

Cyclodextrin particles

The present invention relates to flavouring- and/or fragrance-containing cyclodextrin particles which contain cellulose ethers and have a particle size in the range from 50
5 to 1000 μm , to products containing these particles, to a process for their production and to their use in foodstuffs, pharmaceutical products and commodities.

Cyclodextrins are oligomers of anhydroglucose units which are linked *via* alpha-1,4-
bonds to form a cyclic molecule. According to the number of structural units, a
10 distinction is made between alpha- (6 structural units), beta- (7 structural units) and gamma- (8 structural units) cyclodextrins. They are conventionally produced from starch by enzymatic processes. The cyclic structure of the cyclodextrins permits the formation of inclusion complexes on a molecular level. The inclusion compounds can be formed more or less completely according to the geometry and polarity of the
15 flavourings.

Flavourings are mostly volatile compounds which exhibit high rates of loss, due to evaporation or oxidation, during storage or also during processing operations, for example in the foodstuffs industry. In cyclodextrin complexes, flavourings can be
20 protected from these losses.

Flavourings and fragrances, or flavouring and fragrance mixtures, are generally volatile, mostly liquid substances or complex mixtures of these substances. It is conventional to encapsulate these substances or substance mixtures by spray drying,
25 which, however, yields only relatively fine particles of irregular structure.

A number of methods are known for producing inclusion compounds of flavourings and/or fragrances with cyclodextrins.

30 These methods involve mixing cyclodextrin solutions, suspensions or pastes (conventionally in water) and the flavourings and/or fragrances. Depending on the

polarity of the flavourings and/or fragrances, a two-phase mixture is in most cases obtained thereby. For that reason, high shear forces, e.g. by stirring or kneading, are applied in order to accelerate the process. This step is in most cases followed by a drying step, such as, for example, spray, freeze or fluidised-bed drying.

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According to the known prior art, the operation of drying aqueous flavouring/cyclodextrin complexes by spraying without further additives yields very fine particles.

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EP-A 392 608 describes a method of producing pulverulent cyclodextrin complexes whose particle size is less than 12 μm , preferably less than 5 μm . In that specification, processes such as, for example, spray drying and freeze drying are used.

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The small particle size is disadvantageous for the use of these complexes. Finely divided cyclodextrin complexes can be dispersed in water only with difficulty, and the solubilisation speed is reduced thereby. Moreover, when small (typically < 10 μm) cyclodextrin particles are used in dry mixtures that contain mainly constituents having a particle size of from 50 to 500 μm , there is the risk of separation.

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Small particle sizes have the further disadvantage that the pourability is often lowered and dust readily develops.

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For these reasons it is advantageous for the cyclodextrin complex particles to have particle sizes of at least 50 μm .

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During spray drying, a portion of the flavourings and/or fragrances remains on the particle surface. This so-called surface oil leads to a reduction in the oxidation stability and lowers the pourability still further. A minimal amount of surface oil is desirable.

DE-A 31 05 666 describes a process in which particles having a particle size of from 500 to 1000 μm are produced with the aid of the addition of binders to cyclodextrin complex mixtures in a kneader, with subsequent drying and grinding.

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A disadvantage of such a kneading process is the high proportion of surface oil in the finished granules. In addition, the use of a plurality of process steps (kneading, drying, grinding, sieving) is disadvantageous from the point of view of production costs.

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In EP-A 1 064 856, particles containing carbohydrates and/or polyhydroxy compounds having sizes in the range from 100 to 400 μm are described. The multi-stage process described therein for the production of these particles comprises further steps in addition to spray drying. In one of these steps, the smaller particles
15 formed in the process are recycled, so that they grow to the mentioned particle size range by agglomeration. Disadvantages of these particles are their low stability to abrasion and their surface oil content.

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The object of the present invention was to provide flavouring- and/or fragrance-containing cyclodextrin particles having a size of at least 50 μm , which particles remedy the above-mentioned disadvantages of the prior art, and as simple a process as possible for the production of such particles. A narrow particle size distribution would additionally be advantageous.

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The present invention accordingly provides flavouring- and/or fragrance-containing cyclodextrin particles which have a particle size in the range from 50 to 1000 μm and contain a cellulose ether and which are obtainable from a spray mixture by a single-stage fluidised bed process, wherein the gas inlet temperature is from 80 to 180°C and the gas outlet temperature is from 40 to 95°C.

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The present invention further provides a process for the production of cyclodextrin particles, characterised in that an aqueous spray mixture comprising at least one cyclodextrin, at least one flavouring and/or fragrance and at least one cellulose ether is introduced into a single-stage fluidised bed device.

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The invention relates further to products containing the cyclodextrin particles according to the invention and to the use of the cyclodextrin particles according to the invention in foodstuffs, pharmaceutical products and commodities.

10 Granulation processes known *per se* can be used for producing the particles from the spray mixture. The processes that are suitable according to the invention are single-stage, that is to say the spray mixture is fed to a single apparatus and, when the mixture leaves the apparatus, production is complete and the finished cyclodextrin particles are available. In contrast to multi-stage processes, no intermediate is
15 formed in the single-stage process.

The particles can be produced by continuous fluidised bed spray granulation, for example according to EP-A 163 836, or by discontinuous fluidised bed spray granulation, for example according to EP-A 70 719. It is also possible to employ a
20 process as in WO-A 97/16078 for the production of flavouring granules in a conventional fluid bed rotor granulator with discontinuous operation.

The process is preferably continuous. A continuous process is more suitable for industrial production and exhibits short residence times. With the same material
25 throughput, the bed content in the case of the continuous fluidised bed spray granulation processes is lower than in the case of the discontinuous processes. Instead of allowing all the particle nuclei to grow at the same time, only a small amount of the particle nuclei are sprayed in continuous fluidised bed spray granulation and, once the desired particle size has been reached, they are discharged
30 immediately, for example by way of a sifter. The encapsulated flavouring- and/or fragrance-containing cyclodextrin particles produced according to the invention

exhibit a low particle size distribution; moreover, it is possible to remove the particles (granules) of the desired size selectively.

5 Within the scope of the present invention it is preferred for the fluidised bed to have a small bed height. This is preferably from 3 to 50 cm, particularly preferably from 5 to 20 cm.

10 By means of continuous fluidised bed spray granulation there are obtained from a spray mixture free-flowing, low-dust, granular particles. Ideally, the fundamental operations of nucleus production, drying, shaping and selective discharge of the particles that have reached the desired particle size take place simultaneously in a granulating apparatus.

15 The fundamental principle of continuous fluidised bed spray granulation (Chemie-Ingenieur-Technik, 62nd year (1990), pages 822 to 834) has been realised in numerous variants. A distinction is to be made in particular between the variant with external nucleus formation, in which nuclei from external sifters, grinding apparatus or other solids stores are metered into the bed, and variants with internal nucleus formation.

20 Within the scope of the present invention, processes with internal nucleus supply are preferred. Such a process is described, for example, in EP-A 163 836. This granulating apparatus further has a self-regulating mechanism for regulating the particle size and therefore exhibits a minimal residence time.

25 The spray mixture can be sprayed into the fluidised bed from beneath, from the side or also from above. Numerous variants are possible for separating entrained solids from the exhaust air, which variants differ in the separating method (e.g. cyclone or filter) or in the location of the separation (inside or outside the granulating apparatus).

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Finally, sifters, as described, for example, in EP-A 332 031, are preferably used for discharging the particles. The sifters have the effect that only the coarse particles are able to leave the fluidised bed. The remaining particles are retained in the fluidised bed until they have also reached the desired particle size.

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For the production of the particles according to the invention, an aqueous spray mixture is first prepared. In addition to water, this spray mixture comprises at least one cyclodextrin, flavourings and/or fragrances and at least one cellulose ether.

10 The particles according to the invention are produced from this spray mixture in one process step in a fluidised bed apparatus, with particle sizes greater than or equal to 50 μm .

Particles according to the invention have a particle size of from 50 μm to 1000 μm .

15 Preference is given to particles having a particle size of from 70 μm to 500 μm , particularly preferably from 100 to 300 μm .

Data relating to particle sizes are based on the particle diameter and are taken from cumulative distribution curves. These cumulative distribution curves show the dependency of the cumulative distribution $Q_3(x)$ on the particle diameter x . The cumulative distribution $Q_3(x)$ is the normalised total amount of all particles having a diameter smaller than or equal to x . The particle size $x_{50,3}$ is the particle size at which the cumulative distribution $Q_3(x) = 0.5$. Unless characterised otherwise, data relating to particle size in the present text are based on the particle size $x_{50,3}$. The index 3 indicates that the type of amount measured is the volume (Ullmanns Encyklopädie der technischen Chemie, Volume 2, Verfahrenstechnik I, 4th Edition, Verlag Chemie, Weinheim, 1972, p. 24-34).

25 Particle size determination *via* volume distribution can be carried out by means of laser diffraction (e.g. using the Master Sizer[®] MSS Longbench from Malvern Instruments Ltd., Malvern, UK).

Suitable cyclodextrins are alpha-, beta-, gamma- and substituted cyclodextrins. Alpha-, beta-, gamma-cyclodextrin or mixtures thereof are advantageous, and beta-cyclodextrin is preferred. In a preferred embodiment, the cyclodextrin content of the spray mixture consists only of beta-cyclodextrin.

The amount of cyclodextrin in the spray mixture is advantageously from 5 to 50 wt.%, preferably from 10 to 40 wt.%, particularly preferably from 15 to 30 wt.%.

The amount of water in the spray mixture is advantageously from 40 to 95 wt.%, preferably from 50 to 90 wt.%, particularly preferably from 60 to 80 wt.%.

The amount of flavourings and/or fragrances in the spray mixture is advantageously from 0.0005 to 15 wt.%, preferably from 0.1 to 10 wt.%, particularly preferably from 0.25 to 5 wt.%.

The spray mixture contains binders in the form of cellulose ethers as granulation aids. The cellulose ether is preferably selected from the group comprising methyl cellulose, ethyl cellulose, propyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, carboxymethyl cellulose, carboxymethylhydroxyethyl cellulose and ethylhydroxyethyl cellulose, with carboxymethyl cellulose (CMC) being particularly preferred.

Preference is given to a cellulose ether content in the spray mixture of from 0.1 to 6 wt.%, particularly preferably from 0.2 to 2 wt.%. The dried particles preferably contain from 0.5 to 10 wt.%, particularly preferably from 2 to 4.5 wt.%, cellulose ethers.

Cellulose ethers having a viscosity of from 15 to 200,000 mPas are advantageous; preference is given to those having a viscosity of from 1000 to 50,000 mPas,

particular preference being given to those having a viscosity of from 5000 to 15,000 mPas. The viscosity data are based on a 2 wt.% solution in water at 20°C.

5 The measuring system used was a cone/plate system having a diameter of 40 mm and a cone angle of 4°. The shear rate was 1 s^{-1} , the temperature was 20°C. The viscosity can be determined, for example, using a CVO 120 rheometer (Bohlin Instruments GmbH, Pforzheim).

10 According to the process according to the invention, the content of flavouring and/or fragrance in the finished cyclodextrin particle is from 0.01 to 30 wt.%, preferably from 1 to 15 wt.% and particularly preferably from 5 to 10 wt.%.

15 Methods of determining the loading and the surface oil are known from the literature. In the present case, the determination of the content of flavourings and/or fragrances in the finished cyclodextrin particles for determining the loading and the surface oil was carried out analogously to J. Agric. Food Chem. 1998, 46, 1494-1499. The methods described therein were modified only in respect of the solvents used in the extraction. Ethyl acetate was used instead of n-hexane for determining the loading, and a 2:1 mixture (parts by volume) of n-pentane and diethyl ether was used instead of n-hexane for determining the surface oil content.
20 The loading and surface oil content are given in wt.%.

25 Examples of flavourings and/or fragrances which may be a constituent of the cyclodextrin particles according to the invention are to be found, for example, in S. Arctander, Perfume and Flavor Chemicals, Vol. I and II, Montclair, N.J., 1969, Selbstverlag or K. Bauer, D. Garbe and H. Surburg, Common Fragrance and Flavor Materials, 4th Ed., Wiley-VCH, Weinheim 2001.

30 In detail there may be mentioned: extracts from natural raw materials such as essential oils, concretes, absolutes, resins, resinoids, balsams, tinctures, such as, for example, amber tincture; amyris oil; angelica seed oil; angelica root oil; aniseed oil;

- valerian oil; basil oil; tree moss absolute; bay oil; artemisia oil; benzoin resin; bergamot oil; beeswax absolute; birch tar oil; bitter almond oil; summer savory oil; buchu oil; cabreuva oil; cade oil; calmus oil; camphor oil; cananga oil; cardamon oil; cascarilla oil; cassia oil; cassie absolute; castoreum absolute; cedar leaf oil;
- 5 cedarwood oil; cistus oil; citronella oil; lemon oil; copaiba balsam; copaiba balsam oil; coriander oil; costus root oil; cumin oil; cypress oil; davana oil; dill weed oil; dill seed oil; eau de brouts absolute; oak moss absolute; elemi oil; tarragon oil; eucalyptus citriodora oil; eucalyptus oil; fennel oil; spruce needle oil; galbanum oil; galbanum resin; geranium oil; grapefruit oil; guaiacwood oil; gurjun balsam; gurjun
- 10 balsam oil; helichrysum absolute; helichrysum oil; ginger oil; orris root absolute; orris root oil; jasmine absolute; calamus oil; blue camomile oil; Roman camomile oil; carrot seed oil; cascarilla oil; pine needle oil; spearmint oil; caraway oil; labdanum oil; labdanum absolute; labdanum resin; lavandin absolute; lavandin oil; lavender absolute; lavender oil; lemongrass oil; lovage oil; distilled lime oil; pressed
- 15 lime oil; linaloe oil; litsea cubeba oil; laurel leaf oil; oil of mace; marjoram oil; mandarin oil; massoirinde oil; mimosa absolute; ambrette seed oil; ambrette tincture; clary sage oil; nutmeg oil; myrrh absolute; myrrh oil; myrtle oil; clove leaf oil; clove flower oil; neroli oil; olibanum absolute; olibanum oil; opopanax oil; orange blossom absolute; orange oil; oregano oil; palmarosa oil; patchouli oil; perilla oil;
- 20 Peru balsam oil; parsley leaf oil; parsley seed oil; petitgrain oil; peppermint oil; pepper oil; pimento oil; pine oil; poley oil; rose absolute; rosewood oil; rose oil; rosemary oil; Dalmatian sage oil; Spanish sage oil; sandalwood oil; celery seed oil; spike lavender oil; star anise oil; styrax oil; tagetes oil; fir needle oil; tea-tree oil; turpentine oil; thyme oil; tolu balsam; tonka absolute; tuberose absolute; vanilla
- 25 extract; violet leaf absolute; verbena oil; vetiver oil; juniper berry oil; grapeseed oil; wormwood oil; wintergreen oil; ylang ylang oil; hyssop oil; civet absolute; cinnamon leaf oil; cinnamon bark oil; as well as fractions thereof, or ingredients isolated therefrom;
- 30 individual fragrances from the group of the hydrocarbons, such as, for example, 3-carene; α -pinene; β -pinene; α -terpinene; γ -terpinene; p-cymene; bisabolol;

camphene; caryophyllen; cedrene; farnesene; limonene; longifolene; myrcene; ocimene; valencene; (E,Z)-1,3,5-undecatriene;

the aliphatic alcohols, such as, for example, hexanol; octanol; 3-octanol; 2,6-
5 dimethylheptanol; 2-methylheptanol, 2-methyloctanol; (E)-2-hexenol; (E)- and (Z)-
3-hexenol; 1-octen-3-ol; mixture of 3,4,5,6,6-pentamethyl-3/4-hepten-2-ol and
3,5,6,6-tetramethyl-4-methyleneheptan-2-ol; (E,Z)-2,6-nonadienol; 3,7-dimethyl-7-
methoxyoctan-2-ol; 9-decenol; 10-undecenol; 4-methyl-3-decen-5-ol; the aliphatic
aldehydes and their 1,4-dioxacycloalken-2-ones, such as, for example, hexanal;
10 heptanal; octanal; nonanal; decanal; undecanal; dodecanal; tridecanal; 2-
methyloctanal; 2-methylnonanal; (E)-2-hexenal; (Z)-4-heptenal; 2,6-dimethyl-5-
heptenal; 10-undecenal; (E)-4-decenal; 2-dodecenal; 2,6,10-trimethyl-5,9-
undecadienal; heptanaldiethylacetal; 1,1-dimethoxy-2,2,5-trimethyl-4-hexene;
citronellyloxyacetaldehyde;

15 the aliphatic ketones and their oximes, such as, for example, 2-heptanone; 2-
octanone; 3-octanone; 2-nonanone; 5-methyl-3-heptanone; 5-methyl-3-heptanone
oxime; 2,4,4,7-tetramethyl-6-octen-3-one; the aliphatic sulfur-containing
compounds, such as, for example, 3-methylthiohexanol; 3-methylthiohexyl acetate;
20 3-mercaptohexanol; 3-mercaptohexyl acetate; 3-mercaptohexyl butyrate; 3-acetyl-
thiohexyl acetate; 1-menthene-8-thiol;

the aliphatic nitriles, such as, for example, 2-nonenoic acid nitrile; 2-tridecenoic acid
nitrile; 2,12-tridecadienoic acid nitrile; 3,7-dimethyl-2,6-octadienoic acid nitrile; 3,7-
25 dimethyl-6-octenoic acid nitrile;

the aliphatic carboxylic acids and their esters, such as, for example, (E)- and (Z)-3-
hexenyl formate; ethyl acetoacetate; isoamyl acetate; hexyl acetate; 3,5,5-trimethyl-
hexyl acetate; 3-methyl-2-butenyl acetate; (E)-2-hexenyl acetate; (E)- and (Z)-3-
30 hexenyl acetate; octyl acetate; 3-octyl acetate; 1-octen-3-yl acetate; ethyl butyrate;
butyl butyrate; isoamyl butyrate; hexyl butyrate; (E)- and (Z)-3-hexenyl isobutyrate;

hexyl crotonate; ethyl isovalerate; ethyl-2-methyl pentanoate; ethyl hexanoate; allyl hexanoate; ethyl heptanoate; allyl heptanoate; ethyl octanoate; ethyl (E,Z)-2,4-decadienoate; methyl 2-octinate; methyl 2-noninate; allyl 2-isoamyloxyacetate; methyl 3,7-dimethyl-2,6-octadienoate;

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the acyclic terpene alcohols, such as, for example, citronellol; geraniol; nerol; linalool; lavadulol; nerolidol; farnesol; tetrahydrolinalool; tetrahydrogeraniol; 2,6-dimethyl-7-octen-2-ol; 2,6-dimethyloctan-2-ol; 2-methyl-6-methylene-7-octen-2-ol; 2,6-dimethyl-5,7-octadien-2-ol; 2,6-dimethyl-3,5-octadien-2-ol; 3,7-dimethyl-4,6-octadien-3-ol; 3,7-dimethyl-1,5,7-octatrien-3-ol; 2,6-dimethyl-2,5,7-octatrien-1-ol; and their formates, acetates, propionates, isobutyrate, butyrate, isovalerate, pentanoates, hexanoates, crotonates, tiglinates, 3-methyl-2-butenates;

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the acyclic terpene aldehydes and ketones, such as, for example, geranial; neral; citronellal; 7-hydroxy-3,7-dimethyloctanal; 7-methoxy-3,7-dimethyloctanal; 2,6,10-trimethyl-9-undecenal; geranylacetone; and the dimethyl- and diethyl-acetals of geranial, neral, 7-hydroxy-3,7-dimethyloctanal;

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the cyclic terpene alcohols, such as, for example, menthol; isopulegol; alpha-terpineol; terpinenol-4; menthan-8-ol; menthan-1-ol; methan-7-ol; borneol; isoborneol; linalool oxide; nopol; cedrol; ambrinol; vetiverol; guaiol; and their formates, acetates, propionates, isobutyrate, butyrate, isovalerate, pentanoates, hexanoates, crotonates, tiglinates, 3-methyl-2-butenates;

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the cyclic terpene aldehydes and ketones, such as, for example, menthone; isomenthone; 8-mercaptomenthan-3-one; carvone; camphor; fenchone; alpha-ionone; beta-ionone; alpha-n-methylionone; beta-n-methylionone; alpha-isomethylionone; beta-isomethylionone; alpha-irone; alpha-damascone; beta-damascone; beta-damascenone; delta-damascone; gamma-damascone; 1-(2,4,4-trimethyl-2-cyclohexen-1-yl)-2-buten-1-one; 1,3,4,6,7,8a-hexahydro-1,1,5,5-tetramethyl-2H-

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2,4a-methanonaphthalen-8(5H)-one; nootkatone; dihydronootkatone; alpha-sinensal; beta-sinensal; acetylated cedar wood oil (methyl cedryl ketone);

the cyclic alcohols, such as, for example, 4-tert.-butylcyclohexanol; 3,3,5-trimethyl-
5 cyclohexanol; 3-isocamphylcyclohexanol; 2,6,9-trimethyl-Z2,Z5,E9-cyclododeca-
trien-1-ol; 2-isobutyl-4-methyltetrahydro-2H-pyran-4-ol;

the cycloaliphatic alcohols, such as, for example, alpha-3,3-trimethylcyclohexyl-
methanol; 2-methyl-4-(2,2,3-trimethyl-3-cyclopent-1-yl)butanol; 2-methyl-4-(2,2,3-
10 trimethyl-3-cyclopent-1-yl)-2-buten-1-ol; 2-ethyl-4-(2,2,3-trimethyl-3-cyclopent-1-
yl)-2-buten-1-ol; 3-methyl-5-(2,2,3-trimethyl-3-cyclopent-1-yl)-pentan-2-ol; 3-
methyl-5-(2,2,3-trimethyl-3-cyclopent-1-yl)-4-penten-2-ol; 3,3-dimethyl-5-(2,2,3-
trimethyl-3-cyclopent-1-yl)-4-penten-2-ol; 1-(2,2,6-trimethylcyclohexyl)pentan-3-ol;
1-(2,2,6-trimethylcyclohexyl)hexan-3-ol;

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the cyclic and cycloaliphatic ethers, such as, for example, cineole; cedryl methyl
ether; cyclododecyl methyl ether; (ethoxymethoxy)cyclododecane; alpha-cedrene
epoxide; 3a,6,6,9a-tetramethyldodecahydronaphtho[2,1-b]furan; 3a-ethyl-6,6,9a-
trimethyldodecahydronaphtho[2,1-b]furan; 1,5,9-trimethyl-13-oxabicyclo[10.1.0]-
20 trideca-4,8-diene; rose oxide; 2-(2,4-dimethyl-3-cyclohexen-1-yl)-5-methyl-5-(1-
methylpropyl)-1,3-dioxane;

the cyclic ketones, such as, for example, 4-tert.-butylcyclohexanone; 2,2,5-trimethyl-
5-pentylcyclopentanone; 2-heptylcyclopentanone; 2-pentylcyclopentanone; 2-
25 hydroxy-3-methyl-2-cyclopenten-1-one; 3-methyl-cis-2-penten-1-yl-2-cyclopenten-
1-one; 3-methyl-2-pentyl-2-cyclopenten-1-one; 3-methyl-4-cyclopentadecenone; 3-
methyl-5-cyclopentadecenone; 3-methylcyclopentadecanone; 4-(1-ethoxyvinyl)-
3,3,5,5-tetramethylcyclohexanone; 4-tert.-pentylcyclohexanone; 5-cyclohexadecen-
1-one; 6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone; 5-cyclohexadecen-1-one;
30 8-cyclohexadecen-1-one; 9-cycloheptadecen-1-one; cyclopentadecanone;

the cycloaliphatic aldehydes, such as, for example, 2,4-dimethyl-3-cyclohexene-carbaldehyde; 2-methyl-4-(2,2,6-trimethyl-cyclohexen-1-yl)-2-butenal; 4-(4-hydroxy-4-methylpentyl)-3-cyclohexenecarbaldehyde; 4-(4-methyl-3-penten-1-yl)-3-cyclohexenecarbaldehyde;

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the cycloaliphatic ketones, such as, for example, 1-(3,3-dimethylcyclohexyl)-4-penten-1-one; 1-(5,5-dimethyl-1-cyclohexen-1-yl)-4-penten-1-one; 2,3,8,8-tetramethyl-1,2,3,4,5,6,7,8-octahydro-2-naphthalenyl methyl ketone; methyl 2,6,10-trimethyl-2,5,9-cyclododecatrienyl ketone; tert.-butyl-(2,4-dimethyl-3-cyclohexen-1-yl) ketone;

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the esters of cyclic alcohols, such as, for example, 2-tert.-butylcyclohexyl acetate; 4-tert.-butylcyclohexyl acetate; 2-tert.-pentylcyclohexyl acetate; 4-tert.-pentylcyclohexyl acetate; decahydro-2-naphthyl acetate; 3-pentyltetrahydro-2H-pyran-4-yl acetate; decahydro-2,5,5,8a-tetramethyl-2-naphthyl acetate; 4,7-methano-3a,4,5,6,7,7a-hexahydro-5- or -6-indenyl acetate; 4,7-methano-3a,4,5,6,7,7a-hexahydro-5- or -6-indenyl propionate; 4,7-methano-3a,4,5,6,7,7a-hexahydro-5- or -6-indenyl isobutyrate; 4,7-methanooctahydro-5- or -6-indenyl acetate;

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the esters of cycloaliphatic carboxylic acids, such as, for example, allyl 3-cyclohexylpropionate; allyl cyclohexyloxyacetate; methyl dihydrojasmonate; methyl jasmonate; methyl 2-hexyl-3-oxocyclopentanecarboxylate; ethyl 2-ethyl-6,6-dimethyl-2-cyclohexenecarboxylate; ethyl 2,3,6,6-tetramethyl-2-cyclohexenecarboxylate; ethyl-2-methyl-1,3-dioxolane 2-acetate;

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the aromatic hydrocarbons, such as, for example, styrene and diphenylmethane;

the araliphatic alcohols, such as, for example, benzyl alcohol, 1-phenylethyl alcohol; 2-phenylethyl alcohol; 3-phenylpropanol; 2-phenylpropanol; 2-phenoxyethanol; 2,2-dimethyl-3-phenylpropanol; 2,2-dimethyl-3-(3-methylphenyl)propanol; 1,1-dimethyl-2-phenylethyl alcohol; 1,1-dimethyl-3-phenylpropanol; 1-ethyl-1-methyl-3-

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phenylpropanol; 2-methyl-5-phenylpentanol; 3-methyl-5-phenylpentanol; 3-phenyl-2-propen-1-ol; 4-methoxybenzyl alcohol; 1-(4-isopropylphenyl)ethanol;

the esters of araliphatic alcohols and aliphatic carboxylic acids, such as, for example,
 5 benzyl acetate; benzyl propionate; benzyl isobutyrate; benzyl isovalerate; 2-phenylethyl acetate; 2-phenylethyl propionate; 2-phenylethyl isobutyrate; 2-phenylethyl isovalerate; 1-phenylethyl acetate; alpha-trichloromethylbenzyl acetate; alpha,alpha-dimethylphenylethyl acetate; alpha,alpha-dimethylphenylethyl butyrate; cinnamyl acetate; 2-phenoxyethyl isobutyrate; 4-methoxybenzyl acetate; the araliphatic ethers,
 10 such as, for example, 2-phenylethyl methyl ether; 2-phenylethyl isoamyl ether; 2-phenylethyl 1-ethoxyethyl ether; phenylacetaldehyde dimethylacetal; phenylacetaldehyde diethylacetal; hydratropaaldehyde dimethylacetal; phenylacetaldehyde glycerineacetal; 2,4,6-trimethyl-4-phenyl-1,3-dioxane; 4,4a,5,9b-tetrahydroindeno[1,2-d]-m-dioxine; 4,4a,5,9b-tetrahydro-2,4-dimethylindeno[1,2-d]-m-dioxine;

15 the aromatic and araliphatic aldehydes, such as, for example, benzaldehyde; phenylacetaldehyde; 3-phenylpropanal; hydratropaaldehyde; 4-methylbenzaldehyde; 4-methylphenylacetaldehyde; 3-(4-ethylphenyl)-2,2-dimethylpropanal; 2-methyl-3-(4-isopropylphenyl)propanal; 2-methyl-3-(4-tert.-butylphenyl)propanal; 3-(4-tert.-butylphenyl)propanal; cinnamic aldehyde; alpha-butylcinnamic aldehyde; alpha-amylcinnamic aldehyde; alpha-hexylcinnamic aldehyde; 3-methyl-5-phenylpentanal; 4-methoxybenzaldehyde; 4-hydroxy-3-methoxybenzaldehyde; 4-hydroxy-3-ethoxybenzaldehyde; 3,4-methylenedioxybenzaldehyde; 3,4-dimethoxybenzaldehyde; 2-methyl-3-(4-methoxyphenyl)propanal; 2-methyl-3-(4-methylenedioxyphenyl)-
 20 propanal;
 25

the aromatic and araliphatic ketones, such as, for example, acetophenone; 4-methylacetophenone; 4-methoxyacetophenone; 4-tert.-butyl-2,6-dimethylacetophenone; 4-phenyl-2-butanone; 4-(4-hydroxyphenyl)-2-butanone; 1-(2-naphthalenyl)ethanone; benzophenone; 1,1,2,3,3,6-hexamethyl-5-indanyl methyl ketone; 6-tert.-butyl-1,1-dimethyl-4-indanyl methyl ketone; 1-[2,3-dihydro-1,1,2,6-tetramethyl-3-(1-methyl-

30

ethyl)-1H-5-indenyl]ethanone; 5',6',7',8'-tetrahydro-3',5',5',6',8',8'-hexamethyl-2-acetonaphthone;

the aromatic and araliphatic carboxylic acids and their esters, such as, for example,
5 benzoic acid; phenylacetic acid; methyl benzoate; ethyl benzoate; hexyl benzoate;
benzyl benzoate; methylphenyl acetate; ethylphenyl acetate; geranylphenyl acetate;
phenylethylphenyl acetate; methyl cinnamate; ethyl cinnamate; benzyl cinnamate;
phenylethyl cinnamate; cinnamyl cinnamate; allylphenoxy acetate; methyl salicylate;
isoamyl salicylate; hexyl salicylate; cyclohexyl salicylate; cis-3-hexenyl salicylate;
10 benzyl salicylate; phenylethyl salicylate; methyl-2,4-dihydroxy-3,6-dimethyl
benzoate; ethyl-3-phenyl glycidate; ethyl-3-methyl-3-phenyl glycidate;

the nitrogen-containing aromatic compounds, such as, for example, 2,4,6-trinitro-
1,3-dimethyl-5-tert.-butylbenzene; 3,5-dinitro-2,6-dimethyl-4-tert.-butylaceto-
15 phenone; cinnamic acid nitrile; 5-phenyl-3-methyl-2-pentenoic acid nitrile; 5-
phenyl-3-methylpentanoic acid nitrile; methyl anthranilate; methyl-N-methyl
anthranilate; Schiff's bases of methyl anthranilate with 7-hydroxy-3,7-dimethyl-
octanal, 2-methyl-3-(4-tert.-butylphenyl)propanal or 2,4-dimethyl-3-cyclohexene-
carbaldehyde; 6-isopropylquinoline; 6-isobutylquinoline; 6-sec.-butylquinoline;
20 indole; scatole; 2-methoxy-3-isopropylpyrazine; 2-isobutyl-3-methoxypyrazine;

the phenols, phenyl ethers and phenyl esters, such as, for example, estragole;
anethole; eugenol; eugenyl methyl ether; isoeugenol; isoeugenyl methyl ether;
thymol; carvacrol; diphenyl ether; beta-naphthyl methyl ether; beta-naphthyl ethyl
25 ether; beta-naphthyl isobutyl ether; 1,4-dimethoxybenzene; eugenyl acetate; 2-
methoxy-4-methylphenol; 2-ethoxy-5-(1-propenyl)phenol; p-cresylphenyl acetate;

the heterocyclic compounds, such as, for example, 2,5-dimethyl-4-hydroxy-2H-
furan-3-one; 2-ethyl-4-hydroxy-5-methyl-2H-furan-3-one; 3-hydroxy-2-methyl-4H-
30 pyran-4-one; 2-ethyl-3-hydroxy-4H-pyran-4-one;

the lactones, such as, for example, 1,4-octanolide; 3-methyl-1,4-octanolide; 1,4-nonanolide; 1,4-decanolide; 8-decen-1,4-olide; 1,4-undecanolide; 1,4-dodecanolide; 1,5-decanolide; 1,5-dodecanolide; 1,15-pentadecanolide; cis- and trans-11-pentadecen-1,15-olide; cis- and trans-12-pentadecen-1,15-olide; 1,16-hexadecanolide; 9-hexadecen-1,16-olide; 10-oxa-1,16-hexadecanolide; 11-oxa-1,16-hexadecanolide; 12-oxa-1,16-hexadecanolide; ethylene-1,12-dodecane dioate; ethylene-1,13-tridecane dioate; coumarin; 2,3-dihydrocoumarin, octahydrocoumarin.

Examples of flavourings which may be a constituent of the cyclodextrin particles are, in addition to all the above-mentioned substances, especially the following classes of substance: aliphatic esters (saturated and unsaturated), for example ethyl butyrate, allyl caproate; aromatic esters, for example benzyl acetate, methyl salicylate; organic aliphatic acids (saturated and unsaturated), for example butyric acid, acetic acid, caproic acid; organic aromatic acids; aliphatic alcohols (saturated and unsaturated), for example ethanol, propylene glycol, octenol, 3-octenol, cis-3-hexenol; cyclic alcohols, for example menthol; aromatic alcohols, for example benzyl alcohol; aliphatic aldehydes (saturated and unsaturated), for example acetaldehyde, nonadienal; aromatic aldehydes, for example benzaldehyde; ketones, for example menthone; cyclic ethers, for example 4-hydroxy-5-methylfuranone; aromatic ethers, for example p-methoxybenzaldehyde, guaiacol; phenol ethers, for example methoxyvinylphenol; acetals, for example acetaldehyde diethylacetal; lactones, for example gamma-decalactone; terpenes, for example limonene, linalool, terpinene, terpineol, citral (geranial and neral); sulfur-containing compounds, for example dimethyl sulfide, methylthiol, ethylthiol, allyl isothiocyanate, methylfuranthiol, difurfuryl disulfide; or pyrazines, for example methylpyrazine, acetylpyrazine.

Owing to the very low content of surface oil, the cyclodextrin particles according to the invention are particularly suitable for the encapsulation of substances that are very odour-intensive, readily volatile, readily oxidisable, difficult to meter, difficult to handle and/or irritant. Mention may be made in this connection of, for example,

acetaldehyde, allyl isothiocyanate, limonene, cis-3-hexenol, citral, methylethylpyrazine or methylthiol.

5 The cyclodextrin particles according to the invention may further comprise substances or mixtures of substances having nutritional-physiological activity (nutraceuticals). Examples which may be mentioned include panthenol, pantothenic acid, essential fatty acids, vitamin A and derivatives, carotene, vitamin C (ascorbic acid), vitamin E (tocopherol) and derivatives, vitamins of the B and D group, such as vitamin B₆ (nicotinamide), vitamin B₁₂, vitamin D₁, vitamin D₃, vitamin F, folic
10 acid, biotin, amino acids, compounds of the elements magnesium, silicon, phosphorus, calcium, manganese, iron or copper, coenzyme Q10, unsaturated fatty acids, ω -3-fatty acids, polyunsaturated fatty acids, γ -linolenic acid, oleic acid, eicosapentaenic acid, docosahexaenic acid and derivatives thereof, bisabolol, chloramphenicol, caffeine, capsaicin, prostaglandins, thymol, camphor, extracts or
15 other products of vegetable and animal origin, for example evening primrose oil, borage oil or currant seed oil, fish oils, cod liver oil, ceramides and ceramide-like compounds. Plant extracts, such as, for example, arnica, aloe, beard lichen, ivy, stinging nettle, ginseng, henna, camomile, marigold, rosemary, sage, horsetail or thyme. Oils, such as apricot seed oil, avocado oil, babassu oil, cottonseed oil, borage
20 oil, thistle oil, groundnut oil, gamma-oryzanol, rosehip oil, hemp oil, hazelnut oil, currant seed oil, jojoba oil, cherry kernel oil, salmon oil, linseed oil, corn oil, macadamia nut oil, almond oil, evening primrose oil, mink oil, olive oil, pecan nut oil, peach kernel oil, pistachio kernel oil, rape oil, rice oil, castor oil, safflower oil, sesame oil, soybean oil, sunflower oil, tea-tree oil, grapeseed oil or wheat-germ oil.

25

It is of course possible that the cyclodextrin particles according to the invention may comprise further substances, such as, for example, emulsifiers, colourings, antioxidants, stabilisers, UV filters, vitamins and other ingredients conventional in the foodstuffs, personal care, pharmaceutical or fragrance industry.

30

The spray mixture can be prepared, for example, as outlined in EP-A 1 084 625 or as described hereinbelow.

A complex of cyclodextrin and the flavouring is first formed. For this purpose, the cyclodextrin and the flavouring must be brought at least partly into solution. The solvent used is water having a temperature of from 10°C to 90°C, preferably from 40°C to 70°C, particularly preferably from 50 to 60°C. In the case of flavourings having a particularly low boiling point or high sensitivity to heat, temperatures of from 15 to 30°C are preferred.

Depending on the polarity of the flavourings and/or fragrances, a 2-phase mixture forms in most cases. In order to accelerate the process, shear forces are introduced according to the invention. The introduction of the shear forces can be effected, for example, by stirring or dispersing, for which purpose there are suitable *inter alia* rotor-stator dispersing tools or high-pressure homogenisers.

The shifting of the equilibrium in the direction of the flavouring and/or fragrance/cyclodextrin complex requires time. According to the invention, the mixture is advantageously allowed to rest, after the introduction of the shear forces, for from 0.2 to 24 hours with cooling at from 4 to 25°C, preferably for from 8 to 16 hours with cooling at from 4 to 7°C.

In the case of sensitive flavourings and/or fragrances, the rest period is preferably shortened to from 15 to 30 minutes at from 4 to 7°C.

The addition of the cellulose ether to the spray mixture can be carried out at any desired point in time. This may be before formation of the complex, during formation of the complex, after formation of the complex but before storage at low temperature, during storage at low temperature or after storage at low temperature. It is also possible to mix the cellulose ether with the cyclodextrin powder and only

then add the water. The total amount of cellulose ether can also be divided into several partial amounts, that is to say can be divided into portions, and added at any desired points in time.

5 When preparing the spray mixture, the substances that are used can be added in any desired sequence. For example, it is possible to mix the cyclodextrin and the cellulose ether, then add the water and carry out intensive stirring or dispersing. Flavourings and/or fragrances are then added and the mixture is stirred or dispersed intensively and stored at low temperature. An alternative sequence comprises first
10 intensively mixing the water, cellulose ether and flavourings and/or fragrances and subsequently adding and dispersing the cyclodextrin. In a further example of a variant, the cyclodextrin can be added to water and stirred intensively. The flavour is added and dispersed. After subsequent storage at low temperature, the cellulose ether is added and distributed by stirring or dispersing.

15 Granulation is preferably carried out in a granulating apparatus as described in EP-A 163 836. The temperature of the spray mixture is so chosen that the flavouring or fragrance/cyclodextrin complex does not decompose. The temperature is usually from 5 to 70°C, preferably from 10 to 40°C and particularly preferably from 20 to
20 30°C.

There may be used as the fluidising gas, for example, air, nitrogen, argon or carbon dioxide, preference being given to air and nitrogen. The gas inlet and gas outlet temperatures of the fluidising gas are to be matched to the particular spray mixture in
25 question. The gas inlet temperatures are from 80 to 180°C, preferably from 100 to 140°C and particularly preferably from 120 to 130°C. The gas outlet temperatures are from 40 to 95°C, preferably from 45 to 70°C, particularly preferably from 50 to 60°C.

The cyclodextrin particles according to the invention can be used in a large number of products. In foods and luxury foods they can be used, for example, in confectionery, such as, for example, boiled sweets, chewing gum, breath fresheners, comprimates, hard caramels, confectionery and chocolate, baked goods such as cakes, waffles and biscuits, snacks, instant meals and other instant products (soups, sauces, drinks powders and granules, tea bags, spice mixtures). The cyclodextrin particles are particularly suitable for heated, high-temperature-heated, warmed, sterilised or pasteurised foods, such as, for example, catered meals, fried foods, chips, flavoured panades, ready meals, microwave meals and fruit and vegetable preserves.

Pharmaceutical products may be, for example, lozenges, throat or cough sweets, pharmaceutical powders or granules.

Commodities may be, for example, personal care products, household products, tobacco products (e.g. cigarettes), cosmetic products, washing and cleaning agents, air fresheners, textiles or odour-absorbing agents (e.g. cat litter).

Personal care products may be, for example, oral care products, such as toothpastes, tooth gels, tooth creams, tooth-care chewing gums and mouthwashes.

The following Examples explain the invention:

Unless indicated otherwise, all amounts are by weight.

In the present case, retention (indicated in wt.%) is understood as being the weight-related ratio of the amount of flavouring and/or fragrance in the finished particle to the amount of flavouring and/or fragrance used in the spray mixture.

Examples

Example 1: Limonene/cyclodextrin particles

5 Recipe:

13,143 g of drinking water

4000 g of beta-cyclodextrin (Kleptose® beta-cyclodextrin, Roquette)

431 g of d-limonene

133 g of carboxymethyl cellulose (CMC) (Walocel CRT 10000 GA from Wolff
10 Walsrode); viscosity of the 2 % solution at 20°C, 1 s⁻¹: 10,000 mPas

The water was heated to 25°C, the cyclodextrin was added, and the mixture was mixed for 3 minutes using an Ultra Turrax T50 DPX. The d-limonene is added and the mixture is dispersed for a further 15 minutes.

15

After the mixture had been stored for 6 hours at 6°C, the carboxymethyl cellulose was added and homogenisation was carried out with the aid of the Ultra Turrax T50 DPX. The mixture was then allowed to rest for a further 15 hours at 20°C and was subsequently fed to the fluidised bed granulating apparatus.

20

The above-described spray mixture was granulated in a granulating apparatus of the type described in EP-A 163 836 (having the following features: inflow base diameter: 225 mm, spray nozzle: binary nozzle; separating discharge: zig-zag sifter; filter: internal hose filter). The temperature of the mixture was 35°C. In order to
25 fluidise the bed contents, air was blown in in an amount of 60 kg/h. The inlet temperature of the fluidising gas was 120°C. The temperature of the outlet gas was 55°C. Air in an amount of 1.5 kg/h and having a temperature of 34°C was supplied as the sifting gas. The granulation yield was about 420 g/h. Free-flowing granules having a mean particle size of 131.7 µm and a bulk density of 470 g/l were obtained.

30 The granules had a smooth surface and a spherical, largely ball-shaped geometry.

Because of the constant pressure loss of the filter and the bed contents which likewise remain constant, stationary conditions are to be assumed in respect of the granulation process.

5

- loading: 7.7 %
- retention: 79.2 %
- surface oil: 0.03 %
- particle size distribution (by means of laser diffraction; device: Malvern

10

Master Sizer[®] MSS Longbench):

$$Q_3(x) = 0.1: x = 75 \mu\text{m}$$

$$Q_3(x) = 0.5: x = 132 \mu\text{m}$$

$$Q_3(x) = 0.9: x = 196 \mu\text{m}$$

- bulk density: 470 g/l

15

Example 2: Limonene particles 2

6385 g of drinking water

2000 g of beta-cyclodextrin

20

215.5 g of d-limonene

78 g of carboxymethyl cellulose (CMC), Tylose[®] C 6000 G1 from Clariant;
viscosity of the 2 % solution at 20°C, 1 s⁻¹ mPas: 6000 mPas

25

The water was heated to 50°C, the cyclodextrin was added, and the mixture was mixed for 3 minutes using an Ultra Turrax T50 DPX. The d-limonene was added and the mixture was dispersed for a further 15 minutes.

30

After the mixture had been stored for 30 minutes at 20°C, the carboxymethyl cellulose was added and homogenisation was carried out with the aid of the Ultra Turrax mixer.

The mixture was then allowed to rest for a further 15 hours at 6°C and (storage) was subsequently fed to the fluidised bed granulating apparatus of Example 1. The inlet temperature of the fluidising gas was 125°C. The temperature of the outlet gas was 49°C. The granulation yield was about 570 g/h. Free-flowing granules having a mean particle size of 165.8 µm and a bulk density of 460 g/l were obtained. The cyclodextrin particles had a smooth surface and a spherical, largely ball-shaped geometry.

- 10 - loading: 8.4 %
- retention: 86.4 %
- surface oil: 0.04 %
- particle size distribution (laser diffraction):
 - 15 $Q_3(x) = 0.1: x = 89 \mu\text{m}$
 - $Q_3(x) = 0.5: x = 166 \mu\text{m}$
 - $Q_3(x) = 0.9: x = 272 \mu\text{m}$
- bulk density: 460 g/l

Example 3: Peppermint-flavour particles

- 20 6385 g of drinking water
- 2000 g of beta-cyclodextrin
- 215.5 g of peppermint flavouring
- 62 g of carboxymethyl cellulose (CMC), (Walocel CRT 10000 GA from Wolff
- 25 Walsrode); viscosity of the 2 % solution at 20°C, 1 s⁻¹: 10,000 mPas

The water was heated to 50°C, the cyclodextrin was added, and the mixture was mixed for 3 minutes using an Ultra Turrax T50 DPX. After addition of the peppermint flavouring, the mixture was mixed thoroughly for a further 15 minutes

using the Ultra Turrax T50 DPX. CMC was added and dissolved using the Ultra Turrax.

Storage and further preparation are carried out analogously to Example 2; the granulation yield was 600 g/h. Free-flowing granules were obtained.

- loading: 8.8 %
- retention: 87 %
- particle size distribution (by means of laser diffraction; device: Malvern Master Sizer[®] MSS Longbench):
 - $Q_3(x) = 0.1: x = 103 \mu\text{m}$
 - $Q_3(x) = 0.5: x = 182 \mu\text{m}$
 - $Q_3(x) = 0.9: x = 296 \mu\text{m}$
- surface oil: 0.03 %
- bulk density: 400 g/l

Example 4: Beef-flavour particles

6385 g of drinking water

2000 g of beta-cyclodextrin

200 g of beef flavouring

95 g of methyl cellulose (MC), Methocel[®] A4M FG, Dow Chemical Company;
viscosity of the 2 % solution at 20°C, 1 s⁻¹ mPas: 4000 mPas

After addition of the cyclodextrin to water (10°C), the mixture was mixed for 3 minutes using an Ultra Turrax T50 DPX. The beef flavouring was added and the mixture was dispersed for a further 40 minutes. After the mixture had been allowed to rest for 30 minutes at 20°C, the methyl cellulose was added and homogenisation was carried out using the Ultra Turrax mixer.

Storage and further preparation were carried out analogously to Example 1.

Examples 5 to 14

5 Compositions of spray mixtures; data relate to amounts used in grams.

	5	6	7	8	9	10	11	12	13	14
Water	6200	6000	6000	6385	6385	6500	6500	6385	6800	6900
alpha-Cyclodextrin	660	2000	0	0	0	0	0	0	0	0
beta-Cyclodextrin	660	0	0	2000	2000	2000	2000	2000	2000	2000
gamma-Cyclodextrin	660	0	2000	0	0	0	0	0	0	0
Carboxymethyl cellulose (Walocel® CRT 10000 GA)	55	55	55	0	0	0	0	0	0	0
Hydroxypropylmethyl cellulose Methocel® K4MFG	0	0	0	90	0	0	0	0	0	0
Ethyl cellulose	0	0	0	0	60	0	0	0	0	0
Propyl cellulose	0	0	0	0	0	70	0	0	0	0
Hydroxyethyl cellulose Tylose MH 4000 P2	0	0	0	0	0	0	90	0	0	0
Hydroxypropyl cellulose	0	0	0	0	0	0	0	60	0	0
Ethylhydroxyethyl cellulose	0	0	0	0	0	0	0	0	60	0
Carboxymethylhydrox- ethyl cellulose	0	0	0	0	0	0	0	0	0	90
Lemon oil	200	150	230	10	1	250	100	50	200	75

Example 15: Comparison

In Table 1, the advantages of the particles produced according to the invention over particles produced according to the prior art in terms of oxidation stability, pourability and redispersibility are clear. The better oxidation stability is due to the low content of surface oil.

Table 1:

Cyclodextrin particles containing d-limonene	according to the invention	according to EP-A 392 608	according to DE-A 31 05 666	
Procedure	Example 2	kneading, spray drying	kneading, drying, grinding, sieving	
Process	batchwise preparation of the spray mixture, continuous, simultaneous drying and granulation	batchwise preparation of the spray mixture, continuous drying, no granulation	continuous extrusion and granulation	batchwise preparation of the mixture, batch drying, batch grinding, batch sieving
Particle size	50 µm – 300 µm	0.05 µm – 5 µm	500 – 1000 µm	500 – 1000 µm
Pourability (angle of repose)	32°	63°	52°	47°
Redispersibility at 20°C	4	0	3	3
Surface oil	0.04 %	0.40 %	2.4 %	0.19 %
Retention	86 %	74 %	92 %	86 %
Oxidation sensitivity (after 180 days)	0	3	5	3

10

The pourability was determined according to DIN ISO 4324. An angle of repose < 30° means very good pourability, an angle of repose between 30° and 40° means free flowability, and an angle of repose > 45° means poor flowability (see also

Uhlemann, Möhl: Wirbelschichtsprühgranulation, Springer-Verlag Berlin, 2000, p. 169).

The oxidation sensitivity was evaluated after storage times of one day and 180 days (storage temperature 20°C). In each case, 100 g samples were introduced into a 250 ml plastics bottle, which was closed tightly with a cap. After the particular storage time, the bottles were opened and evaluated in terms of odour. Evaluation was made on a scale of 0 (no oxidation odour) to 5 (strong oxidation odour). After one day, all the particles of Table 1 were still in an odour-free state.

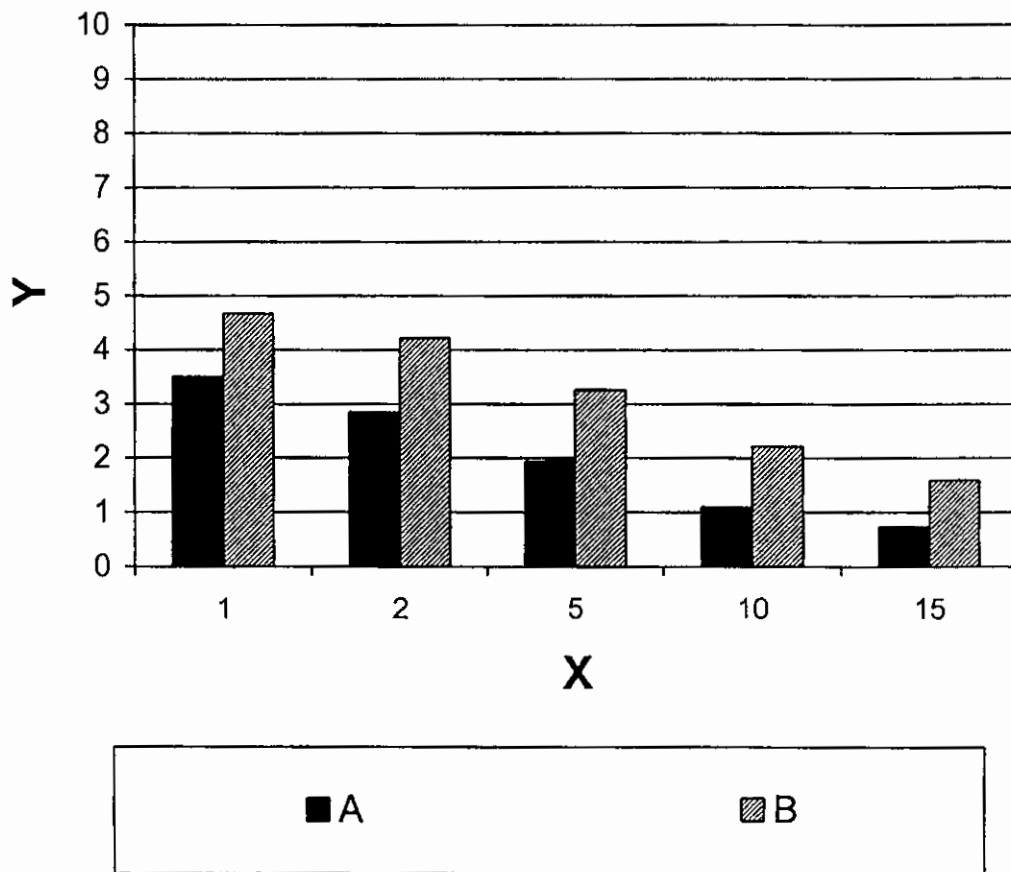
The redispersibility was tested as follows: 20 ml of water (20°C) and 200 mg of the particular particle were placed in a glass beaker and stirred for 1 minute at 200 min⁻¹ using a magnetic stirrer. Evaluation was made on a scale of 0 (very poor redispersibility) to 5 (complete redispersibility). Particles were said to have very poor redispersibility if, after stirring, not all the particles had been wetted with water, large agglomerates had formed and/or, after a standing time of 1 minute, a large number of particles had sunk to the bottom.

Example 16: Chewing gum with peppermint taste

2 wt.% of peppermint flavouring/cyclodextrin particles from Example 3 (corresponding to 0.18 wt.% of flavouring) and 1.12 wt.% of peppermint flavouring in liquid form were incorporated into a chewing gum (B). For comparison purposes, a chewing gum (A) containing 1.30 wt.% of peppermint flavouring in liquid form was prepared.

Sensory time/intensity studies with a group of trained testers (12 people) showed a significantly higher taste intensity overall with chewing gum (B) having peppermint flavouring particles. After 15 minutes, the flavour intensity was twice as high in the sample containing the peppermint flavouring/cyclodextrin particles.

- 28 -



X = chewing time in minutes

Y = intensity of peppermint flavour

A = chewing gum with liquid peppermint flavouring

5 B = chewing gum with liquid peppermint flavouring + peppermint flavouring particles

The intensity of peppermint flavour was evaluated on a scale of 0 (no peppermint flavour) to 10 (very strong peppermint flavour).

10

Example 17: Waffle

The limonene/cyclodextrin particles from Example 2 were added in an amount of 1.2 wt.% (corresponding to 0.1 wt.% of flavouring) to a waffle dough consisting of

15 flour, water, sugar, lecithin, salt and groundnut oil. Waffles were baked for 1 minute

at a temperature of 200°C. For comparison purposes, liquid limonene was incorporated in the same concentration into a dough having the same composition. The sensory evaluation of fresh products (1 day old) gave a higher intensity of flavour in the case of the waffles containing limonene/cyclodextrin particles. It was possible to confirm the sensory evaluation by analysis, as shown in Table 2.

Table 2:

	Waffles containing 0.1 wt.% limonene in the form of a cyclodextrin complex	Waffles containing 0.1 % limonene (liquid)
Limonene content in the baked waffle	2533 ppm	755 ppm
Retention on baking	95 %	38 %
Limonene note (after storage)	3	0
Off flavour	0	4
Sensory description	fresh, citrus-like	musty, oxidised, rancid

The sensory evaluation of the flavour intensity of the limonene note and the off flavour was made after 4-months' storage at 20°C, on a scale of 0 (not perceptible) to 5 (very strong).

In the present case, retention (indicated in %) is understood as being the weight-related ratio of the amount of limonene in the waffle to the amount of limonene used.

Example 18: Instant soup

5 cis-3-Hexenol/cyclodextrin particles produced analogously to Example 1 were added to a powder mixture containing salt, starch, spice powder, fat powder and dried vegetables, in order to reinforce the fresh green note.

10 The following advantages are achieved during the mixing process on account of the set particle size of from 100 to 200 μm : freedom from dust, low risk of separation, good pourability.

During storage, cis-3-hexenol in the cyclodextrin complex is well protected from oxidation, especially on account of the low content of surface oil of the particles after production according to the invention.

15 When water at a temperature of 80°C is poured onto the instant soup mixture, the complex dissolves within a few seconds.

Patent claims

1. Flavouring- and/or fragrance-containing cyclodextrin particles which have a particle size in the range from 50 to 1000 μm and contain a cellulose ether
5 and which are obtainable from a spray mixture by a single-stage fluidised bed process, wherein the gas inlet temperature is from 80 to 180°C and the gas outlet temperature is from 40 to 95°C.
2. Cyclodextrin particles according to claim 1, characterised in that they contain
10 at least one cellulose ether from the group comprising methyl cellulose, ethyl cellulose, ethylhydroxyethyl cellulose, propyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxypropylmethyl cellulose, carboxymethylhydroxyethyl cellulose and carboxymethyl cellulose.
- 15 3. Cyclodextrin particles according to claim 1 or 2, characterised in that they contain carboxymethyl cellulose.
4. Cyclodextrin particles according to at least one of claims 1 to 3, characterised in that the particle size is in the range from 100 to 300 μm .
20
5. Cyclodextrin particles according to at least one of claims 1 to 4, characterised in that the fluidised bed process is fluidised bed spray granulation.
6. Cyclodextrin particles according to at least one of claims 1 to 5, characterised
25 in that they contain as the cyclodextrin alpha-, beta- or gamma-cyclodextrin, preferably beta-cyclodextrin.
7. Cyclodextrin particles according to at least one of claims 1 to 6, characterised in that the content of flavouring and/or fragrance is from 0.01 to 30 wt.%.
30

8. Process for the production of cyclodextrin particles according to at least one of claims 1 to 7, characterised in that an aqueous spray mixture comprising at least one cyclodextrin, at least one flavouring and/or fragrance and at least one cellulose ether is introduced into the single-stage fluidised bed apparatus.
5
9. Process according to claim 8, characterised in that the fluidised bed apparatus is a fluidised bed spray granulation device, preferably with continuous operation.
10. Process according to claim 8 or 9, characterised in that nucleus production takes place in the fluidised bed device.
10
11. Process according to at least one of claims 8 to 10, characterised in that the aqueous spray mixture comprises from 40 to 95 wt.% water, from 5 to 50 wt.% cyclodextrin, from 0.0005 to 15 wt.% flavourings and/or fragrances and from 0.1 to 6 wt.% cellulose ether.
15
12. Process according to claim 11, characterised in that the aqueous spray mixture comprises from 60 to 80 wt.% water, from 15 to 30 wt.% cyclodextrin, from 0.25 to 5 wt.% flavourings and/or fragrances and from 0.2 to 2 wt.% cellulose ether.
20
13. Flavouring- and/or fragrance-containing cyclodextrin particles which have a particle size in the range from 50 to 1000 μm and contain carboxymethyl cellulose.
25
14. Use of cyclodextrin particles according to any one of claims 1 to 7 in foodstuffs, pharmaceutical products and commodities.