that spray-dried particles as described herein are achieved. After spray-drying, the obtained particles may be further dried to determine the loss on drying (LOD). Preferably, however, such additional drying step is not performed because particles having 1-5 weight-% residual water perform better.

A preferred embodiment of the invention relates to a method of producing spray-dried particles with low surface oil and a reduced amount of glucose and/or sucrose, said method comprising the step of spray-drying of an emulsion which comprises or consists of

- water
- oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- at least one antioxidant
- less than 10 weight-% of at least one adjuvant

wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1, and

wherein the viscosity of water containing 20 weight-% of said at least one caseinate is less than 200 Pa·s, preferably less than 100 Pa·s and most preferably less than 50 Pa·s when measured at 25°C at a shear stress of 10 Pa.

An also preferred embodiment of the invention relates to a method of producing spray-dried particles with low surface oil and a reduced amount of glucose and/or sucrose, said method comprising the step of spray-drying of an emulsion which comprises or consists of

- water
- oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- at least one antioxidant
- less than 10 weight-% of at least one adjuvant

wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1, and

wherein the weight ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is from 0.5:1 to 1:1 and is preferably from 0.6:1 to 0.9:1, and

wherein the viscosity of water containing 20 weight-% of said at least one caseinate is less than 200 Pa·s, preferably less than 100 Pa·s and most preferably less than 50 Pa·s when measured at 25°C at a shear stress of 10 Pa.

The most preferred embodiment of the invention relates to a method of producing spray-dried particles with low surface oil and a reduced amount of glucose and/or sucrose, said method comprising the step of spray-drying of an emulsion which comprises or consists of

- water
- oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- at least one antioxidant
- less than 10 weight-% of at least one adjuvant

wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 3:1, and

wherein the weight ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is preferably from 0.6:1 to 0.9:1, and

wherein the viscosity of water containing 20 weight-% of said at least one caseinate is less than 200 Pa·s, preferably less than 100 Pa·s and most preferably less than 50 Pa·s when measured at 25°C at a shear stress of 10 Pa.

When many spray-dried particles according to the present invention are manufactured, a powder is obtained. Such powder is ready-for-sale, is storage stable and does not easily get a fishy off-flavor or off-smell.

Whereas the powder as such could be consumed, it is preferred to add spray-dried particles according to the present invention to food or to use said particles to manufacture a food supplement or a pharmaceutical product.

Such products sell better because they are free of sucrose, contain a limited amount of glucose only and do not have fishy off-flavor or off-smell. The commercial aspect is particularly true for baby food because young parents are very health conscious and often refuse to buy products which are rich in sucrose. The baby's first tooth seems too precious to endanger its existence by feeding products containing a lot of glucose, sucrose, fructose and/or lactose.

Thus, the present invention also applies to an edible composition comprising spray-dried particles according to the present invention, wherein said edible composition is preferably a food supplement, a pharmaceutical product or food, and wherein said edible composition is most preferably baby food.

Examples

The present invention is further illustrated by the following examples.

Example 1:

In example 1, a DHA algal oil comprising approx. 40 weight-% docosahexaenoic acid (DHA) based on the total weight of the oil has been used.

As caseinate, low viscosity sodium caseinate has been used. Viscosity of said caseinate has been determined as 8 Pa·s (water comprising 20 weight-% of said sodium caseinate, measured at 25°C, shear stress 10 Pa).

A mixture of the water, oil, caseinate and the other ingredients (cf. TABLE 1) has been homogenization to obtain an emulsion. Said emulsion has been spray-dried to obtain a powder made of spray-dried particles.

In TABLE 1, details about the composition and the corresponding weight ratios are given. Weight-% are weight-% in dry matter.

The spray-dried particles contained 2.1 weight-% of residual water, based on the total weight of the moist spray-dried particles. Residual water has been determined as loss on drying (LOD) when drying spray-dried particles that contain residual water.

	wt.-%, based on the weight of the total weight of spray-dried particles	weight ratio oil:caseinate	weight ratio oil: (polymers, consisting of 10 or more glucose units)	weight ratio (polymers, consisting of 10 or more glucose units): (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 or more glucose units)
oil	39	1.95:1	2.6:1	
caseinate	20			
glucose (=monosaccharide consisting of 1 glucose unit)	approx. 2			0.7:1
polymers, consisting of 10 or more glucose units	approx. 15			
di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units	approx. 19			
Na-ascorbate	5			

Table 1

Example 2:

Example 1 was repeated, using different quantities of the same ingredients. The details of the composition of the spray-dried particles of example 2 are given in TABLE 2. Weight-% are weight-% in dry matter, as in example 1.

The spray-dried particles of example 2 contained 2.3 weight-% of residual water, based on the total weight of the moist spray-dried particles. As in example 1, residual water has been determined as loss on drying (LOD) when drying spray-dried particles that contain residual water.

	wt.-%, based on the weight of the total weight of spray-dried particles	weight ratio oil:caseinate	weight ratio oil: (polymers, consisting of 10 or more glucose units)	weight ratio (polymers, consisting of 10 or more glucose units): (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 or more glucose units)
oil	28	1.4:1	1.4:1	
caseinate	20			
glucose (=monosaccharide consisting of 1 glucose unit)	approx. 4			0.7:1
polymers, consisting of 10 or more glucose units	approx. 20			
di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units	approx. 23			
Na-ascorbate	5			

Table 2

In contrast to the particles of example 1, the particles of example 2 did not show any self-heating during spray-drying at 100°C. Thus, self-heating during spray-drying can be reduced or avoided by reducing the oil loading to less than 30 weight-%. Such measure is only necessary if very strict fire prevention regulations are in place.

Comparative example 3:

Example 1 and example 2 were to be repeated with a different kind of sodium caseinate. The viscosity of said alternative caseinate has been determined as 218 Pa·s (water comprising 20 weight-% of said sodium caseinate, measured at 25°C, shear stress 10 Pa).

The attempt to repeat examples 1 and 2 failed with said alternative sodium caseinate. At a weight ratio oil:caseinate of 1.95:1 and 1.4:1, respectively, the emulsions formed a solid gel which could not be spray-dried.

Example 4:

The amount of surface oil of the particles of examples 1 and 2 has been determined. In addition, the droplet size, Sauter Diameter D(3,2) has been measured.

The results are given in given in TABLE 3.

Determination of surface oil content:
Weigh exactly an amount of approximately 7-10 g of sample and place it in a 50 ml graduated centrifuge tube. Dilute it to 40 milliliters with cyclohexane. Shake the sample and cyclohexane for exactly 5 minutes using a HS 501D-Schüttelmaschine at 300 hub/min. Filter the mixture through a filter paper (Schleicher&Schuell Nr. 597½, ∅ = 125 mm) to remove all the solids. A 50 ml round bottom flask must be dried in an oven for 1 hour at 105°C and placed in a desiccator until it reaches room temperature. The round bottom flask is weighed accurately to three decimal places. Using a 25 ml pipette, extract 25 ml of the filtrate and transfer it to a clean and tared

50 ml round bottom flask. Place the round bottom flask with the sample on a rotary evaporator and evaporate to dryness. After the cyclohexane is removed, place the round bottom flask with the remaining oil in an oven at 105°C for 1 hour. Remove the round bottom flask from the oven and place it in a desiccator. Allow the round bottom flask to cool to room temperature before weighing. Weigh the round bottom flask to determine the amount of oil extracted.

Calculation:

$$\frac{\text{weight of oil extracted in g} \times 40\text{ ml} \times 100}{\text{weight of sample in g} \times 25\text{ ml}} = \%\text{ surface oil}$$

	weight ratio oil: (polymers, consisting of 10 or more glucose units)	**weight ratio oil:caseinate**	**surface oil**	**Sauter Diameter D(3,2)**
particles of example 1	2.6:1	1.95:1	0.24 weight-%	203 nm
particles of example 2	1.4:1	1.4:1	0.12 weight-%	276 nm

Table 3

The particles of example 1 and 2 are comparable since they comprise the same amount of the same caseinate. The Sauter Diameter D(3,2) of the particles of both examples is below 300 nm. Furthermore, the particles of both examples have a very low glucose content (less than 5 weight-%).

Very little surface oil has been measured for the particles of both examples (0.24 weight-% and 0.12 weight-%, respectively). Thus, the particles of examples 1 and 2 are both very good products.

A comparison of example 1 with example 2 shows that the amount of surface oil can be further lowered by reducing the weight ratio oil:caseinate and/or the weight ratio oil: (polymers, consisting of 10 or more glucose units). An additional advantage of the preferred embodiment of example 2 is the lack of self-heating during spray-drying.

Claims

1. Spray-dried particle, comprising
    - 20-40 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
    - at least one caseinate,
    - glucose,
    - di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
    - polymers, consisting of 10 or more glucose units,

    wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

    wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1, and

    wherein the viscosity of water containing 20 weight-% of said at least one caseinate is less than 200 Pa·s when measured at 25°C at a shear stress of 10 Pa.

2. Spray-dried particle according to claim 1, wherein the weight ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is from 0.5:1 to 1:1 and is preferably from 0.6:1 to 0.9:1.

3. Spray-dried particle according to claim 1 or 2, wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and/or wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 3:1.

4. Spray-dried particle according to any of the preceding claims, wherein the viscosity of water containing 20 weight-% of said at least one caseinate is less than 100 Pa·s and preferably less than 50 Pa·s when measured at 25°C at a shear stress of 10 Pa.

5. Spray-dried particle according to any of the preceding claims, wherein any compound consisting of glucose units is water-soluble.

6. Spray-dried particle according to any of the preceding claims, wherein said spray-dried particle comprises less than 10 weight-%, preferably less than 5 weight-% glucose.

7. Spray-dried particle according to any of the preceding claims, wherein said spray-dried particle comprises 20-30 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil.

8. Spray-dried particle according to any of the preceding claims, wherein said oil comprises docosahexaenoic acid, eicosapentaenoic acid and/or arachidonic acid, and/or wherein the spray-dried particle comprises potassium caseinate and/or sodium caseinate.

9. Spray-dried particle according to any of the preceding claims, wherein the spray-dried particle comprises residual water and/or at least one antioxidant.

10. Spray-dried particle according to any of the preceding claims, wherein the spray-dried particle comprises 1-10 weight-%, preferably 2-8 weight-% of at least one antioxidant, said antioxidant being preferably sodium ascorbate.

11. Spray-dried particle according to any of the preceding claims, wherein said spray-dried particle has a diameter of 50 to 500 microns, preferably of 50 to 200 microns, more preferably of 50 to 120 microns, and/or wherein oil droplets comprised in said spray-dried particle have a droplet size (Sauter Diameter D(3,2)) of less than 450 nm, preferably of less than 300 nm.

12. Spray-dried particle according to any of the preceding claims, consisting of
    - 20-30 weight-% oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
    - at least one caseinate,
    - glucose,
    - di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units
    - polymers, consisting of 10 or more glucose units,

- 1-10 weight-% of at least one antioxidant
- less than 10 weight-% of at least one adjuvant
- residual water

wherein the weight ratio oil:caseinate is from 1:1 to 2:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 2:1, and

wherein the weight-% ratio (polymers, consisting of 10 or more glucose units) : (mono-, di-, tri- and small oligosaccharides, consisting of 1 to 9 glucose units) is from 0.6:1 to 0.9:1, and

wherein any compound consisting of glucose units is water-soluble, and

wherein the viscosity of water containing 20 weight-% of said caseinate is preferably less than 100 Pa·s when measured at 25°C at a shear stress of 10 Pa.

13. Edible composition comprising spray-dried particles according to any of the preceding claims, wherein said edible composition is preferably a food supplement, a pharmaceutical product or food, and wherein said edible composition is most preferably baby food.

14. Method of producing spray-dried particles with low surface oil and a reduced amount of glucose and/or sucrose, said method comprising the step of spray-drying an emulsion which comprises or consists of

- water
- oil, said oil comprising at least 30 weight-% polyunsaturated fatty acids based on the total weight of the oil,
- at least one caseinate,
- glucose,
- di-, tri- and small oligosaccharides, consisting of 2 to 9 glucose units
- polymers, consisting of 10 or more glucose units,
- at least one antioxidant
- less than 10 weight-% of at least one adjuvant

wherein the weight ratio oil:caseinate is from 1:1 to 3:1, and

wherein the weight ratio oil:(polymers, consisting of 10 or more glucose units) is from 1:1 to 5:1, and

wherein the viscosity of water containing 20 weight-% of said at least one caseinate is less than 200 Pa·s when measured at 25°C at a shear stress of 10 Pa.

15. Use of caseinate for producing spray-dried particles having a reduced glucose and/or sucrose content, wherein the viscosity of water containing 20 weight-% of said caseinate is less than 100 Pa·s when measured at 25°C at a shear stress of 10 Pa.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. A23L33/115 A61K9/16 A61K9/50 A23P10/30 A23P10/35 A23L33/12
ADD.
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)
A23L A61K A23P

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, BIOSIS, EMBASE, FSTA, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101 125 133 A (WUHAN MAIKEDE BIOTECHNOLOGY CO [CN]) 20 February 2008 (2008-02-20)	1-3,5-9, 11,13,14
Y	abstract example 1	4,10,12, 14
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Information on patent family members

International application No
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