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DRAGOCO Gerberding & Co. AG
Dragocostraße 1, 37601 Holzminden

Mononuclearly filled microcapsules

The present invention relates to mononuclearly filled microcapsules, food compositions and other articles which contain one or more mononuclearly filled microcapsules and to methods for the production of mononuclearly filled microcapsules.

In the field of the encapsulation of active ingredients (active substances on or in carrier materials) problems, for example incomplete immobilisation of the active substances on or in the carrier material therefor, frequently arise, in particular in the field of foodstuff technology.

In the field of the systems for the functionalisation, in particular the release (liberation) of active ingredients (active substances) from the carrier materials, such problems frequently result from an inappropriate, i.e. either incomplete or,

alternatively, premature or delayed release of the active substances from the carrier material therefor.

It is true that active substance/carrier material combinations that meet the requirements both with respect to the encapsulation efficiency and also with respect to the needs in practice with regard to release have already been found for individual applications, in particular in pharmacology, agricultural chemicals and cosmetics, but in all industrial nations substantial investment continues to be made in searching for systems which in certain fields of application enables (sic) a release of active substances from a carrier material that is in accordance with the need.

Despite extensive efforts, to date only a few functioning systems have been developed for the encapsulation and functionalisation of ingredients in the fields of food technology and food chemistry. This is partly due to the limited approval for possible carrier materials for the ingredients concerned. In particular, however, problems arise with those flavourings which are of complex composition, which is expressed both in the multiplicity of the volatilities and the ranges of polarity of the individual flavour components of the flavouring and in the sensitivity of one or more flavour components to external influences.

Initially, reference may be made to the following documents from the extremely extensive literature on active ingredient release systems:

Brandau, Thorstein; Pharma + Food 3/2001, 8-12:

Microencapsulated active substances and microspheres in pharmaceutical and cosmetic applications are described in this document. The so-called microsphere method, which results in highly spherical granules (solid spheres) with monomodal particle distribution is indicated as method for the production of microspheres. With this method the active substance or active substances is/are uniformly distributed throughout the entire sphere, in a matrix of a carrier material. Furthermore,

microcapsules for the production of which a liquid or liquefied active substance is embedded in a solid shell are described.

WO 93/02785:

This document discloses a method for the production of alginate spheres (solid spheres) from droplets of an alginate solution that are dispensed from a nozzle, wherein the droplets are dripped into an ionic solution such that they solidify. With this method the alginate solution is converted into droplets by vibration excitation. Mononuclearly filled capsules are not disclosed.

WO 98/15191:

This document discloses a method for the production of spheres (beads) as a food additive, wherein these solid spheres are loaded with at least one active ingredient from the group of flavourings. Mononuclearly filled capsules are not disclosed. Data on ingredients from the field of flavourings, in particular water-insoluble flavourings, and technological advantages of the carrier material with respect to stability to heat are disclosed, the release thereof, however, not taking place spontaneously, but continuously during the production or preparation, but in particular during storage of the food.

WO 98/15192:

This document discloses a method for the production of spheres (beads) as a food additive, wherein in a final method step previously prepared water-insoluble gel spheres (solid spheres) are subsequently loaded with at least one active, amphiphilic ingredient.

The encapsulation of flavourings in spheres (beads) leads to the flavourings having an improved thermal stability and insolubility in water during further processing of the beads. However, the flavour release is not instantaneous during chewing or crushing

of the bead particles in the mouth, but is based on a continuous and slow process of diffusion of active flavouring components from the encapsulating material into the food matrix. This is described in particular in WO 98/15191 and in WO 98/15192.

EP 0 513 603 B1:

This document discloses an installation for the production of seamless capsules, in which a fluid stream for the formation of capsules is blown out of a multiple nozzle in such a way that droplets form, which are then brought into contact with a hardening fluid in order to produce the seamless capsules. These seamless capsules are mononuclearly filled. No data are given on the capsule material. Likewise, no data are given on possible ingredients or possible technological advantages of the shell material in use.

JP 11155480 A describes microcapsules filled with oily aromatic ingredients, which are obtained by reaction of polysaccharides such as alginates with calcium or metal ions and which are resistant to heat and water. However, the shell of the capsules described has a high water content of more than 90 %(m/m), based on the capsule shell.

JP 09065853 A describes a microcapsule filled with the flavouring wasabi, which is formed by encapsulating the flavouring with sodium alginate and a polysaccharide as shaping and stabilising adjuvant by means of a twin-flow nozzle and is hardened with calcium chloride. Here again, the hardened capsule shell material has a very high water content of far in excess of 50 %(m/m).

However, as the Applicant's experiments in the context of the present invention have shown for the first time, a high water content in the capsule shell is extremely disadvantageous for the performance of a capsule and in particular for its thermal stability and its flavour retention capacity.

Accordingly, the primary aim of the present invention was to indicate a flavour release system and a method for the production thereof, which is efficient with regard to the primary flavouring encapsulation and, as far as possible, is universally employable in respect of the selection of the flavourings to be encapsulated, i.e. in particular is not restricted to only a few oil-soluble essences.

Furthermore, the method to be indicated should preferably make it possible to produce a flavour release system that is at least essentially insoluble in water and with which the encapsulation of water-soluble filler materials is also possible.

Moreover, in terms of its flavour release the system should preferably have instantaneous characteristics, i.e. enable sudden release of a flavour at the desired point in time, preferably during ingestion of the food (burst effect).

At the same time, the systems to be indicated should be resistant to shear forces, preferably at least to such an extent that they are not destroyed by the shear forces that usually occur during the production or preparation of a food.

Furthermore, the flavour release system to be indicated should be stable to heat and/or stable to boiling and/or stable to deep frying (see below for the definition of these terms).

From the technological standpoint, the method to be indicated should enable the continuous production of release systems that as far as possible are of the same shape.

With respect to the flavour release system, the primary aim is achieved by indicating a mononuclearly filled seamless microcapsule, which comprises

- a capsule shell of a hardened capsule material based on an acid polysaccharide and

- a filler material, comprising a flavouring in an organoleptically effective amount, that is enclosed by the capsule shell on all sides,

wherein the microcapsule is stable to heat and/or stable to boiling and/or stable to deep frying and the water content in the capsule shell has been adjusted to a value of ≤ 50 %(m/m), based on the total mass of the capsule shell.

In this context a mononuclearly filled seamless microcapsule is considered to be stable to heat if it maintains its structural integrity if it is exposed to a water bath at 50°C for 15 minutes. In this context, its structural integrity is retained in particular if the filler material has not seeped from the capsule shell following the treatment of the microcapsule.

A mononuclearly filled seamless microcapsule according to the invention is considered to be stable to boiling if it maintains its structural integrity if it is exposed to a water bath at 100°C for 5 minutes. In this context, its structural integrity is retained in particular if the filler material has not seeped from the capsule shell following the treatment of the microcapsule.

A mononuclearly filled seamless microcapsule according to the invention is considered to be stable to deep frying if it retains its structural integrity if it is exposed to a deep-fry bath of molten palm butter at 180°C for 5 minutes. In this context, its structural integrity is retained in particular if the filler material has not seeped from the capsule shell following the treatment of the microcapsule.

Within the context of the present text, mononuclearly filled (micro)capsules are here understood to be exclusively systems that possess a defined capsule (capsule shell, skin) which completely encloses a single (mono)core (nucleus) of filler material. In this context, the layer thickness of the capsule shell can be variable; preferably the core takes up by far the major proportion of the capsule volume, in order to enable the highest possible loading of the capsule. Thus, in particular, the term "mononuclearly filled microcapsule" is not applicable to "microspheres", such as

have been described, for example, in the cited article in Pharma + Food 3/2001. The latter sphere systems, in which the active substance is embedded in finely divided form as an emulsion or dispersion in the carrier material, are accordingly frequently referred to in the literature as "polynuclear capsules". A microcapsule in the sense of the present text has a maximum volume of 65 mm^3.

A mononuclearly filled seamless microcapsule according to the invention can be produced in particular by a method with the following steps:

- providing a liquid filler material for the microcapsules containing a flavouring in an organoleptically effective amount,

- providing a, preferably aqueous, solution or dispersion of a capsule material, capable of being hardened, based on an acid polysaccharide,

- forming discrete droplets of the liquid filler material for the microcapsules and the solution or dispersion of the capsule (shell) material capable of being hardened, so that the capsule material capable of being hardened surrounds the liquid filler material in the droplets on all sides,

- hardening the capsule (shell) material capable of being hardened, so that seamless polysaccharide capsules are formed, which each mononuclearly surround filler material and are stable to heat and/or stable to boiling and/or stable to deep frying,

- drying the capsule shell formed until the water content in the capsule shell reaches a value of $\leq$ 50 %(m/m), based on the total mass of the capsule shell.

Preferably, the liquid filler material is prepared by preparing a solution or emulsion of the active flavourings to be employed (which together produce the organoleptically effective amount of a flavouring).

It is preferred to produce the discrete droplets of the liquid filler material and the solution or dispersion of the capsule material capable of being hardened by feeding the said liquids through a concentric multi-nozzle arrangement. The discrete droplets then comprise at least two different phases (filler material, capsule material).

Hardening of the capsule material capable of being hardened preferably takes place by bringing the capsule material capable of being hardened, which surrounds the liquid filler material on all sides in the discrete droplets formed, into contact with an aqueous solution of polyvalent cations (for example Ca ions), whereupon the acid polysaccharide reacts with the cations to form a seamless solid shell around the liquid filler material.

After hardening of the capsule material capable of being hardened, the capsules formed are usually separated off from the solution containing polyvalent cations that has been used, and specifically preferably after an only very brief contact time between capsule bath and hardening bath.

Drying of the capsule shell formed preferably takes place at least partially by a water adsorption or absorption process, which can optionally be combined with other drying processes, for example with a convective air drying process.

Prior to drying, the capsules separated off from the hardening bath are preferably also washed in order thus to remove any adhering polyvalent cations from the capsule surface.

Further details on the preferred embodiments of the method are given below.

The present invention also relates to articles, in particular food compositions, which contain one or more mononuclearly filled microcapsules according to the invention and a carrier material for the microcapsule (M).

Mononuclearly filled microcapsules which are suitable for human consumption are already known. In this context the following are to be differentiated: (a) capsules that can be produced by means of multiple nozzle technology, (b) cell capsules and (c) coacervate microcapsules.

With regard to capsule type (a), reference is made in particular to the above statements with regard to the documents JP 11155480 A and JP 09065853 A.

With respect to capsule type (b), i.e. the cell capsules, reference is made to the documents EP 242 135 A2 and EP 528 466 A1, which each disclose the encapsulation of active substances in cell material originating from microorganisms.

With a view to capsule type (c), i.e. coacervate microcapsules, reference is made to the documents WO 93/19621 and WO 93/19622.

Capsule types (b) and (c) and the corresponding methods for their production have certain advantages and certain disadvantages. Disadvantageously, the conventional production methods for both capsule types are still batch methods, so that inexpensive capsule mass production is not possible. Moreover, the preparation of suitable microorganism cells and the encapsulation in such is technically very demanding and susceptible to error, and furthermore the resulting cell capsules are not particularly stable to shear forces. The method for the production of coacervate microcapsules, which is usually carried out using gelatine and an additive such as, for example, gum arabic, is suitable only under the precondition that the flavouring filler material to be encapsulated is completely insoluble in an aqueous solution of the gelatine, which results in a commensurately substantial restriction with regard to complex flavourings that are potentially to be encapsulated. According to the documents WO 93/19621 and WO 93/19622, the active constituents to be encapsulated are restricted to oil-soluble components. Moreover, coacervate microcapsules are as a rule not stable to heat, which further adversely restricts their suitability for use.

To indicate the enormous investment that is being made in the industry to compensate for the described disadvantages of the abovementioned capsule systems and to produce thermally stable active substance release systems with as high as possible a number of flavourings that can potentially be encapsulated, reference is made to the following documents:

US 5,759,599

This document discloses a method for the flavouring and production of foods by the addition of capsules, loaded with flavouring oils, which have been hardened by means of chemical crosslinking and thus have greater stability to heat, which capsules are produced by the coacervation process based on a protein as shell material and are mechanically broken up on chewing. Once again, the capsules can be loaded only with oil-soluble flavouring substances.

WO 99/17871

This document discloses a method for the encapsulation of amphiphilic flavourings in chemically cross-linked coacervate microcapsules, which, on the basis of known distribution coefficients, are subsequently transported from outside into the core of a pre-produced non-flavoured capsule and there are dissolved until a defined equilibrium is reached.

In contrast to the known types of mononuclearly filled capsules, the microcapsules according to the present invention are, in the case of an appropriate embodiment of the production method, stable to shear forces, insoluble in water, have a stable flavour and are stable to heat (capsules are not meltable (sic) in the presence of water) without an additional chemical cross-linking reaction having to be carried out. In this context, the production method according to the invention is significantly simpler than the production of cell capsules or coacervate microcapsules and also leads to significantly more uniform microcapsule products. The capsules according to the invention can be produced in a continuous process and with essentially

constant dimensions. Compared with the microcapsules that are described in the documents JP 11122480 A and JP 09065853 A, the microcapsules according to the invention are characterised in particular by an improved stability to heat and an improved flavour retention.

The hardened capsule (shell) material of the microcapsules according to the invention preferably comprises - as already mentioned - a substance hardened by bringing into contact with monovalent or divalent cations or cations of higher valency. Therefore, a substance that can be hardened correspondingly is preferably used in the method according to the invention, which substance is preferably in the form of a solution for this. Substances that harden in contact with Ca ions, for example after dripping into a bath containing Ca ions, are preferred.

The capsule (shell) material for the microcapsules is advantageously selected from the group comprising alginate, pectate, pectinate, carragheenan, gellan and mixtures thereof. The said materials can be hardened by cations and, in the hardened state, form capsules that are particularly stable to heat and insoluble in water and have a high shear stability. The cations that are suitable for hardening the said materials are know to a person skilled in the art.

The mononuclearly filled seamless microcapsules according to the invention contain an organoleptically effective amount of a flavouring in their filler material. This flavouring preferably comprises one or more flavourings in the sense of the EU Flavourings Directive 88/388/EEC, i.e. one or more substances imparting odour and taste, which either are naturally present in foods (such as, for example, in fruits) or are added to foods in order to impart an attractive odour and taste thereto.

It must be borne in mind that it is particularly advantageous that the flavourings used according to the invention can have an amphiphilic character and do not have to be transported into the filler material from the outside by diffusion after production of the capsule shell.

Within the framework of the present invention it is usually important to take measures that ensure that during production unacceptable amounts of the flavouring do not diffuse out of the filler material into the capsule shell and possibly even diffuse out of the latter. Such measures are, for example, (rapid) separation of the capsules from the hardening bath, washing of the capsules and drying of the capsules (see above). Frequently, the mononuclearly filled seamless microcapsules according to the invention contain a lipophilic solvent (for example a vegetable oil), in which a flavouring is dissolved, as filler material. Moreover, an aqueous solution of a capsule material that is capable of being hardened is usually employed in the production of the microcapsules according to the invention. The distribution of a (for example amphiphilic) flavouring between the filler material and the capsule material during the production of the microcapsules according to the invention can be described by the corresponding distribution coefficients. For reasons of clarity it is, however, more convenient to indicate the distribution coefficients between n-octanol and water, which are usually employed in the literature for the characterisation of substances, instead of the distribution coefficients for the concentration equilibrium between the filler material and capsule material phases. At a given temperature (for example T = 25°C), the ratio of the concentrations of a given flavouring in the two phases n-octanol and water is constant; the distribution coefficient $K_{o/w}$ is a material constant, as is also the common logarithm of the distribution coefficient $\log K_{o/w}$ (also termed $\log P_{o/w}$). $\log K_{o/w}$ (= $\log P_{o/w}$) = $\log_{10}[c_o/c_w]$ where c_o = concentration of a flavouring in n-octanol; c_w = concentration of the same flavouring in water.

For the purposes of the present invention the flavourings can be divided into three groups, depending on their $\log K_{o/w}$, and specifically such that a degree of difficulty for the encapsulation of the flavouring concerned is assigned to each group.

Flavourings with a $\log K_{o/w} \geq 2$ are lipophilic compounds, which are quite easy to encapsulate. A microcapsule according to the invention can contain more than 50 and up to 95 %(m/m) of flavourings with a $\log K_{o/w} \geq 2$ in the filler material (core), based on the total mass of the capsule. This first group of flavourings includes substances such as carvone ($\log K_{o/w}$ = 2.23), gamma-decalactone ($\log K_{o/w}$ = 2.42),

ethyl caproate ($logK_{o/w}$ = 2.83), linalool ($logK_{o/w}$ = 3.28) and beta-pinene ($logK_{o/w}$ = 4.37).

Flavourings with a $logK_{o/w}$ between 1 and 2 can be regarded as amphiphilic compounds and are already more difficult to encapsulate. A microcapsule according to the invention can contain at least 10 %(m/m) and up to 50 %(m/m) of flavourings with a $logK_{o/w}$ between 1 and 2 in its filler material (core), based on the total mass of the capsule. This second group of flavourings includes substances such as ethyl butyrate ($logK_{o/w}$ = 1.77), benzaldehyde ($logK_{o/w}$ = 1.64), isoamyl alcohol ($logK_{o/w}$ = 1.28), ethyl propionate ($logK_{o/w}$ = 1.24) and diacetyl ($logK_{o/w}$ = 1.33).

Flavourings with a $logK_{o/w} \leq 1$ are amphiphilic to hydrophilic substances and are particularly difficult to encapsulate. A microcapsule according to the invention can contain at least 1 %(m/m) and up to 10 %(m/m) of flavourings with a $logK_{o/w} \leq 1$ in its filler material, based on the total mass of the capsule. This third group of flavourings includes substances such as ethyl lactate ($logK_{o/w}$ = 0.88), anisaldehyde ($logK_{o/w}$ = 0.95), butyric acid ($logK_{o/w}$ = 0.78) and ethyl acetate ($logK_{o/w}$ = 0.75).

For organoleptic reasons the flavouring contained, for example in dissolved or dispersed form, in the filler material of a microcapsule according to the invention will frequently contain at least 10 %(m/m), based on the total mass of the flavouring in the filler material, of one or more flavourings with a $logK_{o/w} < 2$. However, if the flavouring is present in the filler material in dissolved form, the proportion of flavourings with a $logK_{o/w} < 1$ should be kept very low, and preferably no more than 1 %(m/m), based on the total mass of the flavouring in the filler material, in order to prevent unacceptable flavour losses. If the flavouring in the filler material is in dispersed, for example emulsified, form, the risk of flavourings passing into the capsule shell is reduced, compared with a dissolved flavouring, so that the flavouring can also contain one or more flavourings with a $logP_{o/w} < 1.0$, for example in a range of 0.5 - 3.0 %(m/m), based on the total mass of the flavouring in the filler material.

Mononuclearly filled microcapsules which have a combination of some or all of the following characteristics can be produced by the method according to the invention:

1. High retention of amphiphilic active substance components (in particular flavourings) in the core during hardening and drying of the shell material up to the finished end product;

2. High stability of encapsulated active substance components during storage;

3. Low interaction between filler material and capsule material;

4. High thermal and/or mechanical and/or chemical stability of the microcapsule to conditions such as usually prevail during the further processing of microcapsules (for example mixing, roasting, baking or boiling).

5. Controlled but sudden release of the active substances contained in the filler material on intended end use of the microcapsule, i.e., for example, on eating a food that contains microcapsules filled with flavourings.

For production of the filler material (i.e. the core of the microcapsule), frequently - as has already been mentioned - (a) a solution, in an oil, of the flavouring to be incorporated or (b) a water-in-oil emulsion that contains the flavouring in the inner aqueous phase is first prepared. Here, the term "oil" includes both liquid vegetable oils and meltable vegetable or animal fats. As a rule it will be advantageous to select an oil which readily dissolves the flavouring to be incorporated and at the same time is suitable for human consumption. If water-in-oil emulsions are used, it can be advantageous to add emulsifiers which are suitable for stabilising the emulsion to the oil phase. By adding a small amount of water, which preferably does not exceed 10 %(m/m) (based on the liquid filler material) and an emulsifier, matched thereto, with an HLB (hydrophilic lipophilic balance) value of preferably less < 5 within the filler material (core system), it is possible to produce a stable water-in-oil emulsion. For this purpose, the emulsifiers are preferably selected from the group that consists

of mono-diglycerides, monoglycerides, polyglycerol esters, sorbitan esters and mixtures thereof. The production of a water-in-oil (w/o) emulsion within the filler material (core phase) improves the retention of the water-soluble flavourings. The emulsifier can also be brought into solution in the oil phase without the addition of water. The emulsifier encloses the more water-soluble flavouring components within the liquid filler material in the form of micelles.

Flavourings which are solid at room temperature can be dispersed in liquid oil, dispersion aids being added if necessary.

To produce the solution or dispersion of a capsule material that is capable of being hardened and is based on an acid polysaccharide, in the method according to the invention the polysaccharide material, for example the sodium salt of the alginic acid, is usually dissolved or dispersed in an aqueous solvent. Non-volatile, water-soluble or water-insoluble dispersible substances can be added at this point in time, for example (a) glycerol, propylene glycol or other agents for improving the mechanical properties of the (dried) mononuclearly filled microcapsules to be produced by plasticising the capsule (shell) or (b) proteins and/or saccharides for modification of the capsule composition.

In a preferred method according to the invention, the solution or dispersion of the capsule material capable of being hardened and the liquid filler material are fed separately from one another to a system, preferably to a multi-nozzle system, this system being so designed that discrete droplets in which the capsule material capable of being hardened surrounds the liquid filler material are formed from the liquid filler material for the microcapsules and the solution or dispersion of the capsule material, capable of being hardened, for the microcapsules. Suitable twin nozzle systems are described in the literature, and in this regard reference is again made to the documents EP 0 513 603 B1 and WO 93/02785.

The said discrete droplets consist of an inner flavouring core (filler material), which is surrounded on all sides by the outer polysaccharide shell (capsule shell). Core, shell

and whole capsule are preferably spherical. The core phase is preferably precisely centered within the capsule shell phase, which means, that the thickness of the capsule shell is the same at every point of the seamless microcapsule. Such an embodiment makes a significant contribution to a high quality capsule. Centering of the capsule core (filler material) can be achieved by suitable selection of the following parameters: ratio of the diameters of inner and outer nozzle; ratio of the flow rates through the inner and the outer nozzle; frequency and amplitude of a vibrator for the multiple nozzle, which is optionally present; intrinsic properties of the liquids used (for filler material and capsule (shell) material).

To harden the discrete droplets formed, these are fed or dripped into a preferably aqueous or aqueous-alcoholic solution of polyvalent cations. The selection of the polyvalent cations depends on the type of capsule material capable of being hardened that is used. Insofar as calcium ions can be used to harden an acid polysaccharide employed, the solution of polyvalent cations preferably contains a dissolved calcium salt, dissolved calcium chloride with a concentration in the range between 1 and 10 %(m/m) (based on the total mass of the liquid hardening bath) being preferred. The solution of polyvalent cations is usually prepared by dissolving the corresponding salts in deionised water or in tap water, to which a low molecular weight alcohol such as ethanol or isopropanal can be added, (a) in order to lower the surface tension of the solution and thus to facilitate the immersion of the discrete droplets produced at the nozzle, (b) to adjust the density of the aqueous solution of the salt (for example calcium salt) containing polyvalent cations and/or (c) to influence the gelling of the capsule material (for example alginate).

As an alternative to feeding or dripping the discrete droplets into a solution of polyvalent cations, the fine droplets can also be sprayed with a solution of the polyvalent cations.

Particularly suitable capsule materials are alginates, i.e. linear copolymers of -L-guluronate (G) and -D-mannuronate (M). The alginate chain can be regarded as a block co-polymer that [lacuna] of "G blocks" (homopolymer regions of guluronic acid

residues), "M blocks" (homopolymer regions of mannuronic acid residues) and "MG blocks" (copolymer regions of mixed alternating sequences of M and G) of variable length. In addition to a variable chemical composition, alginates also have a broad molecular weight distribution, so that the term alginate is a generic term for an entire family of polymers. The properties of a particular alginate are derived from the particular block structure thereof and its molecular weight.

Above a critical molecular weight, the properties of an alginate are essentially determined by its monomer composition and block structure. Generally, an increase of the guluronate content leads to a mechanically more stable gel with increased stability in the presence of non- or anti-gelling ions such as sodium and magnesium, as well as calcium-complexing compounds; alginate gels with a high guluronate content generally have a high porosity and tend to syneresis to only a slight extent during gel formation. In contrast, alginate gels become softer and more elastic as a result of increasing the mannuronate content, and the corresponding gels shrink to a greater extent during gel formation, which results in a lowering of the porosity.

In principle, all alginate types are suitable for the encapsulation of active substances (in particular flavourings); however, those with a mannuronate content of more than 40% are preferred for the production of microcapsules according to the invention for use in food applications because they are comparatively elastic and form smaller pores, which has an advantageous effect for flavouring use at high temperatures and thus on flavour retention during further processing. On the other hand, in the case of an intended continuous release of a flavouring from a capsule according to the invention under the influence of heat, steam or air, i.e. conditions such as frequently exist when tobacco products are used, guluronate-rich alginate gels with large pores are advantageous. Because of their comparatively rapid gelling, high molecular weight alginates are preferred for the encapsulation of flavourings. However, for modulation of the viscosity of an alginate gel it can be advantageous partially to replace high molecular weight alginates by low molecular weight alginates; in addition to other factors, the viscosity of an alginate gel is responsible for the size of the microcapsules that form in the method according to the invention and for the

capsule thickness (shell thickness). Moreover, the viscosity of the alginate gel has a direct influence on the elasticity of the capsule formed.

Calcium ions are preferred for hardening (gelling) alginate, specifically because of their high effectiveness, the low costs associated with use and the fact that they are acceptable from the health standpoint. Other divalent metal ions such as those of zinc, copper, etc. can likewise be used, as can the ions of divalent or trivalent iron, aluminum, etc. For reasons of cost, the salty and slightly bitter tasting chloride is preferred as counterion for calcium; however, acetate and/or lactate are preferred for reasons of taste. A skin of insoluble alginate gel forms immediately when discrete droplets which contain alginate as the capsule material capable of being hardened are brought into contact with calcium ions. Thereafter calcium ions slowly diffuse into the capsule shell. For droplets with a diameter of 100 to 5000 micrometres and an aqueous solution of 1 to 10 %(m/m) calcium chloride, the optimum contact time is less than 1 minute; however, it can also be longer in the individual case and can be, for example, 100 minutes. However, if the flavouring contains water-soluble constituents it is advantageous to remove the capsules that are forming from the calcium bath after only a short time, in order to prevent water-soluble compounds passing into the bath, or at least to keep this within acceptable limits. It is pointed out that the loss of water-soluble flavouring constituents from an alginate capsule proceeds considerably more slowly than the loss of corresponding aroma constituents from a comparable microsphere; these losses in the case of microspheres are described in the document WO 98/15191. The considerations and comments put forward above with regard to calcium ions and alginate apply correspondingly to other pairings of an acid polysaccharide and a monovalent or polyvalent cation.

Although attention was focused above in particular on the various types of alginate and amongst these, in turn, sodium alginate in particular, pectins with a low degree of esterification or other acid polysaccharides can also be used for the production of capsules according to the invention, in particular to produce water-insoluble gel capsules that are stable to heat.

The concentration of the acid polysaccharide (hydrocolloid) in the liquid mixture from which the capsule (shell) is to be produced is preferably in the range of between 0.5 and 4 %(m/m), based on the total mass of the solution. Concentrated solutions are as a rule difficult to process, since they have too high a viscosity. Additives such as, for example, locust bean gum, sucrose, glycerol or propylene glycol can be added to the polysaccharide solution to improve the mechanical properties of the capsule (shell) material. Fillers such as, for example, oligosaccharides, maltrodextrin, starch, gum arabic or cellulose derivatives (for example carboxymethylcellulose) can be dissolved in the polysaccharide solution or dispersed therein to improve the barrier characteristics of the capsules, in that they fill the pores that would otherwise be present in the open structure of the gel subsequently formed.

The hardened gel capsules, or gel capsules in the process of hardening, can be separated off from the suspension (capsules in ion-containing solution), for example by filtration or centrifuging. Moist mononuclearly filled microcapsules result, to which an anti-caking agent can preferably be added, in order to obtain a free flowing product. The product can be dried under atmospheric pressure or reduced pressure while still moist, in order to obtain a capsule product with defined water content. The mechanical stability of the microcapsules can also be adjusted in this way.

The capsules according to the invention have a volume of up to 65 mm^3; but, especially in the field of flavouring technology, distinctly smaller volumes are preferred. Preferred volumes are in the range between 4×10^{-6} m^3 and 2×10^{-9} m^3; in the case of a precisely spherical microcapsule, this corresponds to a diameter of between approximately 200 and approximately 1500 μm. Preferably, the volume of the mononuclearly filled microcapsule according to the invention is in the range between approximately 3×10^{-7} m^3 and 3×10^{-5} m^3; in the case of spherical microcapsules this corresponds to a diameter in the range of approximately 400 to approximately 1200 μm.

The filler material of the mononuclearly filled microcapsules according to the invention contains flavourings. In this context, according to EU Flavourings Directive 88/388/EEC, the term "flavouring" includes natural flavourings, flavourings identical to natural flavourings, artificial flavourings, flavouring extracts, reaction flavourings and smoke flavourings.

A multiplicity of flavourings and flavouring ingredients can be encapsulated using the method according to the invention. The flavourings include compounds such as menthol, natural extracts, essences, complex mixtures of extracts, essential (ethereal) oils, oleoresins or reconstituted natural flavourings, flavourings identical to natural flavourings or artificial flavourings. The group comprising natural extracts, essences and oleoresins includes fruit essences, vanilla extracts, paprika oleoresins, pepper oleoresins, cinnamon oils, oils (sic) of wintergreen, peppermint oil, bay oil, thyme oil, spearmint oil, cassia oil, citrus oils and the like. The group comprising reconstituted natural flavourings, flavourings identical to natural flavourings and artificial flavourings includes apple, cherry, strawberry, peach and also sausage, cheese, tomato, celery and butter flavouring. These flavourings can be used on their own or as mixtures, in accordance with known methods. Depending on their particular $\log K_{o/w}$ value, the flavourings and flavouring ingredients can be incorporated in varying maximum amounts in the capsules according to the invention (see the above remarks regarding the degree of difficulty of encapsulation depending on $\log K_{o/w}$). It is to be stressed that it is particularly advantageous that readily volatile and amphiphilic or water-soluble flavourings, which are required as key compounds for the reconstitution of fresh fruit and vegetable notes, can also be incorporated in a sufficiently high amount in the capsules according to the invention and can be retained therein even during further processing of the capsules.

Filled microcapsules according to the invention, the filler material of which comprises one or more flavourings, are suitable for instant release of this flavouring by mechanical opening of the polysaccharide capsule. The encapsulation is not found to be annoying when eating. A person skilled in the art will determine the thickness and strength of the polysaccharide capsule (shell) in accordance with the

requirements in the particular case; in particular, he will select a suitable capsule material capable of being hardened and use plasticisers if necessary. In this way it is possible, for example, to produce filled microcapsules according to the invention, which have a filler material that comprises one or more flavourings and which, for example, can be incorporated in a food. Spontaneous release of the flavouring then takes place on chewing the food, no or only negligibly small amounts of flavourings being retained by the material of the microcapsule, in contrast to the methods known from the state of the art for flavouring foods.

The microcapsules according to the invention are formulated to be stable to heat and/or stable to boiling and/or stable to deep frying. In this context, these terms have the abovementioned meaning and make it clear that, compared with systems known from the state of the art, the microcapsules according to the invention have particularly good flavour retention in semi-solid or solid foods during boiling, baking, deep frying, roasting, drying, extruding, heating in the microwave, etc. The microcapsules according to the invention afford the flavourings contained therein good protection against decomposition and volatilisation in hot liquid products, especially during pasteurisation and/or sterilisation of products in which they have been integrated.

In principle, a person skilled in the art will be able to modify the composition of many flavourings, in particular with regard to components of an amphiphilic or hydrophilic nature, or to adapt this to the capsule system in such a way that acceptable sensory results are achieved. However, in order to prevent losses of active substances of the amphiphilic or hydrophilic components characteristic for the respective flavour during hardening and drying of the capsules, the method according to the invention is advantageously so designed, using a conventional nozzle system, as is known, for example, from EP 0 513 603 B1, or WO 93/02785 and the documents cited therein, that (a) the capsule material capable of being hardened comes into contact with the (active) substance from the group of flavourings that is contained in the filler material only at the tip of the nozzle and (b) during or after hardening of the capsule material capable of being hardened, the flavouring or flavourings does/do not, or as far as

possible does/do not, diffuse into the capsule surrounding the filler material. On the basis of experiments, a person skilled in the art is able to determine suitable process parameters, on the basis of known or calculated distribution coefficients, which prevent or reduce to a minimum the passage of flavourings into the capsule material and beyond this into the hardening bath or the atmosphere.

It is possible for a person skilled in the art at least essentially to preserve the composition of the flavouring contained in the filler material and the organoleptic profile thereof. Components such as, for example, isoamyl acetate ($logP_{o/w}$ = 2.12), ethyl butyrate ($logP_{o/w}$ = 1.73) and benzaldehyde ($logP_{o/w}$ = 1.64), which are of amphiphilic nature and the solubility in water of which clearly increases in this sequence, are the components that are characteristic or typical of banana, pineapple and cherry flavour, respectively. However, gentle production conditions matched to these flavourings make it possible, within the framework of the invention, for a person skilled in the art to ensure virtually complete retention of these flavourings in the dried microcapsules according to the invention.

The retention of flavourings such as isoamyl alcohol, the $logP_{o/w}$ of 1.22 of which signifies a further increase in the solubility in water compared with the three substances mentioned above, is kept at least within acceptable limits under process conditions according to the invention that are matched thereto, whilst production conditions that are not matched thereto would virtually lead to quantitative losses.

With a $logP_{o/w}$ of -0.16, acetaldehyde, which is responsible for the fresh character of some fruit flavourings, again has a distinctly increased solubility in water compared with isoamyl alcohol. Therefore, quantitative losses of this flavouring can occur on hardening and drying if it is contained in dissolved form in the filler material.

However, even the retention of substances that are readily soluble in water, such as acetaldehyde, can be distinctly increased by appropriate measures, in order to this extent also to retain sensory activity in the core of the capsule, for example by

dispersion of solid flavourings or simple water-in-oil emulsions, micellar systems or liposomes in the case of liquid flavourings.

For applications which require exposure of a final food to heat, free-flowing microcapsules according to the invention that are dry on the outside thereof and have a water content of ≤ 50 %(m/m) in the capsule shell, based on the mass of the capsule shell, are preferred to capsules with a water content of ≥ 50 %(m/m) in the capsule shell. Specifically, with a water content of ≥ 50 %(m/m) flavourings can escape from a microcapsule under the action of heat, together with the water vapour that then forms from excess free water. Dry capsules, for example calcium-hardened capsules, with a water content of □ 50 %(m/m) in the capsule shell, based on the total mass of the capsule shell, can be hydrated only with difficulty, so that even exposure to heat in the presence of water does not immediately result in destruction of the active substance release system; in some cases this is different for capsules according to the invention which have a higher water content of, for example ≥ 50 %(m/m) in the capsule shell, and the solid microspheres known from the state of the art, which contain flavourings embedded in a matrix, are less stable on exposure to heat in the presence of water than the preferred microcapsules according to the invention, which have a water content of ≤ 50 %(m/m) in the capsule shell; in the case of capsules with a filler material content of 80 %(m/m) and a capsule shell content of 20 %(m/m), in each case based on the total mass of the capsule, this corresponds to a water content of less than 10 %(m/m), based on the total mass of the capsule.

According to a preferred embodiment of the process, two-phase discrete droplets are dripped into a hardening bath, the impact of the droplets being cushioned as far as possible, in order to ensure a centered core (of filler material) after hardening of the capsule (shell) material. For this purpose a person skilled in the art will reduce the distance between the multi-nozzle system and the hardening bath and/or, in a first step, spray the discrete droplets with the hardening solution while they are still falling, before the droplets then plunge into the hardening bath, and/or modify the amplitude and frequency of a conventional vibrator assigned to the multi-nozzle

system and/or adapt the intrinsic characteristics of capsule shell and liquid core phase and/or use specific overflow funnel systems or channel systems and/or use surfactant compounds in the hardening bath which produce a foam on the surface of the hardening bath or reduce the surface tension of the hardening bath.

On contact with the polyvalent cations, the polysaccharide solution immediately forms a solid skin around the core material (filler material). The cations then slowly diffuse out of the hardening bath (the hardening spray) into the interior of the capsule shell, so that a hardening gradient is produced, there being a comparatively high hardness on the outside of the capsule shell and a comparatively low hardness on the inside of the capsule shell (in this context see also below). A person skilled in the art will determine at which point in time in the hardening process the gelled microcapsules can be separated off from the hardening bath on the basis of preliminary experiments.

If amphiphilic flavourings are used, it is to be expected that the more hydrophilic compounds within a mixture of flavourings will be those that first diffuse out of the core phase (filler material phase) into the aqueous polysaccharide solution, while the discrete droplets are in the course of formation after issuing from the multiple nozzle, and in a second step diffuse through the capsule shell that is hardening towards the hardening bath. Within the framework of the present invention, the dripping and hardening steps are therefore each preferably carried out within short periods of time. It is known that in contact with polyvalent cations, such as, for example, calcium, polysaccharide solutions based on alginate, gellan or pectin form an inhomogeneous structure. The cations initially react only with the outer surface of the outer polysaccharide phase of the said discrete droplets and then diffuse towards the centre, building up a so-called gel gradient. The capsule shell strength is therefore greater on the outer surface of the microcapsule that has already formed than on the inside, and in the inner part of the gel phase this is of liquid or soft consistency. The molecular chains of the hardening hydrocolloid contract, a certain amount of water being pressed out of the gel at the same time. This phenomenon is known as the syneresis effect, and the shorter the gel time, the smaller is the syneresis effect.

Depending on factors such as the gel time, the polysaccharide solution concentration and the cation solution concentration, the syneresis can amount to between 5 %(m/m) and 60 %(m/m), based on the mass of the original liquid droplets. A certain amount of hydrophilic flavourings can escape into the hardening bath in this way (by syneresis) as a result of the water transport produced. According to a preferred embodiment of the present invention, the gelling time, i.e. the contact time between the forming polysaccharide phase of the capsule and the bath containing polyvalent cations, is reduced to a minimal value, which preferably is less than 1 minute and in particular can be in the range between 5 and 30 seconds. The inhomogeneity of the gel formed and the reduced syneresis effect restrict the migration of the said more hydrophilic flavours out of the core phase (filler material) through said gel phase into the hardening bath. This is an important point of distinction compared with the microcapsules described further above, which are produced by coacervation and with which the contact time between the forming microcapsules and the aqueous reaction bath is hours or even days.

The isolation of the microcapsules formed from the hardening bath is preferably carried out continuously, and specifically preferably by means of a sieving technique or by centrifuging. At the point in time of separation from the hardening bath, the microcapsules are in the wet form. The water content of the moist microcapsules is between 50 and 90 %(m/m), based on the total mass of the particles. The water present is in the form both of water bound to the polysaccharide as well as of free water within the porous structure of the polysaccharide gel and in the form of interstitial water between the microcapsules formed. The water still contains a not insignificant concentration of polyvalent cations. According to a preferred embodiment, a washing step is carried out after separating off the moist (wet) microcapsules from the solution of polyvalent cations (hardening bath). For this purpose, a washing solution is used that preferably consists of deionised water, but can also consist of a mixture of water and an organic solvent, such as, for example, ethanol or isopropanol. The washing step is preferably integrated in the separation step in that a spray nozzle for application of a washing solution is incorporated in the separating device used for separation. In this way the polyvalent ions that are still

present in the interstitial water of the microcapsules and in the outer part of the polysaccharide gel can be washed out very rapidly. This prevents further diffusion of the reactive polyvalent cations into the polysaccharide gel and therefore also prevents a further syneresis effect. After all, microcapsules which are subjected to a method with a short gelling time can lose up to 50 %(m/m) because of the syneresis effect if the microcapsules are left to stand unwashed after separating off from the hardening bath.

Because of the tendency of the more hydrophilic flavourings to issue from the inner phase (core; filler material) of the moist microcapsule through the porous polysaccharide gel structure of the capsule (shell) material, in preferred embodiments of the present invention the microcapsules that are still moist are converted to the dry form as rapidly as possible. The drying process leads to the porous shell structure of the microcapsule contracting further up to a point at which even the more hydrophilic flavourings hardly still diffuse through the dried capsule shell matrix. Drying can be carried out either batchwise or continuously, a continuous process embodiment being preferred, however, in order thus to shorten the period between washing of the moist microcapsules, described above, and the drying process step as far as possible. Each holding time of the moist microcapsules could lead to further syneresis and thus to further transport of hydrophilic flavourings out of the microcapsule.

In the framework of the present invention, the conventional drying processes can be employed, for example using conductive driers (such as standard ovens or vacuum ovens) or convective driers (for example fluidised-bed driers or rotary driers). These technologies are, however, preferably suitable if the filler material (core) contains mainly or even virtually exclusively lipophilic and non-volatile flavourings. If, on the other hand, water-soluble or readily volatile flavourings are to be encapsulated, a significant proportion of these substances will also vaporise in the case of simple evaporation of water, an effect that is critical especially in the case of the convective drying process, with which a particularly high proportion of flavourings is removed from the filler material since substances capable of vaporisation are continuously

transported away by means of a stream of air. In a preferred embodiment of the present invention the said drying technologies are used in a pre-drying step, in which the water content of the capsule shell material still remains high and the co-vaporisation of hydrophilic flavourings thus remains tolerable. Wet microcapsules frequently have a water content that is between 96 %(m/m) and 65 %(m/m), based on the total mass of the capsule shell material. Preferably less than 25% of the total water to be removed is vaporised by means of the pre-drying. In such a way flavourings with a $\log K_{o/w} < 2$, in particular $\log K_{o/w} < 1.5$, are particularly effectively encapsulated.

According to a further alternative embodiment of the present invention a drying technology is employed in which the preferably washed moist microcapsules or the said pre-dried microcapsules are brought into contact with a water-adsorbing or water-binding substance. An inorganic salt, such as, for example, magnesium carbonate, magnesium sulphate or calcium chloride, or compounds such as silicon dioxide, zeolite or starch, is preferably used as water-adsorbing or water-binding substance. In many cases a silicon dioxide, which preferably has an internal specific surface area of 150 m^2/g or more, is preferred. The water adsorption capacity of such a silicon dioxide (also referred to as silica) should be more than 100% and preferably more than 200%, based on its own mass. The still moist or pre-dried microcapsules are usually first of all homogeneously mixed with up to 50 %(m/m) and preferably approximately 25 %(m/m) of the said silica. A drum mixer, spiral mixer, paddle mixer or plough-share mixer can be used for mixing here. After a mixing time, which should not exceed 10 minutes and should preferably be approximately 5 minutes, the microcapsules are separated off from the loaded water-adsorbing or water-binding substance by means of sieving technology. Vibratory or rotary sieves can be used for this purpose. Mixing and sieving can be carried out either batchwise or as a continuous operation. The capsule shell material of the dried microcapsules has a water content of at most 50 %(m/m), based on the mass of the capsule shell. The advantages of such a drying process compared with the abovementioned standard drying technologies are, in particular, to be seen in (a) a shorter process time, (b) the absence of release of a flavouring into the air, (c) the

good flowability of the dried microcapsules even with high flavouring loading and, in particular, (d) in the improvements with regard to the water-soluble and volatile flavouring constituents. Flavourings with a $\log K_{o/w} < 2$ and in particular $\log K_{o/w} < 1.5$ are significantly better encapsulated than when the conventional drying technologies are used. The improvement in respect of the retention in this case can amount to as much as 50 to 90 %(m/m), based on the starting mass of the flavouring components used in the filling material, cf. Example 10.

The microcapsules according to the invention have a water content in the capsule shell of ≤ 50 %(m/m), based on the total mass of the capsule shell. An essential reason for this is that the Applicant's own research has shown that microcapsules with a higher water content in the capsule shell lose an unacceptably high proportion of their more readily volatile and their water-soluble flavourings if they are heated within a food matrix. Specifically, the more readily water-soluble and more volatile compounds are entrained by evaporating water and transported out of the microcapsule, so that there can be said to be a co-distillation. The thermal stability of the microcapsules according to the invention with a water content of ≤ 50 %(m/m) in the capsule shell is based not only on its physical integrity, by virtue of its insolubility in water and its irreversible gel formation. It is also and not least based on the fact that the flavour profile of the originally encapsulated flavouring system is preserved in unchanged form. A microcapsule according to the invention with a filler material that makes up a proportion of at least 80 %(m/m), based on the total mass of the dried capsule, and the capsule shell material of which accordingly makes up a proportion of at most 20 %(m/m), should usually have a water content of no more than 10 %(m/m), again based on the total mass of the dried microcapsules. In the case of a proportion of filler material of 90 %(m/m), the water content should not be more than 5 %(m/m).

The invention will be described in more detail below on the basis of examples.

Example 1

Method for the production of (standard) capsules according to the invention for use in Examples 2 to 5.

Sodium alginate (type Protonal LF20/60, FMC BioPolymer, Drammen, Norway) was dissolved in demineralised water with stirring (15.0 g alginate per 1000 ml water) until a clear solution formed. The stirring time at a water temperature of 8 - 15°C was approximately 30 minutes. The solution was made up at least 3 to 5 hours before processing in order to obtain the desired viscosity of at most 200 mPa·s, and even better on the previous day. Solutions that were more than 24 hours old were no longer used. After the stirring operation, the pH value of the solution was determined and if necessary adjusted to pH 6.5-7.5 using a base. Tank A was filled with this solution.

Neutral oil (for example Miglyol, CONDEA Chemie GmbH, Witten, Germany) or a commercially available vegetable oil (for example soya oil) was added to a selected flavouring concentrate or an essence until a defined degree of dilution was reached to produce a solution or dispersion; this dilute flavouring solution was filled into Tank B and stirred continuously to prevent demixing. The two solutions were pumped separately via pressure lines to a conventional twin-nozzle system which was usually vibrating, the flavouring solution being fed into the inner nozzle with a diameter of 200 micrometres and the alginate solution to the outer nozzle with a diameter of 1000 micrometres. The ratio of the flow rates of the two solutions was controlled by separate pressure adjustment in such a way that a ratio of the liquids A : B of 10 : 1 was obtained.

Standard parameters:
Inner nozzle 0.3 bar / throughput 14.0 = 330 g flavouring per hour
Outer nozzle 0.5 bar / throughput 20.0 = 3300 g alginate per hour
Frequency = 160 Hz, amplitude = 4.8

A two-phase liquid droplet was thus obtained with an average particle diameter of approximately 2.2 mm, with a weight ratio of shell to core of 10 : 1. This droplet is gelled for 5 minutes by gelling with 10% calcium chloride solution (solution of 10 g anhydrous calcium chloride in 100 g demineralised water).

By means of syneresis during gelling of the alginate, a moist capsule with a diameter of approximately 1.6 mm and unchanged flavouring core diameter is obtained. The particles were isolated by filtration and washed briefly with tap water to remove excess calcium ions. The filtered and washed particles were dried in a fluidised bed at an air temperature of 50°C and an amount of air of 10 m^3/min, the average particle diameter of the particles dried by means of this standard drying method being reduced to 1050 micrometres. To assist the fluidisation of the wet and sometimes also sticky capsules, 1% magnesium carbonate was added as antiblocking agent. The average particle diameter, which was most easily determined by measurement of a number of capsules adequate for statistical purposes by means of optical microscopy, showed a modal distribution; the capsule diameter was determined as 1050 ± 100 micrometres. Alternatively a laser diffraction method (Malvern) was used for particle size and particle distribution measurement.

The resulting dry standard capsules had on average a core content of 80 %(m/m) and a shell content of 20 %(m/m), the shell having an average residual water content of 50%, as resulted from drying tests using a halogen drier.

The dilution of the flavouring concentrate with oil in the core of the capsule was so chosen that, in comparison tests using flavouring by means of (a) the corresponding liquid flavouring concentrate or (b) a spray dried form, the same proportions by mass of flavouring were employed in use in each case. In these tests care was taken that, when flavouring with capsules, depending on use and desired release rate a dosage of between 0.2 and 2.0 %(m/m) capsules was set, based on the end use, in order to obtain a uniform picture. Accordingly, the (comparison) flavouring by means of liquid flavouring concentrate took place on the basis of the set dilution of the corresponding flavouring concentrate in the capsule core and the additional dilution by

encapsulation of the shell portion consisting of partially dried alginate gel. When different capsule sizes were used, account was correspondingly taken of the changed dilution and dosage.

Capsules produced in this way were used in the following examples.

Example 2

Chewing gum was produced in accordance with the following formulation.

Formulation type: chewing gum, sugar-free

Table 1:

Chewing composition

Additive	Raw material/ ingredient	%(m/m)
01	Chewing gum base	27.62
02	Xylitol	9.87
03	Sorbitol	48.59
04	Mannitol	11.54
05	Glycerol	2.16
06	Aspartame	0.11
07	Acesulfame-K	0.11
		100.0

	Flavouring:	%(m/m) (based on the total mass of the chewing composition)
08a	Capsules - peppermint oil	1.0*
08b	Capsules – peppermint oil	2.0**
08c	Peppermint oil	0.64

* corresponds to a peppermint oil content of 0.64% for a set average capsule size of 1050 micrometres and a flavouring dilution with oil of 80:20.

** corresponds to a peppermint oil content of 0.64% for a set average capsule size of 800 micrometres and a flavouring dilution with oil of 80:20.

Production method

a - Mixing of 1, 2, 3, 4, 5, 6, 7.
b - Kneading of the composition at a temperature of 50°C until mixture is homogeneous.
c - Addition of the flavouring (0.64% ingredient 08c or 1.0% ingredient 08a or 2.0% ingredient 08b) based on chewing composition (total mass of ingredients 1 to 7).
d - Lamination of the composition.
e - Cutting into strips.

The strips of chewing gum were assessed for odour (aroma by sniffing) and taste (chewing gum in the mouth). The result of the organoleptic test (6 test persons) summarised in Table 2 showed that for both capsule sizes the encapsulated flavouring showed a significantly higher intensity compared with the liquid flavouring for the same proportion by mass.

Table 2:

	Particle size (mm)	Intensity of the flavouring	
		Olfactory	Oral
Alginate capsules (additive 08a)	1.050	5.25	7.00
Alginate capsules (additive 08b)	0.800	6.38	8.40
Not encapsulated (additive 08c)		4.50	4.70

Organoleptic assessment (flavouring strength/intensity):

0 = not discernible, 1 = almost imperceptible, 2 = very weak, type of flavour barely recognisable; 3 = weak, type of flavour just recognisable; 4 = weak, type of flavour clearly recognisable; 5 = acceptable, slightly too weak; 6 = acceptable, optimum strength of flavour; 7 = acceptable, slightly too strong; 8 = flavour much too strong; 9 = flavour extremely strong, irritating.

Example 3 (baking)

Biscuits (crackers) were produced in accordance with the following formulation.

Formulation type: snack biscuit, cheese, salted

Table 3

Additive	Raw material/ingredient	%(m/m)
01	Wheat flour (cracker type)	66.530
02	Vegetable shortening	7.980
03	Cane sugar	1.550
04	Inverted sugar syrup	1.550
05	Salt	1.150
06	Ammonium bicarbonate	0.890
07	Malt syrup extract	0.806
08	Sodium monophosphate	0.665
09	Sodium bicarbonate	0.550
10	Citric acid	0.066
11	Bacterial protease	0.027
12	Sodium metabisulphite	0.016
13	Water	19.370
		100.0

Flavouring: %(m/m) (based on the total mass of the additives 1-13)

14a	Capsules - cheese flavour	1.0*
14b	Capsules – cheese flavour	2.0**
14c	Cheese flavour, top note, liquid	0.08

* corresponds to a cheese top note content of 0.08% for a set average capsule size of 1100 micrometres and a flavouring dilution with oil in the core of 10:90.

** corresponds to a cheese top note content of 0.08% for a set average capsule size of 900 micrometres and a flavouring dilution with oil in the core of 10:90.

Production method

a - Mixing of 2, 3, 4, 5 and 13 (70°C), until all constituents have dissolved.
b - Addition of ingredients 1 and 6-12 to the dough, addition of flavouring 14a or 14b or 14c.
c - Mixing for approximately 10 minutes, until the dough is smooth.
d - Leaving the dough to stand for 2 hours.
e - Lamination of the dough and cutting to size.
f - Addition of granulated salt on top of the biscuit dough (optional).
g - Baking for 4 minutes in an oven at 185°C (initially the temperature should be 210°C). Injection of steam while the biscuits are being introduced into the oven; continuation of the injection until the temperature reaches 190°C.
h - On removal of the biscuits, spray vegetable fat onto the biscuits (optional), until the biscuits acquire a certain shine.

The crackers were assessed for odour (aroma by sniffing) and taste (cracker in the mouth). The result of the organoleptic testing (7 test persons) summarised in Table 4 showed that for both capsule sizes the encapsulated flavouring showed a significantly increased intensity compared with the liquid flavouring for the same proportion by mass.

Table 4:

	Particle size (mm)	Intensity of the flavour	
		Olfactory	Oral
Alginate capsules (additive 14a)	1.100	5.40	7.00
Alginate capsules (additive 14b)	0.900	5.80	8.40
Not encapsulated (additive 14c)		4.50	3.88

Organoleptic assessment:
0 = not discernible, 1 = almost imperceptible; 2 = very weak; 3 = weak, type of flavour just recognisable; 4 = weak, type of flavour clearly recognisable; 5 = acceptable, slightly too weak; 6 = acceptable, optimum strength of flavour; 7 = acceptable, slightly too strong; 8 = flavour much too strong; 9 = flavour extremely strong, irritating.

Example 4 (deep frying)

A panada was produced in accordance with the following formulation:

Formulation type: wet panada

Table 5:

Additive	Ingredients	%(m/m)
01	Turkey breast in pieces, approximately 15g	76.0
02	Salt	1.00
03	Wet panada, BAB 137*	5.80
04	Water	10.2
05	Dry panada, Panko 102*	7.00
		100.0

	Flavouring:	%(m/m) (based on the total mass of additives 1-5)
06a	Flavouring, carrot, liquid	0.16
06b	Flavouring, carrot, capsules	1.0**

** corresponds to a carrot flavouring content of 0.16% for a capsule size of 1050 micrometres and a flavouring dilution with oil in the core of 20:80.

* Griffith Laboratories, B-2200 Herentals

Production Method

a - Disperse wet panada (03) and salt (02) in water and allow to swell.

b - Dispersed (sic) flavouring (06a or 06b) of (sic) the swollen wet panada described in a).

c - Add meat to the flavoured wet panada.

d - Allow to drain off and roll in dry panada (05).

e - Deep fry the panada-coated meat pieces in vegetable fat, approximately 180°C, for approximately 4 minutes.

The deep-fried turkey breast pieces were sampled for odour (aroma by smelling) and taste.

Table 6:

Application: chicken nuggets					
Flavouring: carrot					
#	Form of flavouring	Taste profile			Dosage in %(m/m)
		Profile 1	Profile 2	Profile 3	
06a	Liquid flavouring	Weak carrot	Slight vegetable	Weak green	0.16
06b	Capsules	Typical carrot	Sweet	Vegetable	1.0

Example 5 (steaming, deep-frying)

The noodles were produced in accordance with the following formulation.

Formulation type: instant, Asiatic

Table 7:

Additive	Ingredients	Gram
01	Wheat flour	1000
02	Water	250
03	Salt	13
04	MSG	1.2
05	Kansui***	1.2
06	Guar gum	0.4
		1265.8

	Flavouring:	%(m/m) (based on the total mass of ingredients 1-6)
07a	Leek flavouring, capsules	1.0%*
07b	Leek flavouring, spheres	1.0%**
07c	Leek flavouring, spray-dried product (20 parts flavouring, 80 parts maltodextrin/gum arabicum)	0.25%

* corresponds to a leek flavouring content of 0.05% - corresponding to 0.25% of the corresponding spray-dried product - for a set capsule size of 1050 micrometres and a flavouring dilution by oil in the core of 5:95%.

** corresponds to a leek flavouring content of 0.05% - corresponding to 0.25% of the corresponding spray-dried product - for a set sphere size of 500 micrometre and an embedded flavouring content of 5%.

** (sic) alkaline solution (imparts a fresh, slightly tart, acidic taste to the noodles) consisting of:

05a	calcium carbonate	0.96
05b	sodium carbonate	0.12
05c	sodium polyphosphate	0.12

Production method

a - Mixing and pressing: ingredients 01-07 are blended in a dough kneader. A crumbly mass forms, which is pressed together to give a sheet using a rolling pin.
b - Leave to rest for 5 minutes.
c - Rolling out the dough: the sheet of dough is rolled out ever thinner between two rollers in a domestic noodle machine, max. 1.1 mm.
d - Cutting the noodles (the sheet of dough that has been rolled out is pressed between two corrugated rollers on a perforated plate to give fine noodle strands.
e - Steaming (the perforated plates with the noodles are cooked in a steamer for 3 minutes under approximately 4 bar at 100 - 110°C until not quite done (instant characteristics of the noodles).
f – Deep frying.
g - The noodles are deep-fried for 50 seconds in hot palm oil at 155 - 160°C. Then drain off the excess fat, cool the noodles and pack - as a result of the deep-frying, the noodles become crisper and tastier and keep for longer.

The noodles were assessed for odour (aroma by sniffing) and taste (in the mouth). The result of the organoleptic testing (7 test persons) summarised in Table 8 showed that, compared with the spray-dried flavouring in the same dosage, the encapsulated

flavouring was still clearly discernible and recognisable, whereas the spray-dried flavouring and the flavouring encapsulated in spheres were virtually no longer recognisable as such.

Table 8

	Capsules	Spheres*	Non-encapsulated spray-dried product
After pressing	Onion-like, green, clearly of leek	Weaker than capsules	Slightly of leek, fairly weak
After cutting	Green, leek, weaker than dough sample	Too weak	Slightly onion-like, weak
After steaming	Slight leek, green weak but recognisable	Too weak	Too weak
Finished noodles	Slightly of leek	Too weak	Too weak

* Matrix-embedded flavouring (spheres) was tested here in comparison with capsules, to show the differences between capsules (co-extruded) and spheres (flavouring emulsified, extruded).

Example 6 (drying with silicon dioxide)

15 g sodium alginate (type Protanal LF20/60, FMC Biopolymer) were dissolved in 985 g demineralised water using a high speed mixer of the Ultra-Turrax type until the aqueous solution became clear. The alginate solution was prepared a few hours before it was used to enable complete hydration of the alginate chains. 2 g leek flavouring concentrate were dissolved in 98 g neutral oil (type Miglyol, CONDEA Chemie GmbH). The two solutions were fed separately from two storage tanks to a vibrating two-way nozzle head by means of gear pumps. The nozzle head system comprised an inner nozzle 150 µm in diameter and an outer nozzle 1000 µm in

diameter. The flow rate of the two solutions was adjusted such that they formed a laminar flow from the nozzle; 400 g per hour flavouring solution (leek) through the inner nozzle and 2800 g per hour alginate solution through the outer nozzle. The vibration was adjusted such that it interrupted the steel (sic) and homogeneous discrete droplets formed. At a frequency of 130 Hz, two-phase droplets approximately 2 mm in diameter were formed. The droplets fell into a 10% calcium chloride reaction bath, so that a solid layer immediately formed around the liquid filler material. The calcium bath reactor consisted of a tube system, through which the calcium chloride solution flowed and thus continuously transported the freshly gelled capsules to the separator unit. The flow rate of the pump for the calcium chloride solution was set for a gelling time of approximately 1 minute. The gelled capsules were transported through the tubular reactor and then separated off on an 800 μm sieve. The sieved capsules were washed with tap water. Because of the syneresis, which takes place during the gelling step, the wet gel capsules then had a diameter of only approximately 1.6 mm, with a water content of the shell material of 98%. 520 g of wet capsules were obtained and these were mixed for approximately 10 minutes with 260 g silicon dioxide (Sipernat S50, Degussa) and then separated off from the silicon dioxide on a vibrating 800 μm circular sieve. 120 g dry capsules with a particle size of 1.2 mm were produced. The water content of the shell material of the dry capsules was 49%. The dry microcapsule contained a total of 83 %(m/m) liquid filler material; the water content was 8.4 %(m/m).

Example 7 (pre-drying plus drying with silicon dioxide)

15 g sodium alginate (type Protanal FL 20/60, FMC Biopolymer) were dissolved in 975 g demineralised water using a high speed mixer of the Ultra-Turrax type. 50 g strawberry flavouring and 1 g polyglycerol ester (type PGPR 90, Danisco Cultor) were dissolved in 39 g neutral oil, 10 g tap water were added and the mixture was initially mixed slowly for approximately 5 minutes and then homogenised for approximately 1 minute using a high speed mixer of the Ultra-Turrax type in order to form a stable water-in-oil emulsion. The two solutions were fed to a vibrating two-way nozzle head with an inner diameter of 150 μm and an outer diameter of

1000 µm. The flow rates were set to 300 g per hour for the flavouring solution and to 3000 g per hour for the shell solution and the vibration frequency was set to 180 Hz. Two-phase droplets approximately 1.8 mm in diameter were formed. The droplets fell into a 10% calcium chloride reaction bath. The flow rate of the pump for the calcium chloride reaction bath was set for a gelling time of approximately 1 minute. The gelled capsules were separated off on an 800 µm sieve and washed. The wet gel capsules had a diameter of 1.7 mm and a water content of the shell material of 97%. 605 g wet capsules were obtained and, for the purposes of pre-drying, were pre-dried for approximately 10 minutes in a fluidised bed drier (type STREA 1, Aromatic (sic)) with an air flow of 100 m^3 per hour and an inlet temperature of 50°C. 490 g pre-dried capsules were obtained, mixed with 200 g silicon dioxide (Sipernate S50, Degussa) for approximately 5 minutes and then separated off on a vibrating 800 µm circular sieve. 140 g dry capsules with a particle size of 1.1 mm were produced. The water content of the shell material was 49%. The total microcapsule contained 79.1% liquid filler material; the water content was 10.2%.

Example 8 (drying with silicon dioxide)

15 g sodium alginate (type Protanal LF 20/60, FMC Biopolymer) and 10 g gellan gum (type Kelcogel, Kalco) were dissolved in 975 g demineralised water using a high speed mixer of the Ultra-Turrax type. 500 g of a peppermint flavouring solution were prepared. The two solutions were fed to a vibrating two-way nozzle head with an inner diameter of 200 µm and an outer diameter of 500 µm. The flow rates were set to 500 g per hour flavouring solution and 800 g per hour shell solution and the vibration frequency to 200 Hz. A two-phase droplet approximately 1.4 µm in diameter was formed. The droplets fell into a tubular reactor containing 5% calcium chloride solution. The flow rate of the pump for the calcium chloride reaction bath was set for a gelling time of approximately 10 seconds. The gelled capsules were separated off on an 800 µm sieve and washed. The wet gel capsules had a diameter of 1.2 mm and a water content of the shell material of 96.5%. The 1100 g wet capsules obtained were mixed with 275 g silicon dioxide (Sipernat S50, Degussa) for

approximately 10 minutes and then separated off from the silicon dioxide on a vibrating 800 µm circular sieve. An amount of 540 g dry capsules with a particle size of 0.9 mm was produced. The water content of the shell material was 46%. The total microcapsule contained 93.1% liquid filler material; the water content was 3.2%.

Example 9 (continuous gelling process; short gelling time)

This example serves to demonstrate the improvement that can be achieved in respect of the flavouring component encapsulation in alginate microcapsules if the gelling process is carried out as a continuous one-minute procedure, compared with the encapsulation technologies carried out as a batch procedure, in which the gelled capsules remain in contact with the gelling bath for hours.

50 g sodium alginate were dissolved in 1950 g demineralised water using a high speed mixer of the Ultra-Turrax type. 250 g model flavouring were dissolved in 750 g neutral oil. The model flavouring consisted of flavouring components that covered a broad spectrum of water/oil solubilities indicated by $\log K_{o/w}$ values; see Table 9 below.

Table 9

Component	**Amount % (m/m)**	**Log $K_{o/w}$**
Anisalcohol	5	0.95
Ethyl propionate	5	1.24
Benzaldehyde	5	1.64
Isoamyl acetate	5	2.12
Ethyl caprylate	5	3.9

The two solutions (alginate, flavouring) were fed to a vibrating two-way nozzle head with an inner diameter of 150 µm and an outer diameter of 500 µm. The flow rates were set to 500 g per hour for the flavouring solution and to 1000 g per hour for the shell solution and the vibration frequency was set to 220 Hz.

For the preferred short continuous gelling process, the discrete droplets formed fell into a tubular reactor that was filled with 5% calcium chloride and were transported in such a way that the dwell time was 1 minute. The resulting wet capsules were sieved and washed with tap water.

The result of a one-minute capsule production (corresponding to 8.3 g encapsulated flavouring solution) was then dissolved in 200 ml 1% aqueous sodium citrate solution. The mixture was then extracted with diethyl ether for 4 hours in a perforator. The diethyl ether extract was analyzed by means of HRGC/MS. The results were evaluated based on the surface area of the GC/MS peaks for each component per gram encapsulated flavouring solution.

For the batch gelling process, the discrete droplets formed fell into a reactor containing 5% calcium chloride with a dwell time of two hours. The wet capsules formed were then sieved and washed with tap water. The same analytical protocol as for the short gelling time process was carried out.

10 g model flavouring solution were dispersed in 200 ml 1% aqueous sodium citrate solution. The mixture was extracted with diethyl ether for 4 hours in a perforator and evaluated as described above.

The flavour retention was calculated for each flavouring component during the short continuous gelling process and the long gelling batch process on the basis of the amount of the model flavouring solution that had originally flowed through the nozzle system and theoretically had been encapsulated; the results are summarised in Table 10.

Table 10

Flavour Retention:

Components	Short gelling time (continuous)	Long gelling time (batch)
Anisalcohol	60%	6%
Ethyl propionate	61%	0%
Benzaldehyde	82%	11%
Isoamyl acetate	80%	18.5%
Ethyl caprylate	90%	90%

The flavour retention of the substances with a $\log K_{o/w} < 3.9$ was thus distinctly better in the process with a short gelling time than in the process with a long gelling time.

Example 10 (comparison of different drying processes)

This example serves to demonstrate the difference that exists with regard to flavour retention between a conventional convective drying process (fluidised bed drier) and the drying process using water-binding substances.

A sample of the wet capsule product, produced according to the method with a short gelling time, as has been described in Example 4, was divided into two equal batches of 200 g after washing.

The first batch was dried by adding 100 g silicon dioxide to the wet capsules. The substances were mixed for 10 minutes and the dried capsules were then manually separated off from the silicon dioxide on an 800 µm-sieve. 60 g dried capsules were obtained. The water content of the shell material of the dried capsules was 45% (corresponding to 7% water content and 84.2% liquid filler material based on the mass of the total capsule).

The second 200 g batch was dried in a fluidised bed drier (type STREA 1, Aeromatic) at an inlet temperature of 30°C and an air flow of 100 m^3 per hour, in order to obtain an amount of dried capsules of 60 g. The water content of the shell material of the dried capsules was 62% (corresponding to 14.4% water content and 76.8% liquid filler material based on the mass of the total capsule).

The different amounts of liquid filler material that were found in the two types of dried capsule already show the difference with regard to the flavour retention that is associated with the two drying processes. The capsules dried with silicon dioxide contained 50.52 g (84.2%) liquid filler material; on the other hand, the capsules dried in the fluidised bed contained only 46.08 g (76.8%) liquid filler material.

The details of the retention of each flavouring component are shown in Table 11 below. The analytical method used was identical to that described in Example 9.

Table 11

	Drying [lacuna] "water-binding" substances: % retention	**Convective drying: % retention**
Anisalcohol	33%	5%
Ethyl propionate	50%	4%
Benzaldehyde	80%	52%
Isoamyl acetate	95%	60%
Ethyl caprylate	0%	65%

Example 11 (influence of the water content in the shell on the stability to heat)

This example underlines the importance of the water content that is present within the shell material of the dried capsules in order to guarantee efficient stability of the encapsulated flavouring to heat during a heating process.

Capsules containing cheese flavouring were added to a cracker dough and then baked. The capsules had different water contents (different degrees of drying). The flavouring dosage was kept identical for all tests.

The crackers were prepared in accordance with the following formulation (Table 12):

Table 12

	Additives	**Amount (%)**
1	Vegetable fat	7.98
2	Industrial sugar	1.55
3	Fructose syrup	1.55
4	Salt	1.15
5	Wheat flour (cracker type)	66.53
6	Ammonium bicarbonate	0.89
7	Malt extract syrup	0.806
8	Sodium monophosphate	0.665
9	Sodium bicarbonate	0.55
10	Citric acid	0.066
11	Bacterial protease	0.027
12	Sodium metabisulphite	0.016
13	Water	19.37

Cracker preparation method

1. Mix the ingredients 1, 2, 3, 4 and 13 (70°C) until they have completely dissolved.

2. Add 5-12 and the desired amount of capsules to the dough.

3. Mix for approximately 10 minutes.

4. Allow the dough to stand for 2 hours at room temperature.

5. Roll out the dough (2 mm) and cut into cracker shapes.

6. Bake in an oven at 185°C (preheat the oven to 210°C) for 4 minutes.

The crackers were assessed by a sensory test group (10 persons) in respect of intensity of taste in the mouth. The assessment scale ranged from 1 - 5:

0 no taste
1 very weak flavour note, almost unrecognisable
2 flavour note too weak
3 acceptable taste note
4 good and strong taste note
5 taste note too strong

The results are summarised in Table 13.

Table 13

Capsule type	Mass ratio water/capsule shell	Mass ratio capsule/cracker	Mass ratio flavouring/cracker	Sensory rating
wet	95%	3.5%	0.04%	1
slightly dried	91%	2.7%	0.04%	1
medium-dried	66.7%	1.3%	0.04%	2
dried	38.9%	1%	0.04%	4

Because of their high stability to heat, the dried capsules impart clearly the best sensory results.

Example 12 (effects of different forms of application of flavouring)

This example shows the different sensory ratings of leek taste, which was applied to crackers in liquid form, in spray-dried form and in capsule form.

The crackers were prepared as described in Example 6 and baked, but for 4 minutes at 200°C. The sensory assessment of the three different flavouring embodiments summarised in Table 14 is based on the same scale definition as in Example 11.

Table 14

Type of flavouring	Mass ratio (flavouring and carrier), for example capsule/cracker	Mass ratio flavouring/cracker	Sensory values
Liquid	3.5 %	0.04 %	1
Spray-dried	2.7 %	0.04 %	2
Capsule	1.3 %	0.04 %	4

The leek flavouring encapsulated in alginate capsules showed the best results in respect of stability to baking, compared with the standard flavouring embodiments in liquid and spray-dried form, respectively.

Claims

1. Mononuclearly filled seamless microcapsule, comprising

   - a capsule shell of a hardened capsule material based on an acid polysaccharide and

   - a filler material, comprising a flavouring in an organoleptically effective amount, that is enclosed by the capsule shell on all sides,

wherein the microcapsule is stable to heat and/or stable to boiling and/or stable to deep frying and the water content in the capsule shell has been adjusted to a value of ≤ 50 %(m/m), based on the total mass of the capsule shell.

2. Mononuclearly filled microcapsule according to Claim 1, wherein the hardened capsule material for the microcapsules comprises a substance hardened by bringing into contact with monovalent or divalent cations or cations of higher valency.

3. Mononuclearly filled microcapsule according to one of the preceding claims, wherein the hardened capsule material for the microcapsules is selected from the group comprising alginate, pectate, pectinate, carragheenan, gellan and mixtures thereof

4. Mononuclearly filled microcapsule according to one of the preceding claims, wherein the flavouring contained in the filler material contains at least 10 %(m/m), based on the total mass of the flavouring in the filler material, of one or more flavourings with a $\log K_{o/w} < 2$.

5. Mononuclearly filled microcapsule according to one of the preceding claims, wherein the flavouring contained in the filler material contains at least 10 %(m/m), based on the total mass of the flavouring in the filler material, of one or more flavourings for which the following applies: $1 < \log K_{o/w} < 2$.

6. Mononuclearly filled microcapsule according to one of the preceding Claims 1-4, wherein the flavouring contained in the filler material contains at least 10 %(m/m), based on the total mass of the flavouring in the filler material, of one or more flavourings for which the following applies: $\log K_{o/w} < 1$.

7. Food composition, comprising

- one or more mononuclearly filled microcapsules according to one of the preceding claims and

- a carrier material for the microcapsule(s).

8. Method for the production of mononuclearly filled microcapsules according one of Claims 1-6, with the following steps:

- providing a liquid filler material for the microcapsules containing a flavouring in an organoleptically effective amount,

- providing a, preferably aqueous, solution or dispersion of a capsule material, capable of being hardened, based on an acid polysaccharide,

- forming discrete droplets of the liquid filler material for the microcapsules and the solution or dispersion of the capsule shell material capable of being hardened, so that the capsule material capable of being hardened surrounds the liquid filler material in the droplets on all sides,

- hardening the capsule shell material capable of being hardened, so that seamless polysaccharide capsules are formed, which each mononuclearly surround filler material and are stable to heat and/or stable to boiling and/or stable to deep frying,

- drying the capsule shell formed until the water content in the capsule shell reaches a value of ≤ 50 %(m/m), based on the total mass of the capsule shell.

9. Method according to Claim 8, wherein the seamless polysaccharide capsules are brought into contact with a water-adsorbing or water-binding substance to dry the capsule shell formed.

10. Method according to one of Claims 8 to 9, wherein the capsule shell material capable of being hardened can be hardened by bringing into contact with polyvalent cations, the discrete droplets being brought into contact with a solution that contains the polyvalent cations in order to harden the capsule shell material capable of being hardened.

11. Method according to one of Claims 8-10, wherein the discrete droplets are brought into contact with the solution that contains polyvalent cations for a period of at most 1 minute in order to harden the capsule shell material capable of being hardened.

12. Method according to one of Claims 10 or 11, wherein the seamless polysaccharide capsules formed are washed before drying the capsule shell formed, in order to remove polyvalent cations from the capsule surface.