A tobacco product is provided comprising a core-shell capsule with a capsule shell comprising cellulose acetate and/or a derivative thereof. A method of producing a core-shell capsule with a capsule shell comprising cellulose acetate and/or a derivative thereof by diffusion is also provided.
Products Including Capsules, Uses and Preparation Thereof

Field
The present invention relates to capsules for incorporation into a tobacco product and methods of making the same.

Background
The sensory attributes of a tobacco product can be altered by applying additives to the tobacco product. For example, some tobacco products contain capsules, and the contents of the capsules are released into the tobacco product upon rupture of those capsules. The capsules incorporated in the tobacco products can be manufactured using various materials and by various methods.

Summary
According to a first aspect, there is provided a tobacco product or part thereof comprising a core-shell capsule, wherein the capsule shell comprises cellulose acetate and/or a derivative thereof and the core-shell capsule is formed by a method comprising diffusion.

According to a second aspect, there is provided a use of a core-shell capsule in a tobacco product or part thereof, wherein the capsule shell comprises cellulose acetate and/or a derivative thereof and the core-shell capsule is formed by a method comprising diffusion.

According to a third aspect, there is provided a method for the manufacture of a tobacco product or part thereof comprising a core-shell capsule, the process comprising:

preparing a carrier structure from a carrier material;
encapsulating said carrier structure with a film forming material comprising cellulose acetate and/or a derivative thereof so as to form a shell completely surrounding the carrier structure;
exposing said encapsulated carrier structure to a medium in which said carrier material is soluble or dispersible, so that the carrier material is at least partially removed from within the shell by diffusion;
removing the resultant core-shell capsule from said medium; and
incorporating the core-shell capsule into a tobacco product or part thereof.
In some embodiments of the method, the resultant core-shell capsule comprises an additive. In some embodiments, said additive is present in the medium and at least some of the additive diffuses into the capsule through the shell as the carrier material is at least partially removed. Additionally or alternatively, the additive is present in the carrier material and at least some of the additive remains within the capsule as the carrier material is at least partially removed.

In some embodiments of the first, second and/or third aspects, the tobacco product is a smoking article or a smokeless oral tobacco product. In some embodiments, the tobacco product part is a filter or a filter element, or is a rod or portion of tobacco.

**Brief Description of the Figures**

Embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

- Figure 1 is a schematic illustration of a cross-section of a smoking article containing a core-shell capsule according to some embodiments of the present invention;
- Figure 2 is a schematic illustration of a cross-section of a smoking article containing a plurality of core-shell capsules according to some embodiments of the present invention;
- Figure 3 is a schematic illustration of a cross-section of a smokeless oral tobacco product containing a core-shell capsule according to some embodiments of the present invention; and
- Figure 4 is a schematic illustration of a cross-section of a core-shell capsule according to some embodiments of the present invention.

**Detailed Description**

There is provided a tobacco product or part thereof comprising a core-shell capsule, the capsule shell comprising cellulose acetate and/or a derivative thereof.

As used herein, the term "core-shell capsule" includes capsules that comprise a core and a shell.

As used herein, the term "tobacco product" includes smokeless oral tobacco products and smokeable tobacco products, such as smoking articles.
As used herein, the term "smoking article" includes smokeable products such as cigarettes, cigars and cigarillos whether based on tobacco, tobacco derivatives, expanded tobacco, reconstituted tobacco or tobacco substitutes and also heat-not-burn products (i.e. products in which flavour is generated from a smoking material by the application of heat without causing combustion of the material) and other articles capable of generating tobacco-derived aerosols. Typically, smoking articles are provided with filters for removing constituents from the gaseous flow.

As used herein, the term "smokeless oral tobacco product" includes any smokeless tobacco product designed to be placed in the oral cavity of a user for a limited period of time, during which there is contact between the user's saliva and the product.

The core-shell capsule is formed by a method which involves diffusion. In some embodiments, the core-shell capsule is formed by a method based on diffusional exchange.

As used herein, the term "diffusional exchange" is used to refer to the exchange of one or more substances across a barrier or membrane by diffusion.

In some embodiments, the core-shell capsule is not produced by electrospraying or electroprocessing.

Figure 1 shows a cross-section of a smoking article 10 in which a core-shell capsule 1 is incorporated into the filter 2 of the smoking article 10, in accordance with an embodiment of the invention. The smoking article 10 comprises a rod of smokeable material 6 and a filter 2. The rod of smokeable material 6 and filter 2 shown in Figure 1 are attached to each other by tipping paper 3, although other means for attaching the rods of smokeable material to a filter that are known in the art may be employed in the alternative. In the illustrated embodiment, the filter 2 is wrapped in a length of tipping paper 3 which is longer than the filter 2 and connects the rod of smokeable material 6 to the filter 2 in a manner well known in the art. The filter 2 of the smoking article 10 may be wrapped in a plugwrap 4 in addition to the tipping paper 3. The rod of smokeable material 6 may be formed from cut rag tobacco, reconstituted and/or pelletised tobacco and is circumscribed by a wrapper 5.
The core-shell capsule 1 may be positioned largely centrally along the length of the filter 2 of the smoking article 10. Alternatively, the core-shell capsule may be positioned towards or at one end of the filter 2, such as towards the end of the filter 2 adjacent to the rod of smokeable material 6 of the smoking article 10, or towards the end of the filter 2 which forms the mouth end of the smoking article 10.

The core-shell capsule 1 may be positioned largely along the longitudinal axis of the filter 2 of the smoking article 10. Alternatively, the core-shell capsule may be positioned towards the periphery of the filter 2 of the smoking article 10 (not shown).

The filter 2 can comprise two or more filter elements. The filter or filter elements may be any conventional filter or filter element known to a person skilled in the art. For example, the filter or element may comprise any filter material or combination of filter materials. A smoking article may comprise multiple filter elements and at least one cavity, the cavity being positioned between two filter elements or at one end of the filter.

In some embodiments, the tobacco product comprises a single core-shell capsule 1. In alternative embodiments, the tobacco product comprises a plurality of core-shell capsules 1.

Figure 2 shows a cross-section of a smoking article 20 containing a plurality of core-shell capsules n arranged in a spaced configuration along the longitudinal axis of the smoking article 20, in accordance with an embodiment of the invention. In some embodiments, the capsules n are positioned peripherally or in a more random configuration.

In Figure 2, the capsules n are positioned wholly within the rod of smokeable material 16. In other embodiments, some or all of the capsules n may be positioned within one or more other component(s) of the smoking article 20, such as the filter 12.

In some embodiments (not shown), one or more capsule(s) 11 are positioned between one or more of the component(s) of a smoking article 20. For example, one or more capsules 11 may be positioned between the filter 12 and the rod of smokeable material 16 of the smoking article 20.
In some embodiments (not shown), the capsules 11 may be positioned so that they are partially within the tobacco product or part thereof.

Figure 3 shows a cross-section of a smokeless oral tobacco product 30 containing a core-shell capsule 21 arranged within the tobacco-containing material 26 of the product 30, in accordance with an embodiment of the invention. In some embodiments (not illustrated) the product has a plurality of capsules distributed within the tobacco-containing material 26. The capsules may all be the same or they may be different, for example containing different additives and/or having different configurations, for example some having an outer coating and some not.

The capsules incorporated into different products or into different parts of products, such as those described with reference to Figures 1 to 3 above, may be different. For example, the physical characteristics of the capsules may be different and may be selected to be optimised for the particular use. As an example, capsules incorporated into the filter of a smoking article may differ to those that are incorporated into the rod of smokeable material of a smoking article; they might have a smaller diameter. Additionally or alternatively, capsules of a smaller diameter may be used where a plurality of capsules are to be incorporated into a single product.

Figure 4 shows a cross-section of a core-shell capsule 31 according to some embodiments. The capsule illustrated in Figure 4 and described below may, in some embodiments, be used in any of the embodiments illustrated in Figures 1 to 3 and described herein. The core-shell capsule 31 comprises a shell 32 and an internal core 33. In this embodiment, the shell is coated with an outer coating 34.

The shell 32 of the core-shell capsule 31 comprises cellulose acetate and/or a derivative thereof. Suitable cellulose acetate derivatives will be known to the person skilled in the art. In some embodiments, the shell 32 comprises cellulose acetate phthalate, referred to herein as cellulose phthalate. In some embodiments, the shell 32 comprises cellulose triacetate. In some embodiments, the shell material consists essentially of cellulose acetate and/or derivatives thereof. In some embodiments, the shell material comprises cellulose derivatives. In some embodiments, the shell material does not comprise gelatin.
In some embodiments, the shell 32 comprises a continuous layer or film of shell material. In other words, the shell material may form a continuous coating around the internal core 33 of the capsule without the need to plug any holes in the shell or to seal one or more edges or sections of the shell material together.

In some embodiments, the shell 32 of the core-shell capsule 31 is coloured. In some embodiments, the colouring is food grade colouring. In some embodiments, the shell 32 is a different colour from the core 33 of the core-shell capsule 31. Such an arrangement may be advantageous for determining whether the core 33 is completely coated by the shell 32.

In some embodiments, the internal core 33 of the core-shell capsule 31 comprises an additive. The additive may be any substance that modifies and/or enhances the characteristics of the tobacco product, such as the sensory attributes of a tobacco product. For example, when the core-shell capsule 31 is incorporated into a smoking article, the additive may be anything which may be added to smoke and/or which may modify the composition of smoke.

The additive may be in solid, liquid and/or gaseous phase. In some embodiments, the additive is in liquid phase. In some embodiments in which the core-shell capsule 31 is placed in a smoking article, the additive changes phase during use of the smoking article. Such an arrangement may advantageously release more additive during use of the smoking article. In some embodiments, the additive in the core-shell capsule 31 changes from solid phase to liquid phase during use of the smoking article.

The additive may be a flavour or flavourant (where permitted by local regulations), a deodoriser, a diluent, an adsorbent, or any other substance that is capable of modifying the tobacco product. The additive may comprise, consist essentially of and/or consist of water. The additive may comprise at least 50% water, at least 75% water, at least 80% water, at least 85% water, at least 90% water, at least 95% water and/or 100% water.

As used herein, the terms "flavour" and "flavourant" refer to materials which, where local regulations permit, maybe used to create a desired taste or aroma in a product for adult consumers. They may include extracts (e.g., licorice, hydrangea, Japanese white bark magnolia leaf, chamomile, fenugreek, clove, menthol, Japanese mint, aniseed, cinnamon, herb, wintergreen, cherry, berry, peach, apple, Drambuie, bourbon, scotch,
whiskey, spearmint, peppermint, lavender, cardamon, celery, cascarilla, nutmeg, sandalwood, bergamot, geranium, honey essence, rose oil, vanilla, lemon oil, orange oil, cassia, caraway, cognac, jasmine, ylang-ylang, sage, fennel, piment, ginger, anise, coriander, coffee, or a mint oil from any species of the genus Mentha), flavour enhancers, bitterness receptor site blockers, sensorial receptor site activators or stimulators, sugars and/or sugar substitutes (e.g., saccharin, aspartame, acesulfame potassium, saccharine, cyclamates, lactose, sucrose, glucose, fructose, sorbitol, or mannitol), and other additives such as charcoal, chlorophyll, minerals, botanicals, or breath freshening agents. They may be imitation, synthetic or natural ingredients or blends thereof. They may be in any suitable form, for example, oil, liquid, or powder.

In some embodiments, the additive comprises menthol. The additive may comprise at least 50% menthol, at least 75% menthol, at least 80% menthol, at least 85% menthol, at least 90% menthol, at least 95% menthol and/or approximately 100% menthol.

In some embodiments, the additive comprises Kreteks-style flavours, clove extract and/or any natural or synthesised compound that may be present in cloves or clove extract, such as eugenol.

In some embodiments, the additive may be mixed with a solvent. Suitable solvents will be known to the person skilled in the art. In some embodiments in which the additive comprises menthol, propylene glycol may be a suitable solvent.

Alternatively or in addition, the additive in the internal core 33 of the core-shell capsule 31 may comprise a carrier material. In some embodiments, the carrier material is and/or comprises polyethylene glycol (also known as PEG).

The internal core 33 of the core-shell capsule 31 may contain a single type of additive. Alternatively, the internal core 33 may contain a plurality of types of additive. In some embodiments, the internal core 33 comprises two different types of additives. For example, the different additive types may be different flavourants, or, one type may be a flavourant and another type may be an additive which is not a flavourant.

In some embodiments, the core-shell capsule 31 may be coated with an outer coating 34. This outer coating is optional, but may be preferred in some embodiments. In some embodiments, the outer coating 34 may be a moisture-impermeable coating. The moisture-impermeable layer may serve to ensure that any additive in the inner core 33
is retained in the core-shell capsule 31 until it is desirable for the additive to be released. In embodiments in which the internal core 33 of the core-shell capsule 31 comprises an additive material that is water-soluble, or includes or is water, the outer coating 34 may be impermeable or substantially impermeable to water.

The core-shell capsule 31 may comprise more than one outer coating 34. In these embodiments, the plurality of outer coatings 34 may have the same or substantially the same composition of materials. Alternatively, the composition of the plurality of the outer coatings may be different.

Suitable materials for the outer coating 34 will be known to the person skilled in the art. In some embodiments, the outer coating 34 comprises wax, such as castor wax, bees wax, carnauba wax, or a combination thereof.

Alternatively or in addition, the outer coating 34 may comprise cellulose acetate and/ or one or more cellulose derivatives. Suitable cellulose derivatives will be known to the person skilled in the art, and may comprise hydroxypropyl methylcellulose (HPMC) and/or carboxymethyl cellulose (CMC).

Alternatively or in addition, the outer coating 34 may comprise one or more plasticiser(s). As used herein, the term 'plasticiser' includes softeners but does not include water.

The one or more plasticiser(s) may be used to effect and/or assist in the impermeabilisation of the outer coating 34 of the core-shell capsule 31. The one or more plasticiser(s) may achieve this by limiting or reducing the leakage of the internal core 33 to outside of the core-shell capsule 31.

Alternatively or in addition, the shell 32 of the core-shell capsule 31 may comprise one or more plasticiser(s). The one or more plasticiser(s) may be used to effect and/or assist in the impermeabilisation of the shell 32 of the core-shell capsule 31. The one or more plasticiser(s) may achieve this by limiting or reducing the leakage of the internal core 33, when it is in a liquid or gaseous phase, to outside of the core-shell capsule 31.

In embodiments in which the shell 32 of the core-shell capsule 31 comprises one or more plasticiser(s), if the material of the shell 32 of the core-shell capsule 31 is a
substance that could also be considered to be a plasticiser, the at least one plasticiser is a substance different from the material of the shell 32 of the core-shell capsule 31.

In some embodiments, the at least one plasticiser is impermeable to water and/or is liposoluble. In some embodiments, the at least one plasticiser is impermeable to fats and/or is water-soluble.

The at least one plasticiser may be selected from a group comprising triacetin, dibutyl phthalate, dibutyl sebacate, diethyl phthalate, dimethyl phthalate, acetyltributyl citrate, acetyltriethyl citrate, diacetylated monoglycerides, dibutyl sebacate, mineral oil, benzyl benzoate, chlorbutanol, glycerin monostearate, lanolin alcohols and cellulose acetate phthalate compatible plasticisers. These compounds are particularly suitable when it is desirable for the shell 32 and/or the outer coating 34 of the core-shell capsule 34 to be liposoluble.

Alternatively or in addition, the at least one plasticiser may be selected from a group comprising polyvinylpyrrolidone (PVP) and polyvinyl alcohol (PVA).

Alternatively or in addition, the at least one plasticiser may be selected from a group comprising triethyl citrate, triacetin, benzyl benzoate, dibutyl phthalate and 2,5-dimethylpyrazin.

In some embodiments, the core-shell capsule 31 comprises 0.1 to 30 wt.% plasticiser. The core-shell capsule may comprise 0.5 to 20 wt.%, 1 to 15 wt.% and/or 2 to 10 wt.% plasticiser. The core-shell capsule 31 may comprise 4 to 8 wt.% plasticiser.

In some embodiments, the outer coating 34 of the core-shell capsule 31 comprises more than 15 wt.% more than 20 wt.%, more than 25 wt.% more than 30 wt.% more than 35 wt.% more than 40 wt.% or more than 45 wt.% plasticiser said percentage referring to the weight of the outer coating 34. In some embodiments, the outer coating 34 of the core-shell capsule 31 comprises at least 15 wt.%, at least 20 wt.%, at least 25 wt.%, at least 30 wt.%, at least 35 wt.%, at least 40 wt.% or at least 45 wt.% plasticiser.

In some embodiments, the shell 32 of the core-shell capsule 31 comprises less than 40 wt.% plasticiser, said percentage referring to the weight of the shell 32. The shell 32 may comprise less than 30 wt.%, less than 20 wt.%, less than 10 wt.%, less than 5 wt.%
or less than 3 wt.% plasticiser. In some embodiments, the shell 32 of the core-shell capsule 31 is free or substantially free from plasticiser.

In some embodiments, the shell 32 of the core-shell capsule 31 comprises at least 1 wt.%, at least 2 wt.% at least 5 wt.% or at least 10 wt.% plasticiser, said percentage referring to the weight of the shell 32.

In some embodiments, the outer coating 34 of the core-shell capsule 31 comprises one or more plasticiser(s) and the shell 32 of the core-shell capsule 31 is free or substantially free of plasticiser. In some embodiments, the outer coating 34 comprises a greater amount of plasticiser in percent by weight than the shell 32 of the core-shell capsule 31.

In some embodiments, the shell 32 of the core-shell capsule 31 is substantially free of plasticiser and the outer coating 34 comprises at least 1 wt.%, at least 3 wt.%, at least 5 wt.%, at least 8 wt.% or at least 10 wt.% plasticiser, said percentage referring to the weight of the outer coating 34.

In some embodiments in which the additive in the internal core 33 of the core-shell capsule 31 comprises water, the core-shell capsule 31 is impermeable to water, so that, when stored for 1 month at 25°C at a relative humidity (rH) of 75%, at least some of the water is retained in the internal core 33 of the core-shell capsule 31. Under these conditions, at least 40 wt.%, at least 50 wt.% or at least 60 wt.% of the water may be retained in the internal core 33 of the core-shell capsule 31, compared to the start of said 1-month period and/ or to the initial water content.

In some embodiments in which the additive in the internal core 33 of the core-shell capsule 31 comprises water, the core-shell capsule 31 is impermeable to water, so that, when stored for 2 months at 25°C at a relative humidity (rH) of 75%, at least some of the water is retained in the internal core 33 of the core-shell capsule 31. Under these conditions, at least 40 wt.%, at least 50 wt.%, at least 60 wt.% or at least 70 wt.% of the water may be retained in the internal core 33 of the core-shell capsule 31, compared to the start of said 2-month period and/or to the initial water content.

In some embodiments in which the additive in the internal core 33 of the core-shell capsule 31 comprises water, the core-shell capsule 31 is impermeable to water, so that,
when stored for 3 months at 25°C at a relative humidity (rH) of 75%, at least some of the water is retained in the internal core 33 of the core-shell capsule 31. Under these conditions, at least 40 wt.%, at least 50 wt.%, at least 60 wt.% or at least 70 wt.% of the water may be retained in the internal core 33 of the core-shell capsule 31, compared to the start of said 3-month period and/or to the initial water content.

In some embodiments in which the additive in the internal core 33 of the core-shell capsule 31 comprises water, the core-shell capsule 31 is impermeable to water, so that, when stored for 4 months at 25°C at a relative humidity (rH) of 75%, at least some of the water is retained in the internal core 33 of the core-shell capsule 31. Under these conditions, at least 40 wt.%, at least 50 wt.%, at least 60 wt.% or at least 70 wt.% of the water may be retained in the internal core 33 of the core-shell capsule 31, compared to the start of said 4-month period and/or to the initial water content.

In some embodiments in which the additive in the internal core 33 of the core-shell capsule 31 comprises water, the core-shell capsule 31 is impermeable to water, so that, when stored for 5 months at 25°C at a relative humidity (rH) of 75%, at least some of the water is retained in the internal core 33 of the core-shell capsule 31. Under these conditions, at least 40 wt.%, at least 50 wt.%, at least 60 wt.% or at least 70 wt.% of the water may be retained in the internal core 33 of the core-shell capsule 31, compared to the start of said 5-month period and/or to the initial water content.

In some embodiments in which the additive in the internal core 33 of the core-shell capsule 31 comprises water, the core-shell capsule 31 is impermeable to water, so that, when stored for 6 months at 25°C at a relative humidity (rH) of 75%, at least some of the water is retained in the internal core 33 of the core-shell capsule 31. Under these conditions, at least 40 wt.%, at least 50 wt.%, at least 60 wt.% or at least 70 wt.% of the water may be retained in the internal core 33 of the core-shell capsule 31, compared to the start of said 6-month period and/or to the initial water content.

The core-shell capsule 31 may be a suitable size to be incorporated into a tobacco product.

In some embodiments, optionally including the embodiments described above and illustrated in Figures 1 to 3, the core-shell capsule has a diameter within the range 1.5 to 10 mm, and optionally within the range 2 to 8 mm. In some embodiments, the core-
shell capsule has a diameter in the range 3 to 5 mm, optionally 3.4 to 4.8 mm and further optionally 3.5 to 4.5 mm. In some embodiments, the core-shell capsule has a diameter in the range of 2.5 to 4 mm. In some embodiments, the core-shell capsule has a diameter of about 3.5 mm. In some embodiments, the core-shell capsule has a diameter of 1 mm, at least 1.5 mm, at least 2 mm, at least 2.5 mm, at least 3 mm, at least 3.1 mm, at least 3.2 mm, at least 3.3 mm, at least 3.4 mm, at least 3.5 mm, at least 3.6 mm, at least 3.7 mm, at least 3.8 mm, at least 3.9 mm, at least 4 mm, at least 4.5 mm, at least 5 mm, at least 6 mm, at least 7 mm, at least 8 mm, at least 9 mm, or at least 10 mm. In some embodiments, the core-shell capsule has a diameter of at least 2 mm. In some embodiments, the core-shell capsule has a diameter of greater than 1 mm, greater than 2 mm, greater than 3 mm or greater than 4 mm.

In some embodiments, the core-shell capsule is not a microcapsule or a nanocapsule. As used herein, the terms "microcapsule" and "nanocapsule" refer to capsules with a diameter of less than 1 mm and less than 1 µm, respectively.

The average capsule size may be determined by laser diffraction analysis, in particular as specified in the international standard ISO 13320-1. For example, a Malvern Mastersizer 3000 may be used. This methodology is useful for determining average capsule sizes in the range of 0.2 µm to 3.5 mm. For larger diameters (such as diameters greater than 3.5 mm), the average diameter can be determined by manually measuring, if applicable using a microscope, a statistically representative sample of the capsules. The average is the arithmetic mean for the purpose of this specification.

In some embodiments the core-shell capsule is spherical or substantially spherical. Alternatively, the core-shell capsule may be elongate, optionally with a longitudinal axis extending parallel to a longitudinal axis of the tobacco product.

Generally, the contents of the core-shell capsule are to be released prior to and/or during use, and in some circumstances even after use of the tobacco product or part thereof into which the capsule has been incorporated. The contents of the core-shell capsule may be released by any suitable means. In some embodiments, the contents of the core-shell capsule are released by rupturing the capsule, so as to release the additive at a predetermined moment. In other words, the core-shell capsule may be rupturable.
In some embodiments in which the core-shell capsule 31 is in a tobacco product, the user can break the capsule by breaking the shell 32 and/or the outer coating 34 of the capsule 31 by applying pressure to the part of the tobacco product which surrounds the core-shell capsule 31. For example, in embodiments in which the core-shell capsule 31 is positioned within a filter of a smoking article, the shell 32 and/or the outer coating 34 of the capsule 31 may be ruptured by applying pressure to the external surface of the filter.

The core-shell capsules of the present invention are produced by a process that is based on diffusion through the shell of core-shell capsules. Surprisingly, by using a multiple step process, the inventors have overcome the limitations of prior art methods, which are virtually all limited to a small range of capsule sizes.

In some embodiments, the method comprises the steps of producing a shell of core-shell capsules, exposing said shell to a medium comprising an additive and allowing the diffusion and/or osmosis of the additive through said shell.

In some embodiments, the method comprises the steps of: producing a precursor core-shell capsule comprising a carrier structure or core encapsulated by a film-forming material forming a shell; and exposing said precursor core-shell capsule to conditions that result in the diffusion and/or osmosis of at least part of the material of the carrier structure from the core through the shell to the outside of the shell.

In some embodiments, the method comprises the steps of: producing a precursor core-shell capsule comprising a carrier structure or core and an additive encapsulated by a film-forming material forming a shell; exposing said precursor core-shell capsule to conditions that result in the diffusion and/or osmosis of at least part of the material of the carrier structure from the core through the shell to the outside of the shell, while at least some of the additive remains in the core of said capsule.

In some embodiments, the method of preparing a core-shell capsule with a core comprising an additive comprises:

preparing a solid carrier structure from a carrier material that is dissolvable in a solubilising medium;

encapsulating said solid carrier structure so as to obtain an encapsulated carrier structure surrounded by a shell (a precursor core-shell capsule);
exposing said encapsulated carrier structure to said medium for a duration sufficient to at least partially replace at least some of the material of the carrier structure by said medium, thereby obtaining a core-shell capsule with a core comprising said medium and a shell; and removing the core-shell capsule from the medium.

In some embodiments, an additive is mixed with the carrier material before and/ or during formation of the carrier structure. Alternatively or in addition, in some embodiments, an additive is contained in the solubilising medium.

In some embodiments, the method of preparing core-shell capsules by countercurrent flow diffusion comprises the steps of:
- preparing substantially spherical, self-sustained carrier beads from a carrier material, said carrier beads having a diameter in the range of 1 µm to 1 cm;
- encapsulating said self-sustained carrier beads with an appropriate film-forming material to form a semi-permeable shell in order to obtain precursor core-shell capsules;
- exposing said precursor core-shell capsules to a solubilising medium containing an additive, wherein said carrier material is soluble and/ or dispersible in said medium, so as to favour diffusion of the dissolved and/or dispersed carrier material out of said precursor core-shell capsules and diffusion of said additive into the precursor core-shell capsules, thereby obtaining core-shell capsules comprising an additive.

In some embodiments, the core-shell capsule comprises a core comprising an additive, wherein at least part of said core and/or said additive has properties of or comprises a liquid at 65°C.

In some embodiments, the core-shell capsule comprises a core comprising an additive, wherein at least part of said core and/or said additive is a liquid at 65°C.

In some embodiments, the core-shell capsule comprises a core, at least part of which is liquid, comprises a liquid or has properties of a liquid at 45°C, 35°C and/or 25°C, and a shell, and comprising an additive, said shell comprising cellulose acetate and/or a derivative thereof.
In some embodiments, the methods of the invention may comprise a step of preparing carrier structures, carrier cores or carrier beads from a carrier material. As used herein, the terms "carrier structure", "carrier bead", "carrier core" and "primary core", "primary beads", "primary compound", "precursor beads" and "precursor cores" are interchangeable and may be used for describing the same principle. The expression "core" expresses the fact that said carrier beads and/or cores will form the core of intermediate or precursor core-shell capsules. The expression "primary" expresses that said carrying structure is transient and will generally be replaced by the additive or a medium as specified elsewhere in this specification. In some embodiments, said carrier beads are self-sustained. The feature of being self-sustained refers to the fact that said beads are sufficiently compact so as to function as a framework, allowing for the formation of a shell around them in a further step. Said carrier beads may thus actually be liquid, for example in the form of liquid beads that are suspended in a medium, so that said shell can be formed around said carrier cores. According to one embodiment, however, said beads are in a solid state, for example in the form of a crystal or a non-crystalline solid state, for example in a glassy state. Said feature of being self-sustained, for example solid, refers to the status when being subjected to the step of shell-formation as being described elsewhere in this specification.

One of the innovative aspects of the method of the present invention is the making of a primary, self-contained structure (core, beads), which serves as a scaffold to create a membrane around the primary core, as will be described further below.

In some embodiments, in a still further, subsequent step said beads may be exposed to conditions in which the beads are substantially disintegrated, for example solubilised and/or suspended.

In some embodiments, said carrier beads are substantially spherical.

The carrier beads may be prepared from any suitable material. Suitable characteristics in terms of melting point, solubility and diffusion characteristics of the material that is used for preparing the carrier beads are discussed elsewhere in this specification.

According to an embodiment, said carrier material of said carrier beads is selected from PEG, polyvinyl alcohol (PVA), including fully, intermediate or partially hydrolysed
PVA, water soluble saccharides, in particular water soluble mono-, di-, oligo-, and polysaccharides, lipids, fats, and waxes, for example.

In some embodiments, said carrier material has a melting point that is greater than 5°C, greater than 10°C, greater than 15°C, greater than 20°C, greater than 25°C, greater than 30°C, greater than 35°C, greater than 40°C, greater than 45°C, greater than 50°C and/or greater than 60°C.

While there exist many ways for producing carrier beads that may be used in the methods of this invention, the solidification of droplets of liquefied carrier material is cited as an example for the purpose of illustration. Accordingly, in some embodiments, said carrier beads are obtained by providing liquid carrier material (for example, liquefied carrier material) and adding droplets of liquid carrier material into a solidification medium, thereby obtaining said carrier beads by solidification of said droplets. For example, said droplets may be obtained by pumping said liquid carrier material through a nozzle into said solidification medium and/or by dropping them into the solidification medium. In some embodiments, said solidification medium is a liquid. In some embodiments, said solidification medium has a temperature that is below the melting point of said carrier material when said droplets of liquid carrier material are added.

In some embodiments, said carrier material has a melting point that is higher than the melting point of said (liquid) solidification medium. Therefore, when being contacted with the liquid solidification medium at a temperature that is below the melting point of said carrier material, said liquefied carrier material solidifies and forms said self-sustained carrier beads.

In some embodiments, an additive is added to said carrier material in said carrier beads. Said additive maybe admixed with said carrier material before and/or when forming said carrier beads. According to an embodiment, said additive is added to liquid carrier material. According to this embodiment, the carrier beads comprise a mixture of carrier material and an additive. In this embodiment, said carrier bead may comprise, for example, 50 to 99 wt.%, 60 to 98 wt.%, 70 to 97 wt.% or 80-96 wt.% of carrier material and 1 to 50 wt.%, 2 to 40 wt.%, 3 to 30 wt.% or 4 to 20 wt.% of additive.
According to another embodiment, said carrier beads are substantially free of said additive, and said additive is added at a later moment, as disclosed elsewhere in this specification.

According to an embodiment, said carrier beads, comprising or not said additive, may be washed with appropriate solvents, such as acetone, and/or with a blend of solvents, for example. This washing step is conducted, for example, before the subsequent encapsulation step.

In some embodiments, the methods of the invention may comprise any one or a combination of two or more of the steps selected from: producing a shell of core-shell capsules; encapsulating said carrier beads with an appropriate film-forming and/or polymeric material so as to obtain carrier core-shell capsules; encapsulating said solid carrier core so as to obtain carrier core-shell capsules; and encapsulating said self-sustained carrier beads with an appropriate film-forming medium to form a semi-permeable shell in order to obtain precursor core-shell capsules.

In some embodiments, said carrier beads are encapsulated with an appropriate material that is capable of forming a shell. In this manner, the term "carrier core-shell capsules", also interchangeably referred to as "precursor core-shell capsules" may be obtained. The core of said carrier or precursor core-shell capsules thus may comprise, consist essentially of and/or consist of the carrier material, which are optionally admixed with an additive in the embodiments in which the additive is added to the carrier beads.

Said film-forming and/or polymeric material for forming said shell may be selected, according to an embodiment, from materials comprising one or more selected from polysaccharides, polysaccharide-based materials, protein-based materials, polyvinyl alcohol, polyvinyl acetate, polylactic-co-glycolic acid, polylactic acid, and combinations comprising two or more of the aforementioned.

Examples of proteins and protein-based materials include milk proteins, such as whey protein and/or casein protein, cereal proteins, such as wheat protein and zein protein from corn, and gelatin.
Examples of polysaccharides and polysaccharide-based materials include cellulose acetate, cellulose triacetate, cellulose phthalate, hydroxypropylcellulose, ethyl cellulose, cellulose derivatives in general, including cellulose derivatives other than those specified herein, chitosan, chitin, Arabic gum, alginate, pectin, pullulan, maltodextrin, cyclodextrin (e.g. cyclodextrin α, β and/or γ), starch, modified starch, and combinations comprising two or more of the aforementioned.

According to an embodiment, said film-forming and/or polymeric material is or comprises cellulose and/or a derivative of cellulose, such as cellulose acetate, or a derivative of cellulose acetate, such cellulose acetate phthalate and/or cellulose triacetate, for example. Cellulose and cellulose acetate derivatives may be advantageous in certain situations as they generally have a weak solubility in many common solvents such as pure water. They are, however, soluble in di- or triacetin and acetic acid solutions.

As will become apparent further below, the material for preparing the shell may be carefully selected with respect to the membrane characteristics of the shell obtained with the material. As described below, the shell material has to allow diffusion from the core into the solubilising medium and/or, once the shell is at least partially, but maybe substantially "emptied" from its primary core, the core medium may be replaced totally or partially by the flow of the solubilising medium and/or additive into the membrane. Alternatively or in addition to the selection of the material from which it is prepared and the encapsulating technique used to optimise diffusion characteristics and/or the permeability of the shell, the thickness of the shell may be adjusted in order to optimise diffusion characteristics and/or the permeability of the shell.

Having the above in mind, said shell maybe prepared in any suitable manner. According to an embodiment, said step of encapsulating said carrier beads comprises the step of applying said film-forming and/or polymeric material onto the solid carrier beads. According to some embodiments, the step of encapsulating said carrier beads with an appropriate film-forming and/or polymeric material comprises the step of coating said carrier core. The coating maybe performed by any suitable apparatus. For example, the coating may be performed by using any apparatus selected from the group consisting of a fluidized bed, a drum coater and a Lodige coater. If a coating technique is used for preparing said shell and/or encapsulating said core beads, said coating may be a first coating, and any one of the methods of the invention may comprise a step of
applying a second coating, for example in order to change (and in particular reduce) the permeability or diffusion characteristics of the shell, as is specified elsewhere in this specification.

Diffusion characteristics and/or the permeability of the shell are closely related to the characteristics of pore size, pore morphology and pore distribution of the membranes or shells. As mentioned above, also membrane or shell thickness may play role in the flow into and/or out of the capsules. These parameters should be kept in mind and/or should be determined or tested, in order to provide a shell that can be used for the purpose of the present invention.

The membrane or shell thickness may be adjusted so as to achieve the permeability and/or diffusion characteristics as desired with respect to the invention, in particular as required for the step of exposure to the solubilising medium, where the carrier core should move to the outside of the capsule. The permeability generally depends on the thickness of the shell, and more specifically decreases with increasing thickness. The skilled person may adjust the thickness of the shell so as to optimise diffusion characteristics, optionally also with regard to the material (additive) to be encapsulated.

In accordance with the invention, the weight ratio between said carrier core and said shell of said carrier core-shell capsules is in the range of 1-40 wt.% shell and 60-99 wt.% core material, or 2-30 wt.% shell and 70-98 wt.% core material, or 3-25 wt.% shell and 75-97 wt.% core material, or 5-20 wt.% shell and 80-95 wt.% core material, or 8-15 wt.% shell and 85-92 wt.% core material, for example about 10 wt.% shell material. These weight ratios may also apply to the final core-shell capsules comprising an additive as discussed further below, possibly after a second coating step. In this case, the weight of the carrier core is simply replaced by the mass of the core comprising the additive.

In some embodiments, the thickness of the shell of the carrier core-shell capsule may be between 30 and 500 μm, or between 50 and 200 μm.

According to an embodiment, the shell of the carrier core-shell capsules and/or precursor core-shell capsules comprises pores, optionally after further processing of the capsules obtained after encapsulating said carrier beads.
According to an embodiment, the shell of the carrier core-shell capsules and/or precursor core-shell capsules is semi-permeable, optionally after further processing of the capsules obtained after encapsulating said carrier beads.

According to an embodiment, the shell of the carrier core-shell capsules and/or precursor core-shell capsules has or is further processed to have membrane characteristics allowing for diffusion and/or osmosis of said solubilising medium and/or of a liquefied and/or dissolved carrier material through said shell.

In embodiments in which a particular processing step is required in order to render the shell permeable and/or porous as specified above, such a step may comprise a physical and/or a chemical treatment that brings about said permeability. For example, the carrier core-shell capsules may be exposed to a solution that is corrosive to the shell, resulting in pore formation or increase of permeability after a given time of exposure, for example. For example, a solution having a particular pH may be used to provide the necessary diffusion/permeability characteristics of the shell. Generally, physical and/or a chemical treatment that may be used include the exposure to pressure, to a change of temperature (increased and/or lowered temperatures), a change of pH and/or combinations of two or more of these, for example.

As will be specified further below, the methods of invention may comprise a further step of chemically and/or physically treating the capsules to affect the diffusion and/or permeability properties of the capsules, but with the opposed goal, in particular, in order to decrease diffusion through the shell and/or permeability. In embodiments in which there are two steps of physical and/or chemical treatment to modify the membrane permeability properties, the step for increasing diffusion/permeability may be a first step of chemically and/or physically treating or processing said shell, and said later step of decreasing said membrane diffusion/permeability properties may be a second, different step of chemically and/or physically treating or processing said shell.

In some embodiments, at this stage, optionally after said further processing step, the membrane characteristics of the shell of said carrier core-shell capsules are such that said shell is permeable to at least the carrier material, optionally after solubilising or suspending the carrier material. In some embodiments, the membrane characteristics
of the shell at this stage are such that the shell is permeable to an additive, which is to be encapsulated or which maybe present in the capsules at this stage already.

In some embodiments, the membrane of said carrier core-shell capsules has or is processed to have properties that optimise and/or favour the diffusion of the additive into the capsules and/or the diffusion of a solubilised (for example melted or dissolved) and/or suspended carrier material from the inside to the outside of the capsules, in particular under conditions as specified below.

According to an embodiment, the methods of the invention may comprise the step of exposing said precursor core-shell capsules to conditions that result in the diffusion and/or osmosis of at least part of the carrier core through the shell to the outside of the shell. For example, these conditions maybe provided by a medium.

The invention takes into consideration that optimal pore characteristics for diffusion out of the capsule may be different from the characteristics favouring the diffusion into the capsule.

According to an embodiment, the methods of the invention may comprise the step of exposing said carrier core-shell capsules to a solubilising medium, which may be a liquid medium.

In some embodiments, said carrier material is soluble or dispersible in said medium, whether the medium is liquid or gaseous, for example.

According to an embodiment, said carrier material of said carrier beads, said additive and said (optionally liquid) solubilising medium are selected so that said carrier material and said additive are both soluble or dispersible in said medium, optionally following chemical and/or physical treatment of said medium. For example, the solubilising medium may be provided at a temperature that is above the melting point of said carrier material. In this manner, the carrier material is exposed to said temperature when said carrier core-shell capsules are exposed to said medium. In some embodiments, said medium is liquid at said temperature.
According to an embodiment, said additive and/or said carrier material are soluble and/or dispersible in liquid water, optionally following heating said water to a temperature of up to 100°C, up to 90°C, up to 70°C, or up to 60°C.

According to an embodiment, said solubilising medium is liquid at a temperature of 70°C, 60°C, 50°C, 40°C, 30°C, 25°C, 20°C, 15°C, 5°C, at 0°C, or possibly even at -5°C, for example.

According to an embodiment, said medium is a liquid medium selected from the group consisting of an aqueous solution, an alcohol-containing solution, a hydrophobic solvent, oils, and mixtures comprising one or more of the aforementioned.

An exemplary way of exposing said carrier core-shell capsules to said solubilising medium comprises placing the carrier core-shell capsules inside a bath comprising said liquid medium. The carrier core-shell capsules may simply be transferred, for example by dropping into said liquid medium.

In some embodiments, during said step of exposing said carrier core-shell capsules to a liquid medium, a substantial part of said carrier material is liquefied, for example dissolved, melted and/or suspended.

In some embodiments, during said step of exposing said carrier core-shell capsules to said solubilising medium, said carrier material diffuses through said shell to the outside of said capsules. In some embodiments, the liquid or solubilising medium may diffuse through said shell into the capsules. If an additive was added to the medium, said additive may diffuse into the capsules together with said liquid medium. In particular, said medium may comprise, consist essentially of or consist of said additive. For example, said liquid medium may be an essence, an essential oil, an extract, for example a plant extract, or any other type of liquid additive.

In some embodiments, said carrier core-shell capsules are exposed to said solubilising medium for a time that is sufficient to allow for diffusion or osmosis of a substantial part of said carrier material through said shell to the outside of said shell.

In some embodiments, said carrier core-shell capsules are exposed to said liquid and/or solubilising medium for a duration sufficient to at least partially replace said
carrier core of said core-shell capsules by said liquid medium, thereby obtaining core-shell capsules with a liquid core comprising said liquid medium. During this step, a substantial part of said carrier material moves by diffusion and/or osmosis through said shell to the outside of said shell. For example, more than 40 wt.%, more than 50 wt.%, more than 60 wt.%, or 70 wt.% or more of said carrier material moves out of said carrier core-shell capsules. While it may, in some embodiments, be preferred that essentially all of the carrier material (up to 100 wt.%) is removed from the inside of the capsules, it is generally observed that small or residual amounts of the carrier material remain within the capsules.

The solubilising medium, optionally comprising an additive, may move, for example diffuse to the inside of the shell at the same time while said carrier material is moving from the inside to the outside of said shell. In this event, a diffusional exchange occurs through the membrane of said shell of said carrier core-shell capsules. In other words, at least a partial replacement of the carrier material by said solubilising medium and/or said additive takes place.

In accordance with the above said, in an aspect or an embodiment, the methods of the invention may be directed to methods of encapsulation and/or methods of providing core-shell capsules having an additive by counter-current flow diffusion and/or diffusional exchange.

Alternatively, it is envisaged that the carrier material moves and/or diffuses outside in a first step, and said solubilising medium and/or an additive moves and/or diffuses to the inside of the shell in a subsequent, separate step. It is also envisaged that a separate step is provided specifically for letting the additive, or a solution or dispersion containing it, into the shell, following a preceding step in which the carrier material was removed from the carrier core-shell capsules.

Furthermore, the invention also encompasses the embodiment in which the additive is present together with said carrier core and during exposure to the solubilising medium only or substantially only the carrier material diffuses out of the capsule shell, while the additive is retained within the shell.
In some embodiments, by exposure of the carrier core-shell capsules to the solubilising medium, and/or to a medium comprising an additive, core-shell capsules comprising a liquid core and/or an additive are obtained.

In an embodiment, the methods of the invention comprise a step of removing said core-shell capsules with a liquid core, for example as obtained in the preceding step, from said solubilising and/or liquid medium. Conveniently, said capsules may be separated by filtration, for example.

According to an embodiment, the methods of the invention comprise a step of removing residual liquid and/or solubilising medium and additive, if applicable, from the surface of said core-shell capsules by washing the capsules, for example.

It is also possible to dry the surface of the core-shell capsules as obtained following the exposure to the medium and/or following the above, optional washing step. In some embodiments, said core-shell capsules are dried with air or a gas having an appropriate temperature, for example in an air and/or gas stream. Alternatively, or in addition, residual medium or solvent may be removed from the surface of said core-shell capsules with the aid of an appropriate absorbing medium, such silicate powder, for example.

Optionally, the invention encompasses ways of further processing said capsules, in particular in order to adjust or modify the release characteristics and to control the release.

According to an embodiment, the methods of the invention may comprise the step of chemically and/or physically treating or processing said shell of said core-shell capsules comprising an additive so as to modify the diffusion properties through the shell of said core-shell capsules. If the method of the invention comprises a previous, first step of chemical and/or physical treatment, the present step may be a second step of chemical and/or physical treatment. This time, the capsules comprise an additive and the carrier core has been substantially removed.

Accordingly, the methods of the invention may comprise the step of exposing said core-shell capsules to conditions resulting in the change of the diffusion characteristics of the shell of the capsules obtained in the preceding step, so as to reduce the capacity of
the additive to diffuse through said shell and/or to the outside of the capsules, once at least part of the carrier core has been moved out of said shell.

In some embodiments, the treatment and/or processing of this step results in a reduction of permeability of the membrane of the shell. This treatment may result in a better retention of the core comprising the additive within the shell.

Chemical and/or physical treatment for modifying permeability and/or diffusion characteristics of the shell include, for example, exposure to a change of temperatures (exposure to a higher and/or a lower temperature), exposure to pressure, exposure to a pH change, and/or applying a coating onto the core-shell capsules.

The methods of the invention may comprise the step of applying a coating on said core-shell capsules comprising an additive. This step may be conducted following the step of exposing the cells to said liquid and/or solubilising medium, optionally after an intermediate washing step. At this stage, the core-shell capsules already comprise, in their core, the additive, and the carrier core may have been substantially removed.

In embodiments in which the step of encapsulating said carrier beads involved a coating step, the step of coating core-shell capsules comprising the additive may be referred to as a second coating, while the former coating may be referred to as a first coating. Alternatively, the step of coating core-shell capsules comprising the additive may be referred to as an outer coating 34, while the former coating may be referred to as a shell 32.

Said chemical and/or physical treatment, for example said coating, may result in a change of the pore and/or permeability characteristics and in particular may improve the retention of the additive inside the capsules.

The solvent, such as acetic acid, in which the cellulose acetate is applied to the carrier structure to form the shell of the core-shell capsules may be removed. In some embodiments, this removal of the solvent is by evaporation. This evaporation may be as a result of an evaporation step in which the capsules or their precursors may be exposed to conditions which encourage or enhance evaporation of the solvent used.
In some embodiments, if a second coating is performed, such coating maybe made by way of any suitable film-forming and/or polymeric material. In some embodiments, a plasticiser is used. For example, said capsules maybe coated with a substance comprising, consisting essentially of or consisting of a lipid, for example a wax and/or a fat, a lacquer, and/or any other film-forming and/or polymeric material, such as cellulose acetate, cellulose acetate phthalate, cellulose triacetate, and/or cellulose derivatives such as hydroxypropyl methylcellulose (HPMC) and/or carboxymethyl cellulose (CMC), for example. Other suitable plasticisers are discussed elsewhere in this specification.

Examples of suitable waxes include carnauba wax, bees wax, castor wax, candellila wax and paraffin wax. Examples of other lipids are hydrogenated oil, such as hydrogenated soybean or palm oil, mono glycerides, diglycerides, acetic acid esters, datem, ascorbyl palmitate, calcium stearate, magnesium stearate and potassium stearate, for example.

The material of the second coating, second or subsequent layer, for example, may be chosen in dependence of the desired release characteristics. The stability, integrity and/or susceptibility of the second or subsequent coating/layer determine the retention and/or the release of the additive from the core, and may be selected accordingly. If release is to take place only after mechanical damage of the capsule, the material for the second or subsequent coating/layer may be selected so as to be relatively stable with respect to fluctuations of environmental parameters, such as the temperature and/or pH, for example. In addition, in this case the capsule material may be rigid, resisting little or not at all to mechanical constraints and/or pressure.

When the core of the capsule comprises water and/or a water-soluble material, the material of the second coating, second or subsequent layer maybe impermeable to water and/or liposoluble. When the core of the capsule comprises a liposoluble material, the material of the second coating, second or subsequent layer may be impermeable to fats and/or water-soluble.

Said first and second coatings or layers of the core-shell capsules of the invention may be made from the same or different layers.

The invention relates to a tobacco product comprising capsules that are obtainable by any one of the methods of the invention. Such tobacco products include smoking
articles and smokeless oral tobacco products. Alternatively and/or in addition, the invention relates to a filter element comprising a core-shell capsule for a smoking article obtainable by any one of the methods of the invention. The core-shell capsule(s) may be incorporated into the tobacco product and/or filter element by any suitable method known in the art.

According to an embodiment, the invention provides a core-shell capsule comprising a core comprising an additive, wherein at least part of said core and/or said additive has properties of or comprises a liquid and/or at least part of said core and/or said additive, is a liquid at 60°C, at 50°C, at 40°C, at 35°C and/or at 30°C, and/or at room temperatures (25°C), or at even lower temperatures, such as 22°C, 20°C, 15°C, 10°C and 5°C.

According to an embodiment, at least a part of said core and/or said additive has the properties of a liquid or comprises a liquid. In some embodiments, substances that comprise a liquid encompass compositions that comprise different substances which are present in different conditions of aggregation, respectively, at least one substance being present in the form of a liquid. For example, in some embodiments the core and/or additive may comprise a gel or a liquid that is mixed with a solid.

Examples of substances of matter that comprise a liquid and that may function as an additive and/or core of the capsules of the invention are a gel, a wet spongy structure, a suspension, an emulsion, a dispersion, a colloid, an aerosol and a foam.

Substances that have properties of a liquid, including liquids, are substances that do not resist strongly to a change of form, but which generally resist to exposure of pressure. Liquids can generally hardly be compressed. According to a general definition, a liquid is a form of matter with a definite volume but no fixed shape. Examples of substances of matters that are not strictly liquids but which have properties of a liquid and which may be used as at least part of the core and/or additive in the capsules of the invention may be selected from semi-solids, such as liquid crystals and plastic crystals. Semi-solids, or quasi-solids are also known as amorphous liquids.

According to an embodiment, a liquid, and a substance having the properties of a liquid (such as semi-solids) is a substance having a viscosity in the range of 0.005 to 15,000
centipoises at 60°C, at 50°C, at 40°C, at 35°C and/or at 30°C, and/or at room temperatures (25°C), or at even lower temperatures, such as 22°C, 20°C, 15°C, io°C and 5°C.

According to an embodiment, a liquid, and a substance having the properties of a liquid (such as semi-solids) is a substance having a viscosity in the range of 0.005 to 3,000 centipoises at 60°C, at 50°C, at 40°C, at 35°C and/or at 30°C, and/or at room temperatures (25°C), or at even lower temperatures, such as 22°C, 20°C, 15°C, io°C and 5°C.

According to an embodiment, a liquid, and a substance having the properties of a liquid (such as semi-solids) is a substance having a viscosity in the range of 0.005 to 1,000 centipoises at 60°C, at 50°C, at 40°C, at 35°C and/or at 30°C, and/or at room temperatures (25°C), or at even lower temperatures, such as 22°C, 20°C, 15°C, io°C and 5°C.

According to an embodiment, a liquid, and a substance having the properties of a liquid (such as semi-solids) is a substance having a viscosity in the range of 0.005 to 500 centipoises at 60°C, at 50°C, at 40°C, at 35°C and/or at 30°C, and/or at room temperatures (25°C), or at even lower temperatures, such as 22°C, 20°C, 15°C, io°C and 5°C.

According to an embodiment, a liquid, and a substance having the properties of a liquid (such as semi-solids) is a substance having a viscosity in the range of 0.005 to 200 centipoises at 60°C, at 50°C, at 40°C, at 35°C and/or at 30°C, and/or at room temperatures (25°C), or at even lower temperatures, such as 22°C, 20°C, 15°C, io°C and 5°C.

Viscosity maybe determined using a Brookfield DV-II+ viscometer on 0.50 mL of sample at a temperature as specified above, (e.g. 60°C, 50°C, 40°C, 35°C, 30°C, 22°C, 20°C, 15°C, io°C, 5°C, 25°C, as applicable).

According to an embodiment, in the above viscosity ranges expressed in centipoises, the value of 0.005 is replaced by 0.899 centipoises, which is the viscosity of water.
In some embodiments, at least part of said core, for example at least 50 wt.%, at least 60 wt.% or at least 70 wt.%, 80 wt.% and/or 90 wt.% of said core remains liquid and/or keeps the liquid properties during a shelf life of three months when stored at 25°C and at a relative humidity of 50%.

In some embodiments, at least part of said core, for example at least 50 wt.%, at least 60 wt.% or at least 70 wt.%, 80 wt.% and/or 90 wt.% of said core remains liquid and/or keeps the liquid properties during a shelf life of six months when stored at 25°C and at a relative humidity of 50%.

In some embodiments, at least part of said core, for example at least 50 wt.%, at least 60 wt.% or at least 70 wt.%, 80 wt.% and/or 90 wt.% of said core remains liquid and/or keeps the liquid properties during a shelf life of nine months when stored at 25°C and at a relative humidity of 50%.

In some embodiments, the core of said core-shell capsules comprises residual and detectable amounts of said carrier material. For example, if said carrier material is PEG, said core may comprise residual PEG, in addition to the additive.

In some embodiments, the shell of said core-shell capsules comprises cellulose acetate and/or a derivative thereof, such as cellulose acetate phthalate, for example. Other shell materials are mentioned elsewhere in this specification.

In some embodiments, the shell of said core-shell capsules is multi-layered, comprising at least two, or at least three or more distinguishable layers. Said different layers may comprise and/or consist of different materials and/or different compositions. The first layer may be referred to as the shell 32, and any subsequent layers may be referred to as coatings 34.

**Examples**

The following examples are provided to assist in the understanding of the invention and are not intended to limit the scope of the invention.

Example 1: Preparation of a support and additive core
Polyethylene glycol (PEG) 2000 having a melting point of 45-50°C (Merck, Germany) was melted and maintained at a temperature of 60-65°C. 15 wt.% of menthol oil was mixed with the PEG.

A cooling bath was prepared with sunflower oil and kept at 10-15°C. The PEG-menthol mixture was extruded through a nozzle of 1400 µm (Nisco, Zurich, Switzerland) and dropped in a drop-wise manner in the cooling bath.

Beads with a diameter of 2-4 mm were harvested with a sieve from the cooling bath and washed with acetone.

**Example 2: Formation of a shell**

15 g cellulose acetate (Sigma Aldrich®, CAS no. 9004-35-7) was dissolved in 100 ml acetic acid. Once the cellulose acetate was completely dissolved, 80 ml isopropanol was added progressively to the solution. The beads with the core structure of Example 1 were coated in a fluidized bed (MP-i, Aeromatic, Niro, Germany) by atomization of the cellulose acetate solution, with a weight ratio of 90% beads to 10% cellulose acetate.

**Example 3: Replacement of carrier substrate from core**

The coated beads of Example 2 were put in a water bath of 70°C and kept therein until liquefaction of the core and absorption of water in the core.

**Example 4: Wax-sealing of the coated capsules with liquid core**

A proportion of the capsules comprising a shell and a liquid core of Example 3 were coated with castor wax in a fluidized bed (same apparatus as in Example 2), up to a weight ratio of 5% wax and 95% capsules.

**Example 5: Cellulose acetate-sealing of the coated capsules with liquid core**

The remaining proportion of the capsules of Example 3 were fluidized-bed coated with cellulose acetate instead of wax. In particular, 15 g cellulose acetate was dissolved in 100 ml acetic acid. Once the cellulose acetate was completely dissolved, 80 ml isopropanol was added progressively to the solution.

The capsules obtained in Examples 4 and 5 were stored for 6 months at 25°C at a relative humidity (rH) of 70. Upon rupturing individual capsules, the liquid content of
the capsules was released. The additive remained liquid in the capsules during the 6 months.

**Example 6: Preparation of a support and additive core**

PEG 3000 (melting point of 50-56°C) and PEG 1500 (melting point 42-48°C) in 80/20 proportion was melted and maintained at a temperature of 65-70°C. 15 wt.% of menthol oil was mixed with the PEG mixture. Beads with a diameter of 2-4 mm were prepared and washed as described in Example 1.

**Example 7: Formation of a shell**

15 g cellulose phthalate (cellulose acetate phthalate, Sigma Aldrich®, CAS no. 9004-38-0) was dissolved in 100 ml acetic acid. Once the cellulose phthalate was completely dissolved, 80 ml isopropanol was added progressively to the solution. The beads with the core structure of Example 6 were coated in a fluidized bed by atomization of the cellulose phthalate solution, with a weight ratio of 90% beads to 10% cellulose phthalate.

**Example 8: Replacement of carrier substrate from core**

The coated beads of Example 7 were put in a water bath of 70°C and kept therein until liquefaction of the core and absorption of water in the core.

**Example 9: Wax-sealing of the coated capsules with liquid core**

A proportion of the capsules comprising a shell and a liquid core of Example 3 were coated with a mixture of waxes in a fluidized bed, up to a weight ratio of 5% wax and 95% capsules. The wax mixture was composed of 33.3% bees wax, 33.3% castor wax and 33.3% carnauba wax, which waxes were melted in a mixture and sprayed on the capsules.

**Example 10: Cellulose phthalate-sealing of the coated capsules with liquid core**

The remaining proportion of the capsules of Example 8 were fluidized-bed coated with cellulose phthalate instead of wax. 15 g cellulose phthalate was dissolved in 100 ml acetic acid. Once the cellulose phthalate was completely dissolved, 80 ml isopropanol was added progressively to the solution.
The capsules obtained in Examples 9 and 10 were stored for 6 months. Upon rupturing 30 individual capsules, the liquid content of the capsules was released. The additive remained dispersed in the capsules during the 6 months.

Example 11: Preparation of a support and additive core
PEG 2000 (melting point of 45-50°C) is melted and maintained at a temperature of 60-65°C. 15 wt.% of menthol oil is mixed with the PEG.

A cooling bath is prepared with sunflower oil and kept at 10-15°C. The PEG-menthol mixture is extruded through a nozzle of 500 μm and dropped in a drop-wise manner into the cooling bath.

Beads with a diameter of 1-2 mm are harvested with a sieve from the cooling bath and washed with acetone.

Example 12: Formation of a shell
The beads with the core structure of Example 11 are coated with a weight ratio of 90% beads to 10% cellulose acetate exactly as discussed in Example 2.

Example 13: Replacement of carrier substrate from core
The coated beads of Example 12 are put in a water bath of 70°C and kept therein until liquefaction of the core and absorption of water into the core.

Example 14: Fat-sealing of the coated capsules with liquid core
A proportion of the capsules comprising a shell and a liquid core of Example 13 are coated with fat in a fluidized bed, up to a weight ratio of 5% fat and 95% capsules. The fat used is Bergazid fat (C1852, from Berg and Schmidt, Hamburg, Germany), which is melted and sprayed on the capsules.

Example 15: Cellulose acetate-sealing of the coated capsules with liquid core
The remaining proportion of the capsules of Example 13 are fluidized-bed coated with cellulose acetate as discussed in Example 5.

The capsules obtained in Examples 14 and 15 are stored for 6 months at 25°C at 70% rH. Upon rupturing individual capsules, the liquid content of the capsules is released. The additive remains liquid in the capsules for up to 6 months.
Example 16: Preparation of a support and additive core
A mixture of PEG 3000 (melting point of 50-56°C) and PEG 1500 (melting point 42-48°C) in 80/20 proportion was melted and maintained at a temperature of 65-70°C. No additive was added at this stage. Beads with a diameter of 2-4 mm were prepared and washed as discussed in Example 1.

Example 17: Formation of a shell
The beads with the core structure of Example 16 were coated in a fluidized bed with cellulose phthalate as discussed in Example 7.

Example 18: Replacement of carrier substrate from core
The coated beads of Example 17 were put in an emulsion bath of 60°C composed of water 90% w/w, menthol oil 8% w/w, tween® 20 1.5% w/w, Span® 40 0.5% w/w and kept therein until liquefaction of the core and absorption of the emulsion into the core.

Example 19: Wax-sealing of the coated capsules with liquid core
A proportion of the capsules comprising a shell and a liquid core of Example 18 were coated with a wax mixture as used in Example 9 in a fluidized bed, up to a weight ratio of 5% wax and 95% capsules.

Example 20: Cellulose phthalate-sealing of the coated capsules with liquid core
The remaining proportion of the capsules of Example 18 were fluidized-bed coated with cellulose phthalate as discussed in Example 10.

The capsules obtained in Examples 19 and 20 were stored for 12 months at 70% rH, at room temperature. Upon rupturing individual capsules, the liquid content of the capsules was released. The additive remained dispersed in the capsules during the storage period.

Example 21: Preparation of a support and additive core
Beads with a diameter of 2-4 mm were prepared and washed as discussed in Example 16.

Example 22: Formation of a shell
The beads with the core structure of Example 21 were fluidized-bed coated with cellulose phthalate solution as discussed in Example 7.

**Example 23: Replacement of carrier substrate from core**

The coated beads of Example 22 were put in a flavour bath of 60°C composed of thyme essential oil and kept therein until liquefaction of the core and absorption of the flavour in the core.

**Example 24: Wax-sealing of the coated capsules with liquid core**

A proportion of the capsules comprising a shell and a liquid core of Example 23 were coated with the wax mixture discussed in Example 9 in a fluidized bed.

**Example 25: Cellulose phthalate-sealing of the coated capsules with liquid core**

The remaining proportion of the capsules of Example 23 were fluidized-bed coated with cellulose phthalate as discussed in Example 10.

The capsules obtained in Examples 24 and 25 were stored for 12 months at 70% rH, at room temperature. Upon rupturing individual capsules, the liquid content of the capsules was released. The additive remained dispersed in the capsules for up to 12 months.

**Example 26: Uncoated capsules with cellulose acetate shell and additive core**

A cellulose acetate core-shell capsule was produced with the following composition:

- 5% cellulose acetate
- 5% PEG 400
- 80% PEG 1500
- 15% menthol oil

**Example 27: Preparation of a further support core**

PEG 3000 and PEG 400 were mixed at a weight ratio of 85% to 15% to achieve a melting point of 45-50°C. The mixture was melted and maintained at a temperature of 60-65°C. The melted PEG was extruded into a cooling bath as described in Example 1 and capsules with an average diameter of 2-4 mm were harvested with a sieve from the cooling bath and washed with acetone.
Example 28: Formation of a shell with cellulose acetate

The capsules with the core structure of Example 27 were coated as described in Example 2, with a weight ratio of 90% capsules to 10% cellulose acetate.

Example 29: Formation of a different shell with cellulose triacetate

15 g cellulose triacetate (Sigma Aldrich, CAS no. 9012-09-3) was dissolved in 200 ml acetic acid. Once the cellulose triacetate was completely dissolved, the capsules with the core structure of Example 27 were coated in a fluidized bed by atomization (see Example 2) of the cellulose triacetate solution, with a weight ratio of 90% capsules to 10% cellulose triacetate.

Example 30: Replacement of carrier substrate from core

The coated capsules of Example 28 and 29 were put in a water bath at 35°C and kept therein until liquefaction of the core and diffusion of water into the core. In this example, water alone is used as the active agent.

Examples 31 to 40: Sealing of core-shell capsules of Example 30

In a series of experiments, the liquid core-shell capsules of Example 30 (with both types of coatings) were subjected to a further treatment for sealing the shell and making it impermeable to the water (the encapsulate) retained within the shell of the capsule. In these further examples, the coating material, or a mixture of a coating material and plasticiser, were dissolved in one or two solvents and the capsules of Example 30 were coated in a fluidized bed (MP-i, Aeromatic, Niro, Swiss) by atomization. Table 1 below lists the details in terms of the sealing materials, plasticisers, solvents used and quantity.

In these examples, the sealing provides a second coating and/or a further layer on the shell of said core-shell capsules.
Table 1: Solvents and coating materials for Examples 31 to 40

<table>
<thead>
<tr>
<th>Ex. no.</th>
<th>Solv. 1 (ml)</th>
<th>Coating material</th>
<th>Amount coating material (g)</th>
<th>Solv. 2 (ml)</th>
<th>Plasticiser</th>
<th>Amount plasticiser (g)</th>
<th>Weight ratio*</th>
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Solv. 1: acetic acid; Solv. 2: isopropanol;
*weight ratio of core-shell capsules obtained in Example 30: coating material (Examples 31 and 32) or core-shell capsules obtained in Example 30: plasticiser (Examples 33-40);

Coating materials: A = cellulose acetate; B = cellulose triacetate;
Plasticisers: C = benzyl benzoate; D = triacetin; E = triethyl citrate; F = dibutyl phthalate.

For instance, Example 34 was conducted as follows: 15 g cellulose triacetate was dissolved in 200 ml acetic acid. Once completely dissolved, 12.5 g of benzyl benzoate plasticiser was added progressively to the solution. It is noted that cellulose triacetate is not compatible with isopropanol, which is why the dilution of acetic acid with isopropanol is not conducted in this example. The liquid core-shell capsules of Example 30 were coated in a fluidized bed by atomization of the cellulose triacetate solution, with a weight ratio of 89% core-shell capsules (Example 30), 6% cellulose triacetate and 5% benzyl benzoate (11% of second coating altogether).

In Examples 33, 35, 37 and 39, isopropanol was added progressively to the solution of the first solvent and the coating material. Then, the plasticiser was added to the solution comprising the two solvents and the coating material dissolved therein. Then,
the capsules of Example 30 were coated using the mixture of solvents, coating material and plasticiser as described above. Example 31 was conducted as Example 2.

In Examples 31 to 40 sealed core-shell capsules or core-shell capsules comprising two separate coatings (multi-layer core-shell capsules) were obtained. The capsules were stored for 6 months at 25°C at a relative humidity (rH) of 75%. Upon rupturing individual capsules, the liquid content of the capsules was released. The water remained inside the capsules during the 6 months.

In order to address various issues and advance the art, the entirety of this disclosure shows by way of illustration various embodiments in which the claimed invention(s) may be practiced and provide for superior containment of additive. The advantages and features of the disclosure are of a representative sample of embodiments only, and are not exhaustive and/or exclusive. They are presented only to assist in understanding and teach the claimed features. It is to be understood that advantages, embodiments, examples, functions, features, structures, and/or other aspects of the disclosure are not to be considered limitations on the disclosure as defined by the claims or limitations on equivalents to the claims, and that other embodiments may be utilised and modifications may be made without departing from the scope and/or spirit of the disclosure. Various embodiments may suitably comprise, consist of, or consist essentially of, various combinations of the disclosed elements, components, features, parts, steps, means, etc. In addition, the disclosure includes other inventions not presently claimed, but which may be claimed in future.
Claims

1. A tobacco product or part thereof comprising a core-shell capsule, wherein the capsule shell comprises cellulose acetate and/or a derivative thereof and the core-shell capsule is formed by a method comprising diffusion.

2. A tobacco product according to claim 1, wherein the capsule core comprises an additive, optionally wherein the additive comprises menthol.

3. A tobacco product according to claim 1 or 2, wherein the capsule core comprises an additive and the additive consists essentially of water.

4. A tobacco product according to claims 1 to 3, wherein the capsule core comprises an additive and the additive comprises clove extract and/or Kreteks-style flavours.

5. A tobacco product according to any of the preceding claims, wherein the core-shell capsule has a diameter of greater than 1 mm.

6. A tobacco product according to any of the preceding claims, wherein the core-shell capsule has a moisture-impermeable coating.

7. A tobacco product according to claim 6, wherein the moisture-impermeable coating comprises one or more plasticiser(s).

8. A tobacco product according to any of the preceding claims, wherein the core-shell capsule is rupturable.

9. A tobacco product according to any of the preceding claims, wherein the tobacco product is a smoking article or a smokeless oral tobacco product.

10. A tobacco product according to any of the preceding claims, wherein the tobacco product part is a filter or a filter element, or is a rod or portion of tobacco.
11. Use of a core-shell capsule in a tobacco product or part thereof, wherein the capsule shell comprises cellulose acetate and/or a derivative thereof and the core-shell capsule is formed by a method comprising diffusion.

12. A use according to claim 11, wherein the tobacco product is a smoking article or a smokeless oral tobacco product.

13. A use according to claim 11, wherein the tobacco product part is a filter or a filter element, or is a rod or portion of tobacco.

14. A process for the manufacture of a tobacco product or part thereof comprising a core-shell capsule, the process comprising:
   preparing a carrier structure from a carrier material;
   encapsulating said carrier structure with a film forming material so as to form a shell completely surrounding the carrier structure;
   exposing said encapsulated carrier structure to a medium in which said carrier material is soluble or dispersible, so that the carrier material is at least partially removed from within the shell;
   removing the resultant core-shell capsule from said medium; and
   incorporating the core-shell capsule into a tobacco product or part thereof, wherein said film forming material comprises cellulose acetate and/or a derivative thereof, wherein said medium and/or said carrier material comprises an additive and wherein said resultant core-shell capsule comprises said additive.

15. A process according to claim 14, wherein said additive comprises menthol.

16. A process according to claim 14 or 15, wherein said additive consists essentially of water.

17. A process according to any one of claims 14 to 16, wherein the capsule core comprises clove extract and/or Kretteks-style flavours.

18. A process according to any one of claims 14 to 17, wherein said carrier material comprises polyethylene glycol.
19. A process according to any one of claims 14 to 18, wherein said carrier material diffuses to the outside of the capsule and said medium diffuses to the inside of the capsule, wherein said medium comprises said additive.

20. A process according to any one of claims 14 to 19, comprising the step of applying a coating onto said core-shell capsules.

21. A process according to claim 20, wherein the coating comprises one or more plasticiser(s).

22. A process according to any one of claims 14 to 21, wherein said core-shell capsules have a diameter of greater than 1 mm.

23. A process according to any one of claims 14 to 22, wherein the tobacco product is a smoking article or a smokeless oral tobacco product.

24. A process according to any one of claims 14 to 23, wherein the tobacco product part is a filter or a filter element, or is a rod or portion of tobacco.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**


ADD.

According to International Patent Classification (IPC) into both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

A24B A24D B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents:

  *A* document defining the general state of the art which is not considered to be of particular relevance.

  *E* earlier application or patent but published on or after the international filing date.

  *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified).

  *O* document referring to an oral disclosure, use, exhibition or other means.

  *P* document published prior to the international filing date but later than the priority date claimed.

  *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention.

  *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone.

  *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

  *Z* document member of the same patent family.

**Date of the actual completion of the international search**

22 April 2014

**Date of mailing of the international search report**

29/04/2014

**Name and mailing address of the ISA**

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**Authorized officer**

Dimoul a, Kerasi na

Form PCT/ISA/210 (second sheet) (April 2005)
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