

## **SMOKING COMPOSITION COMPRISING FLAVOUR PRECURSOR**

This disclosure relates to smoking compositions having enhanced sensory components, and articles and methods related to such smoking compositions.

5 Smoking articles that heat tobacco or other sources of nicotine, without combustion of the tobacco or nicotine source, have been proposed. Such articles generate aerosols that can deliver nicotine and other tobacco constituents to a user. However, a user may perceive significantly different flavour notes from those experienced with conventional smoking articles such as cigarettes.

10 Accordingly, it may be desirable to incorporate flavour compounds into tobacco or other sources of nicotine that are used in non-combustion smoking articles to better approximate an experience associated with smoking a conventional cigarette. A variety of flavour compounds are known for addition to tobacco products. However, the volatility of such compounds presents challenges for incorporating the compounds into tobacco or  
15 smoking articles. For example, losses may occur during production or storage due to the volatility of the compounds.

In one aspect of the disclosure, there is provided a smoking article comprising an aerosol forming substrate, a heating element configured to heat, but not combust, the aerosol forming substrate, a flavour precursor compound added to the aerosol forming  
20 substrate, wherein the flavour precursor compound releases a thiol-containing flavour compound upon heating of the aerosol forming substrate by the heating element.

As described herein, smoking articles, in which the tobacco or other source of nicotine is heated but not combusted, deliver to a user an aerosol containing a flavour to provide the user with an experience similar to that of smoking a conventional cigarette. The  
25 articles contain a flavour composition that includes a flavour precursor, which does not have a significant odour. The flavour precursor converts into one or more flavour compounds or intermediates for flavour compounds upon heating to produce flavour notes that provide the composition with a profile more closely resembling that of conventional cigarettes.

Smoking articles described herein may provide one or more advantages. For  
30 example, the smoking articles described herein provide an enhanced flavour experience relative to smoking articles that do not include a flavour precursor. Upon heating, the flavour precursors described herein release flavour compounds or intermediates of flavour compounds comprising a thiol group. Thiol-containing flavour compounds or intermediates, such as hydrogen sulfide, methanethiol, and furfurylthiol, are more volatile than the flavour

precursor compounds. Because the flavour precursors are not volatile or are less volatile than the flavour compounds, losses during production may be mitigated and the articles may have a longer shelf life. Further, because the flavour precursor compounds are less odourous than the flavour compounds, the article does not impart substantial sulfur notes

5 when it is not in use.

As used herein, "thiol" means a compound of the formula RSH, where R is H or an organic group.

As used herein, "thiol-containing flavour compound" and "flavour compound" mean a thiol-containing flavour compound that is released from the flavour precursor compound or that is generated from the reaction of a thiol-containing intermediate with an aerosol forming substrate.

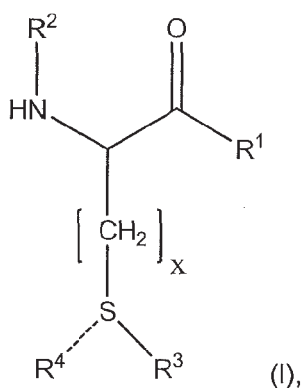
As used herein, "thiol-containing intermediate" and "intermediate" mean any thiol-containing compound that is released from the flavour precursor compound and that can react with an aerosol forming substrate, such as tobacco or other nicotine source to generate a thiol-containing flavour compound.

The thiol-containing flavour compound or intermediate is a compound that is more volatile than the flavour precursor compound. Preferably, the flavour compound has flavour properties that enhance the experience of non-combustible smoking articles to, for example, provide an experience more similar to that resulting from smoking a combustible smoking article. For instance, the flavour compound can enhance flavour properties such as complexity and mouth fullness. Complexity is generally known as the overall balance of the flavour being richer without dominating single sensory attributes. Mouth fullness is described as perception of richness and volume in the mouth and throat of the smoke. The released or generated thiol-containing flavour compounds may provide one or more of these or other flavour properties. In embodiments, the released or generated thiol-containing flavour compound is selected from the group consisting of hydrogen sulfide, methanethiol, 3-methyl-2-butene-1-thiol and furfurylthiol. Hydrogen sulphide and methanethiol are particularly preferred for their generation of flavour notes particularly associated with tobacco smoke.

Any suitable test may be employed to determine whether the thiol-containing flavour compound produces a flavour component that is typically perceptible with smoking of cigarettes. For example, a compound that invokes a subjective perception of a flavour note, associated with smoking of cigarettes would be considered to have or to produce a flavour for purposes of the present disclosure. In embodiments, trained flavourists may determine whether a flavour compound is released or generated on heating a flavour precursor compound, such as in the presence of an aerosol forming compound during smoking of a non-combustible smoking article. In embodiments, randomly or non-randomly selected people may be chosen to determine whether they perceive the compound to produce a flavour. By way of example, if 25% or more, e.g., 50% or more, 60% or more, 70% or more,

or 80% or more of the selected people perceive a flavour, the compound will be determined to be flavour producing.

Any suitable sulfur-containing flavour precursor compound may be employed to release a thiol-containing flavour compound or intermediate. In embodiments, the flavour precursor compound has a structure of Formula I, as follows:



where:

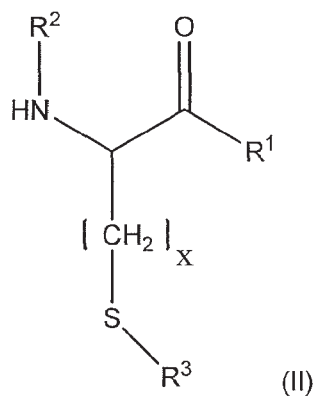
- 10       $\text{R}^1$  is OH or an amino acid residue,  
           $\text{R}^2$  is H,  $\text{C}(\text{O})\text{CH}_3$ , or an amino acid residue,  
           $\text{R}^3$  is H or C1-C3 unsubstituted alkyl,  
           $\text{R}^4$  is optional and, if present, is C1-C3 unsubstituted alkyl, and  
          x is an integer from 1 to 3.

15

$\text{R}^1$  is preferably OH or a glycine residue.  $\text{R}^2$  is preferably H,  $\text{C}(\text{O})\text{CH}_3$ , or a glutamate residue.  $\text{R}^3$  is preferably H or  $\text{CH}_3$ .  $\text{R}^4$  is preferably  $\text{CH}_3$ , if present, to produce a positively charged sulfur species. Preferably,  $\text{R}^4$  is not present. X is preferably 1 or 2.

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In embodiments, the flavour precursor compound has a structure of Formula II, as follows:



where:

R<sup>1</sup> is OH or an amino acid residue,

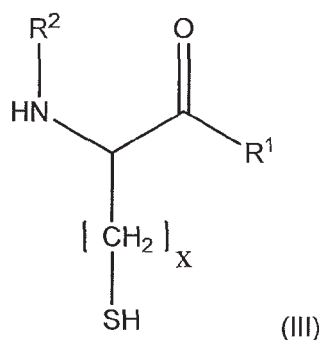
R<sup>2</sup> is H, C(O)CH<sub>3</sub>, or an amino acid residue,

5 R<sup>3</sup> is H, C1-C3 unsubstituted alkyl or an amino acid residue, and

x is an integer from 1 to 3.

R<sup>1</sup> is preferably OH or a glycine residue. R<sup>2</sup> is preferably H, C(O)CH<sub>3</sub>, or a glutamate residue. R<sup>3</sup> is preferably H, CH<sub>3</sub> or a cysteine residue. X is preferably 1 or 2.

10 In embodiments, the flavour precursor compound has a structure of Formula III, as follows:



where:

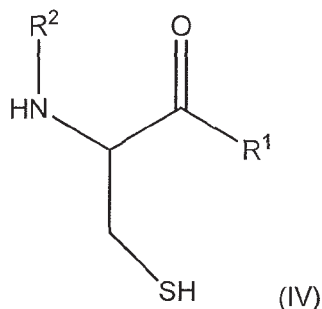
15 R<sup>1</sup> is OH or an amino acid residue,

R<sup>2</sup> is H, C(O)CH<sub>3</sub>, or an amino acid residue, and

x is an integer from 1 to 3.

R<sup>1</sup> is preferably OH or a glycine residue. R<sup>2</sup> is preferably H, C(O)CH<sub>3</sub> or a glutamate residue. X is preferably 1 or 2.

In embodiments, the flavour precursor compound has a structure of Formula IV, as follows:



where:

R<sup>1</sup> is OH or an amino acid residue, and

R<sup>2</sup> is H, C(O)CH<sub>3</sub>, or an amino acid residue.

R<sup>1</sup> is preferably OH or a glycine residue. R<sup>2</sup> is preferably H, C(O)CH<sub>3</sub>, or a glutamate residue.

It will be understood that, with regard to Formulas I-IV presented above, that an amino acid residue may be bound to the core structure via a peptide bond or via a suitable side chain, such as a carboxylic acid group.

In embodiments, the flavour precursor compound is a compound selected from the group consisting of cysteine (CAS No. 3374-33-9), cysteine (CAS No. 56-89-3), glutathione (CAS No. 70-18-8), methionine (CAS No. 59-51-8), DL methionine methylsulfonium (CAS No. 582174), N-acetyl cysteine (CAS No. 616-91-1), S-methyl cysteine (CAS No. 1187-84-4), DL-homocysteine (CAS No. 454-29-5), N-acetyl methionine (CAS No. 65-82-7), Farnesyl-Met-Ome (CAS No. 218962-72-2), albumin (CAS No. 9006-59-1) and 2-hydroxy-4-(methylthio)butyric acid (CAS No. 922-50-9).

Disclosure of a compound herein, whether by name, structure, reference number or the like, refers to the particular disclosed compound, as well as suitable salts, polymorphs, isomers, etc. thereof.

In embodiments, the flavour precursor compound is a compound comprising a cysteine residue. Examples of such compounds include cysteine, glutathione, N-acetyl cysteine, S-methyl cysteine, and cysteine.

Preferably, the flavour precursor compound is cysteine or glutathione. More preferably, the flavour precursor compound is cysteine.

As used herein, a flavour composition is a composition comprising a flavour precursor compound and a further compound typically used in flavour compositions, for example. In particular, the composition may comprise one or more flavour compounds known in the art, which include but are not limited to, menthol, spearmint, peppermint, eucalyptus, vanilla, cocoa, chocolate, coffee, tea, spices (such as cinnamon, clove and ginger), fruit extracts, and combinations thereof. In embodiments, the flavour composition further comprises menthol or eugenol. Such flavourants are commonly used to provide a refreshing flavour to the smoke of a smoking article. The composition may also comprise adjuvants that allow the composition to meet technical requirements, such as stability or tonality persistence.

A delivery system may be provided, which encapsulates a flavour composition or flavour precursor compound. The delivery system protects the flavour composition or flavour precursor compound during manufacture and upon storage.

In embodiments, a delivery system may take any suitable form which is capable of retaining the flavour composition or flavour precursor compound within the structure of the system until the release is desired.

Preferably, the delivery system comprises a closed matrix or network structure, which traps the flavour precursor compound within the closed structure. For example, the flavour composition or precursor may be trapped in domains within a matrix structure. Upon compression or deformation of the material, the flavour composition or precursor is forced out from the matrix structure, for example, through the breakage of the surrounding structure. In embodiments, the delivery system comprises a polymer matrix comprising one or more matrix-forming polymers. For example, the gradual breakdown of the polymer matrix with increasing compressive force, temperature, or both provides the controlled release of the flavour precursor compound from the delivery system. The release of the flavour precursor compound can thus vary as a function of temperature or the deformation resulting from the compressive or shear force that is applied to the delivery system.

The delivery system may advantageously be provided within smoking articles in a variety of different forms so that there is flexibility in the way in which the composition or precursor can be incorporated into the smoking article. In embodiments the delivery system is provided in the form of particles, beads or capsules. The particles, beads or capsules may be formed into any suitable shape, but are preferably substantially cylindrical or spherical.

In various embodiments, the flavour precursor is synthesized or purified prior to its addition to the flavour composition or flavour delivery composition.

A flavour precursor compound, as described above, may be included in a smoking composition in any suitable manner and in any suitable amount. The term "smoking composition" is used to describe a composition that produces an aerosol when it is heated, and is used to make a smoking article. The term "smoking article" includes articles that heat the smoking composition directly or indirectly, or smoking articles that neither combust nor heat the smoking composition, but rather use air flow or a chemical reaction to deliver nicotine, a flavour compound or other materials from the tobacco or other nicotine source. As used herein, the term "smoke" is used to describe an aerosol produced by a smoking article. An aerosol produced by a smoking article may be, for example, produced by non-combustible smoking articles, such as heated smoking articles or non-heated smoking articles.

A flavour delivery system can controllably release a flavour precursor compound to its surrounding environment by any suitable methods, for example by deformation of the flavour delivery system or by changing the temperature. The amount of flavour precursor compound released over a time interval, as well as the start or end of the interval(s) can be controlled. The amount of flavour precursor compound released during each interval and the length of time intervals need not be equal.

A smoking composition of the invention comprises a flavor precursor compound or a flavor composition, the composition or precursor optionally being provided as part of a delivery system. A smoking composition may comprise, for example, one or more of: powder, granules, pellets, shreds, strips or sheets comprising one or more of: herb leaf, tobacco leaf, tobacco stems, fragments of tobacco ribs, homogenized tobacco, reconstituted tobacco, processed tobacco, extruded tobacco and expanded tobacco. The smoking composition may be in loose form, or may be provided in a suitable container or cartridge. For example, the smoking composition may be contained within a paper or wrap and have the form of a plug.

Smoking articles that include aerosol-generating devices typically comprise an aerosol-forming substrate that is assembled, often with other components, in the form of a rod. Typically, such a rod is configured in shape and size to be inserted into an aerosol-generating device that comprises a heating element for heating the aerosol-forming substrate.

“Aerosol-forming substrate” as used herein is a type of smoking composition that can be used in an aerosol-generating device to produce an aerosol. The aerosol-forming substrate can release a flavor compound upon heating. The aerosol-forming substrate can be in solid form or liquid form. The substrate can comprise both liquid and solid components.

5 The aerosol-forming substrate may comprise tobacco and a flavour composition wherein a flavor precursor compound or a disassociated flavor compound is released from the substrate upon heating. In embodiments, the aerosol-forming substrate does not include tobacco, but does include a flavor composition wherein a flavor precursor compound as described herein or a disassociated flavor compound is released from the substrate upon heating, and optionally nicotine. The aerosol-forming substrate may further comprise an aerosol former. Examples of suitable aerosol formers are glycerine and propylene glycol. Optionally, the aerosol-forming substrate may be provided on or embedded in a carrier which may take the form of powder, granules, pellets, shreds, spaghetti strands, strips or sheets. The aerosol-forming substrate may be deposited on the surface of the carrier in the form of, for example, a sheet, foam, gel or slurry. The aerosol-forming substrate may be deposited on the entire surface of the carrier, or alternatively, may be deposited in a pattern in order to provide a non-uniform flavor delivery during use.

Smoking articles may comprise a filter which may be a single segment filter or a multi-component filter comprising two or more connected or unconnected filter segments. Any suitable filter or filter segment may be included in a smoking article described herein. One or more of the filter segments may each comprise a flavor precursor compound or a flavor composition, the precursor or composition optionally being provided in a delivery system. Smoking articles may be packaged in containers for sale, for example in soft packs or hinge-lid packs, with an inner liner coated or impregnated with a flavor compound, a flavor composition or a delivery system.

A smoking composition comprising a flavor precursor compound or a flavor composition, the precursor or composition optionally being provided in a delivery system, can be manufactured using any suitable technique. For example, a flavour composition comprising a flavour precursor compound, may be sprayed on tobacco. To facilitate spraying, the flavor precursor compound can be added to a liquid carrier to form a mixture, such as solution, suspension or slurry, and the slurry can be applied onto the tobacco. Slurries comprising the flavor precursor compound can include any liquid or liquid mixtures suitable for dispersing and dispensing (e.g., spraying) particles comprising the flavor

precursor compound. A preferred liquid is water (e.g., deionized water), though other liquids, such as alcohols, can be used.

In some embodiments, tobacco may be dipped in a solution, suspension or dispersion comprising the flavour precursor. A solid such as a powder or crystals comprising the flavour precursor may be added to tobacco. The smoking composition can then be processed for use in a smoking article.

In some embodiments, the flavor precursor compound may be added to cut filler tobacco stock supplied to a cigarette-making machine or applied to a pre-formed tobacco column prior to wrapping a cigarette wrapper around the tobacco column.

The concentration of a flavor precursor compound in the slurry can be any amount suitable for dispensing the slurry onto tobacco. Slurries comprising a dispersion of a flavor precursor compound in a liquid can comprise from about 0.01 to about 2% by weight of a flavor precursor compound. The flavor precursor compound can be provided in the form of a dried powder and applied to tobacco as such. If dried powder is used, it can be dusted onto tobacco. Another technique for incorporating the flavor precursor compound in a tobacco smoking composition involves adding the flavor precursor compound to a slurry of ingredients used to make reconstituted tobacco. The slurry, including the flavor precursor compound, can be formed into a reconstituted tobacco sheet and the sheet can be cut to shreds for incorporation as cut filler of a rod of smoking composition or other forms of smoking article.

Homogenized tobacco can also be used to make aerosol-forming substrate for use in smoking articles that are being heated in an aerosol-generating device. As used herein, the term "homogenized tobacco" denotes a material formed by agglomerating particulate tobacco. Tobacco dust created by tobacco breakage during shipping and manufacturing, leaf lamina, stems and other tobacco by-products that are finely ground may be mixed with a binder to agglomerate the particulate tobacco. Homogenized tobacco may comprise other additives in addition to a flavor precursor or flavour composition, including but not limited to, aerosol-formers, plasticisers, humectants, and non-tobacco fibers, fillers, aqueous and non-aqueous solvents and combinations thereof. Homogenized tobacco can be cast, extruded, or rolled. A number of reconstitution processes for producing homogenized tobacco materials are known in the art. These include, but are not limited to: paper-making processes of the type described in, for example, US5,724,998; casting processes of the type described in, for example, US5,724,998; dough reconstitution processes of the type

described in, for example, US3,894,544; and extrusion processes of the type described in, for example, in GB983,928.

It will be appreciated that aerosol-forming substrates may have different shapes and sizes depending upon, for example, the type of smoking article in which they are intended to be used. Aerosol-forming substrates may be substantially three-dimensional. For example, aerosol-forming substrates may be bricks or plugs comprising a plurality of strands of homogenized tobacco material. Alternatively, aerosol-generating substrates may be substantially two-dimensional. For example, aerosol-generating substrates may be mats or sheets comprising a plurality of strands of homogenized tobacco.

The amount of flavour precursor compound desired in a smoking composition may vary depending on the final product in which the smoking composition is to be included. For example, the flavour precursor compound may be added to tobacco to enhance the flavour or aroma of conventional smoking articles, such as cigarettes, cigars, and the like. As such articles may already produce a similar flavour or aroma when smoked, flavour precursor compounds that release flavour compounds having similar flavour qualities may be added in relatively low concentrations or amounts. In contrast, it may be desirable to add higher concentrations or amounts of flavour precursor compounds to smoking compositions, such as tobacco-containing aerosol-forming substrates, that will be used in smoking articles in which constituents are aerosolized without combustion. Smoking articles having tobacco-containing aerosol-forming substrates for use with an aerosol-generating device typically provide flavour characteristics that differ from those of combustible smoking articles. It may also be desirable to include higher concentrations or amounts of flavour compounds to smoking compositions that do not include tobacco, such as non-tobacco containing aerosol-forming substrates. Preferably, the flavour precursor compounds are included in the smoking composition for use in smoking articles in amounts that provide a user with a perceived note similar to a combustible smoking article, such as a cigarette. For example, the flavour precursor may be included in a non-combustion smoking article or a smoking article that does not include tobacco in an amount that results in the release or delivery of the flavour compound in a concentration or amount similar to that delivered to a user of a conventional smoking article such as a cigarette.

In embodiments, the amount of flavour compound delivered to a user may be determined on a per puff basis. Any suitable method may be used to determine the amount of flavour compound delivered per puff. For example, ISO, Health Canada Intense, or other standard or automated procedures may be employed or modified to determine content per

puff. Examples of ISO methods that may be employed or modified include: (i) ISO 4387:1991 Cigarettes – Determination of total and nicotine free dry matter using a routine analytical smoking machine, 1991-10-15; (ii) ISO 8454:1995 Cigarettes – Determination of carbon monoxide in the vapour phase of cigarette smoke – NDIR method, 1991-11-15; (iii) 5 ISO 10315:1991 Cigarettes – Determination of nicotine in smoke condensates – Gas-chromatographic method, 1991-08-01; and (iv) ISO 10362-1:1991 Cigarettes – Determination of water in smoke condensates – Part 1: Gas-chromatographic method, 1991-09-15. The Health Canada Intensive method refers to: Health Canada – Official Method T-115, Determination of “Tar”, Nicotine and Carbon Monoxide in Mainstream Tobacco Smoke, 10 December 1999. Regardless of the method employed, it may be desirable to determine the amount of a flavour compound that is delivered per puff of a conventional cigarette and formulate a non-conventional smoking article that aerosolizes tobacco or other constituents without combustion so that it delivers similar amounts of the flavour compound per puff. The amount of flavour precursor compound added to a smoking composition for such articles 15 may be varied and tested to determine how much flavour precursor is needed to deliver a similar amount of the flavour compound.

Of course, the desired amount of flavour compound delivered per puff will depend on the flavour compound itself. In embodiments, a smoking article is configured to deliver about 5 nanograms or more of the flavour compound per puff. In embodiments, a smoking article 20 is configured to deliver from about 10 nanograms of the flavour compound per puff to 1 milligram of the flavour compound per puff, such as from about 50 nanograms per puff to about 750 nanograms per puff or from about 75 nanograms per puff to about 500 nanograms per puff.

The amount of flavour precursor compound added to a smoking composition to 25 deliver a desired amount of disassociated flavour compound to a user will depend on the components and configuration of the article and the flavour precursor compound.

Of course, a flavour precursor may be added to a smoking composition in any suitable amount or concentration. In embodiments, a smoking composition comprises 0.001 weight % or greater, based on the total weight of tobacco, of the flavour precursor 30 compound. In embodiments, a smoking composition includes 0.005 weight % or greater of the flavour precursor compound. In embodiments, a smoking composition includes 0.01 weight % or less of the flavour precursor compound. In embodiments, a smoking composition includes from about 0.001 weight % to about 2 weight % of the flavour precursor compound, such as from about 0.005 weight % to about 1 weight % of the flavour

precursor compound or from about 0.01 weight % to about 0.25 weight % of the flavour precursor compound.

The flavour precursor compound may be added to tobacco at any suitable time, such as before or during processing of the tobacco for incorporation into a smoking article or the like. Preferably the flavour precursor compound is stable (that is, the flavour compound is not released or generated) under such processing.

In embodiments, one or more flavour precursor compounds is dissolved in a food grade solvent and then applied to a tobacco substrate or other suitable substrate in concentrations up to 1000ppm. The substrate may then be equilibrated at room temperature to a humidity of approximately 60 % for at least 48 hours. For application during the substrate generation (e.g. cast leaf process, extrusion) the compounds can be added directly as solid material to any available food grade solvent system required in the process. In case the application as a solid is not feasible, the compound can be applied as a solution, suspension, etc. created as described above. The concentration to the substrate during generation may reach 1 % of the total dry weight.

In embodiments, the reconstitution of tobacco is performed by drying and casting homogeneous slurry of tobacco powder, water, glycerin, binder and cellulose fibres. This type of process is known as cast leaf process and is widely used by the tobacco industry for the manufacturing of reconstituted or homogenized tobacco for use in conventional cigarette. A cast leaf process may involve applying temperatures of up to about 140°C, such as between about 90°C and about 140°C. Accordingly, if the smoking composition that includes the flavour precursor compound is to be manufactured in a cast leaf process, the flavour precursor compound is preferably stable at such temperatures.

Preferably, the flavour precursor compound releases the flavour compound or the intermediate under general use conditions of the article in which the flavour precursor compound is incorporated. By way of example, smoking articles that heat, but do not combust, tobacco to aerosolize tobacco constituents typically heat the tobacco at about 200°C to about 450°C. Accordingly, the flavour precursor compound preferably releases the flavour compound at a temperature from about 200°C to about 450°C when a smoking composition having the flavour precursor compound is included in such articles. By way of another example, combustion of tobacco typically occurs at a temperature of about 450°C. Accordingly, the flavour precursor compound preferably releases the flavour compound at a temperature below about 450°C when a tobacco composition having the flavour precursor compound is included in combustible smoking articles such as cigarette or cigars.

In embodiments, the flavour precursor compound releases the flavour compound at a temperature of about 150°C or greater. In embodiments, the flavour precursor compound releases the flavour compound at a temperature of about 450°C or less. In embodiments, the flavour precursor compound releases the flavour compound at a temperature of from about 100°C to about 450°C, such as from about 150°C to about 450°C or from about 200°C to about 450°C.

Tobacco compositions, as used herein refer to smoking compositions that include tobacco and a flavour precursor. For example, the tobacco composition may be used in combustible smoking articles or non-combustible smoking articles in which an aerosol-forming substrate is used. The tobacco composition can be reconstituted tobacco containing various tobacco types of different origins, as well as binders and humectants. The humectants facilitate the production of an aerosol. When heated, the humectants evaporate and re-condense into small droplets to generate a visible aerosol. Preferably, the flavour precursor composition releases the flavour compound under use conditions, but not under storage, processing, or manufacturing conditions.

In the case of combustible smoking articles such as cigarettes, the smoking composition may be used in any portion of the smoking article having a tobacco substrate, for example in the tobacco rod of a conventional cigarette, or in one or more segments of the filter of a conventional cigarette. In the case of smoking articles in which the smoking composition, or a component thereof, is not combusted, the smoking composition may be used in any portion of the smoking article having an aerosol-forming substrate.

By way of example and with reference to **FIG. 1**, a schematic drawing of a smoking article **102** in which the smoking composition is not combusted is shown. As shown in **FIG. 1**, the smoking article **102** includes a combustible heat source **104**, an aerosol-forming substrate **106**, an elongate expansion chamber **108** and a mouthpiece **110** in abutting coaxial alignment, which are overwrapped in an outer wrapper of cigarette paper **112** of low air permeability.

The combustible heat-source **104** is a pyrolysed porous carbon-based heat source. The combustible heat source **104** is cylindrical and comprises a central airflow channel **116** that extends longitudinally through the combustible heat source **104**. A substantially air impermeable, heat resistant coating **114** of iron oxide is provided on the inner surface of the central airflow channel **116**. The aerosol-forming substrate **106** is located immediately downstream of the combustible heat source **104** and comprises a cylindrical plug of homogenised tobacco material **118** comprising a flavor precursor compound and glycerine

as aerosol former and circumscribed by filter plug wrap **120**. The homogenized tobacco material **118** consists of longitudinally aligned filaments of extruded tobacco material.

A heat-conducting element **122** consisting of a tube of aluminum foil surrounds and is in contact with a rear portion of the combustible heat source **104** and an abutting front portion of the aerosol-generating substrate **106**. As shown in FIG. 1, a rear portion of the aerosol-generating substrate **106** is not surrounded by the heat-conducting element **122**.

The elongate expansion chamber **108** is located downstream of the aerosol-generating substrate **106** and comprises a cylindrical open-ended tube of cardboard **124**. The mouthpiece **110** of the smoking article **102** is located downstream of the expansion chamber **108** and comprises a cylindrical plug of cellulose acetate tow **126** of very low filtration efficiency circumscribed by filter plug wrap **128**. The mouthpiece **110** may be circumscribed by tipping paper (not shown). The dimensions of the smoking article **102** may be similar to a conventional cigarette.

In use, a user ignites the combustible carbon-based heat source **4** and then draws air through the central airflow channel **116** downstream towards the mouthpiece **110**. The front portion of the aerosol-generating substrate **106** is heated primarily by conduction through the abutting non-combusting rear portion of the combustible heat source **104** and the heat-conducting element **122**. The drawn air is heated as it passes through the central airflow channel **116** and then heats the aerosol-forming substrate **106** by convection. The heating of the aerosol-forming substrate **106** releases volatile and semi-volatile compounds, including the disassociated flavor compound, and glycerine from the aerosol forming substrate **118**, which are entrained in the heated drawn air as it flows through the aerosol-forming substrate.

The heated air and entrained compounds pass downstream through the expansion chamber **108**, cool and condense to form an aerosol that passes through the mouthpiece into the mouth of the user (at about ambient temperature).

To make the smoking article **102**, a rectangular piece of the heat-conducting element **122** is glued to cigarette paper **112**. The heat source **104**, the plug of the aerosol-forming substrate **106** and the expansion chamber **108** are suitably aligned and positioned on the cigarette paper **112** with the attached heat-conducting element **122**. The cigarette paper **112** with the attached heat-conducting element **122** is wrapped around the rear portion of the heat source **104**, the aerosol-generating substrate **106** and the expansion chamber **108** and glued. The mouthpiece **110** is attached to the open end of the expansion chamber using known filter combining technology.

In another example of a heated smoking article, the smoking composition comprising the flavor precursor compound is brought into direct contact with a heat source that is not combusted, such as an electrical heat source. **FIG. 2** shows a smoking article that is heated by an electrical heat source when engaged with a device for consumption. The smoking article **101** comprises a front-plug **103**, an aerosol-forming substrate **111**, a hollow cellulose acetate tube **109**, a transfer section **107**, and a mouthpiece filter **105**. These five elements are arranged sequentially and in coaxial alignment and are assembled by a cigarette paper **115** to form a rod. The rod has a mouth-end, which a user inserts into his or her mouth during use, and a distal end located at the opposite end of the rod to the mouth end. When assembled, the rod is 52 mm long and has a diameter of 7.2 mm. The front-plug **103** is a cylindrical portion of cellulose acetate tow. The aerosol-forming substrate **111** is located downstream of the front-plug **103** and comprises a bundle of crimped cast-leaf tobacco wrapped in a filter paper. The cast-leaf tobacco includes additives, including glycerine as an aerosol former. The tube **109** is located immediately downstream of the aerosol-forming substrate **111** and is formed from cellulose acetate. The transfer section **107** allows volatile substances including the flavor compound released from the aerosol-forming substrate **111** to pass along the rod towards the mouth end. The volatile substances may cool within the transfer section **107** to form an aerosol. The mouthpiece filter **105** is a conventional mouthpiece filter formed from cellulose acetate tow. The elements identified above are assembled by being tightly wrapped within a cigarette paper **115**.

The aerosol-generating device **119** comprises a sheath **121** for receiving the smoking article **101** for consumption. A heating element **113** is located within the sheath **121** and positioned to engage with the distal end of the smoking article **101**. The heating element **113** is shaped in the form of a blade terminating in a point. As the smoking article **101** is pushed into the sheath the point of the heating element **113** engages first with the front-plug **103** and then penetrates into the aerosol-forming substrate **111**. When the smoking article **101** is properly engaged with the aerosol-generating device **119**, the heating element **113** is located within the aerosol-forming substrate **111**. Heat generated by the heating element **113** is transferred by conduction and convection to the aerosol-forming substrate **111** which comprises the flavor precursor compound. An insulating collar **117** may surround a portion of the heating element **113** that is in contact with and protect the front-plug **103** from burning or melting. Of course, it will be understood that the smoking articles described with regard to **FIG. 1** and **FIG. 2** are just two examples of a smoking article that may employ a smoking composition comprising a flavor precursor compound as described herein. It will be further

understood that methods for making a smoking article having a smoking composition that includes a flavor precursor compound other than those described in connection with **FIG. 1** and **FIG. 2** may be employed.

Any suitable method for making a smoking article having a smoking composition that includes a flavor precursor compound may be employed. In general, a method for making a smoking article having a smoking composition that includes a flavor precursor compound includes adding or incorporating the flavor precursor compound or a flavor delivery composition into a smoking composition, such as tobacco or other substrate; and incorporating the smoking composition into a smoking article.

In general and as described herein, a method for enhancing flavor of a smoking composition comprises adding a flavor precursor compound, optionally encapsulated in a delivery system, to the smoking composition. The flavor precursor compound releases or dissociates a flavor compound or intermediate upon heating. As used herein "release" and "dissociate" are used interchangeably. The heating of the flavor precursor compound occurs when a smoking article is used (combusted or heated) by a smoker.

All scientific and technical terms used herein have meanings commonly used in the art unless otherwise specified. The definitions provided herein are to facilitate understanding of certain terms used frequently herein.

As used in this specification and the appended claims, the singular forms "a", "an", and "the" encompass embodiments having plural referents, unless the content clearly dictates otherwise.

As used in this specification and the appended claims, the term "or" is generally employed in its sense including "and/or" unless the content clearly dictates otherwise.

As used herein, "have", "having", "include", "including", "comprise", "comprising" or the like are used in their open ended sense, and generally mean "including, but not limited to". It will be understood that "consisting essentially of", "consisting of", and the like are subsumed in "comprising," and the like.

Non-limiting examples illustrating certain aspects of the compounds, compositions, processes and articles described in this disclosure are provided below.

## Examples

### Example 1

5 A variety of non-volatile sulfur compounds, as shown in table 1, are screened by (ATD) GC-MS on a cellulose filter to determine whether and how much hydrogen sulfide and methanethiol they release upon heating.

The compounds are also added to non-combusted smoking articles to assess the change in sensory attributes of such compounds during aerosolisation of such articles in the  
10 presence and absence of the compounds.

Certain of the non-volatile sulfur compounds are also applied to a blended tobacco by syringe injection and used for non-combusted smoking substrates. The tobacco with the non-volatile sulfur compounds is formed into sticks and equilibrated for at least 12 hours prior to assessment.

15 The ortho-nasal impact of the selected compounds is evaluated in different concentrations on global aroma by usage of the smoke simulator in pushing mode. Selected compounds are then selected for sensory testing.

20 **Table 1: Non-volatile sulfur compounds**

| non-volatile thiol-containing compounds      | CAS No.     | category                     |
|----------------------------------------------|-------------|------------------------------|
| Cysteine                                     | 3374-33-9   | amino acid                   |
| Cystin                                       | 56-89-3     | amino acid derivate          |
| Glutathione                                  | 70-18-8     | natural antioxidant in cells |
| Methionine                                   | 59-51-8     | amino acid                   |
| DL-Methionine methylsulfonium chloride       | 582174      | amino acid derivate          |
| N-Acetyl L-cysteine                          | 616-91-1    | amino acid derivate          |
| S-methyl L-cysteine                          | 1187-84-4   | amino acid derivate          |
| DL-Homocysteine                              | 454-29-5    | amino acid derivate          |
| N-Acetyl L-methionine                        | 65-82-7     | amino acid derivate          |
| Farnesyl-Met-Ome                             | 218962-72-2 | amino acid derivate          |
| Egg albumin                                  | 9006-59-1   | sulfur rich protein          |
| 2-Hydroxy-4-(methylthio)butyric acid Ca salt | 922-50-9    | non-amino acid sulfur source |

Aqueous solutions are prepared according to table 2. Additionally 1:10 and 1:100 dilutions are prepared for validation.

**Table 2: Stock solution preparation of tested compounds**

| non-volatile sulfur compounds                | weight (g) | mL of H <sub>2</sub> O |
|----------------------------------------------|------------|------------------------|
| Cysteine                                     | 1.00       | 10                     |
| Cystin                                       | n/a        | n/a                    |
| Glutathione                                  | 1.00       | 10                     |
| Methionine                                   | 0.50       | 20                     |
| DL-Methionine methylsulfonium chloride       | 1.08       | 10                     |
| N-Acetyl L-cysteine                          | 1.50       | 10                     |
| S-methyl L-cysteine                          | 0.98       | 20                     |
| DL-Homocysteine                              | 0.50       | 10                     |
| N-Acetyl L-methionine                        | 1.91       | 10                     |
| Farnesyl-Met-Ome                             | 1 $\mu$ L  | 20 $\mu$ L             |
| Egg albumin                                  | 0.50       | 10                     |
| 2-Hydroxy-4-(methylthio)butyric acid Ca salt | 1.00       | 20                     |

ATD-GC-MS analyses are performed using following instrumental set-up:

5 **Table 3: ATD-GC-MS instrumentation**

| Instrument         | Details                                        |
|--------------------|------------------------------------------------|
| Injector           | Perkin Elmer Thermal Desorber Turbo Matrix 350 |
| Gas chromatograph  | Agilent 7890A GC                               |
| Column             | 60m x 0.25 $\mu$ m, FFAP                       |
| Mass chromatograph | Agilent 5975C                                  |

**Table 4: ATD-GC-MS parameters**

| ATD parameters          | Value                    |
|-------------------------|--------------------------|
| tube temperature        | 250°C                    |
| trap temperature        | -40°C                    |
| temperature gradient    | 99°C per second to 275°C |
| desorption time         | 5 min                    |
| N <sub>2</sub> pressure | 170 kPa; constant        |

10 Of each compound solution (stock, 1:10, 1:100) 20 $\mu$ L are spiked on a pre-equilibrated Cambridge pad piece which is then inserted into glass tube. Tubes are ortho-nasally assessed after thermal desorption and detected aroma notes determined. The results are given in Table 5.

**Table 5: Flavour Evaluation**

| non-volatile sulfur compounds                | comments and ortho-nasal evaluation                                                           |
|----------------------------------------------|-----------------------------------------------------------------------------------------------|
| Cysteine                                     | fresh tubes (250°C heated) gave burnt phenolic roasty impression with weak sulfury meaty note |
| Glutathione                                  | fresh tubes (350°C heated) gave only weak roasty impression                                   |
| Methionine                                   | fresh tube (350°C heated) smelled cooked potato and meaty-like                                |
| N-Acetyl L-methionine                        | Methanethiol note stronger than hydrogen sulfide note                                         |
| Farnesyl-Met-Ome                             | cooked potato-like                                                                            |
| Egg albumin                                  | Methanethiol and hydrogen sulphide balanced out                                               |
| 2-Hydroxy-4-(methylthio)butyric acid Ca salt | fresh tubes (250°C heated) smelled cooked potato-like with a sulfury roasty aspect            |
| DL-Methionine methylsulfonium chloride       | green, cabbage, fishy, sulfury green                                                          |
| N-Acetyl-Cysteine                            | popcorn, meaty, roasty                                                                        |
| DL-Homocysteine                              | roasty, very weak                                                                             |
| S-Methyl-L-Cysteine                          | cabbage, sulfury                                                                              |

The results indicate that there are mainly two families of compounds, the first generating predominantly hydrogen sulphide ( $H_2S$ ) and the second generating predominantly methanethiol (MSH). The exception is egg albumin for which the generation seems to be similar.

The tubes of those candidates generating mostly  $H_2S$  were ortho-nasally evaluated after heating as being sulfury, roasty or burnt.  $H_2S$  could not be directly detected. In contrast the methanethiol generating compounds all were judged having a potato-like aroma, indicating the presence of methional as side product.

### Example 2

Orthonasal & smoking evaluation of selected non-volatile sulfur compounds is performed using a smoke simulator in pushing mode. The following prototypes are tested:

**Table 6: Prototypes to be tested**

| non-volatile sulfur compounds                | concentration spiked in mg (concept A) | concentration spiked in mg (concept B) |
|----------------------------------------------|----------------------------------------|----------------------------------------|
| Cysteine                                     | 1.82                                   | 0.182                                  |
| Glutathione                                  | 1.75                                   | 0.175                                  |
| Methionine                                   | 0.47                                   | 0.047                                  |
| 2-Hydroxy-4-(methylthio)butyric acid Ca salt | 0.94                                   | 0.094                                  |
| DL-Methionine methylsulfonium chloride       | 1.00                                   | 0.10                                   |
| S-Methyl-L-Cysteine                          | 2.07                                   | 0.20                                   |

Testing is performed as follows. The smoking regime is Health Canada. The power setting of smoke simulator is 54W. Smoking evaluation is performed for concepts showing preference in ortho-nasal evaluation. Smoking evaluation is performed by comparison of untreated blend versus treated concept

For submission to sensory testing in Expert Panel only Cysteine and Glutathione were selected. For Glutathione Concept B and Cysteine Concept B was chosen.

**Table 7: Observations recorded during the experimental run**

| Thiol-containing compound                     | Concept | Panel description                                             |
|-----------------------------------------------|---------|---------------------------------------------------------------|
| Cysteine                                      | A       | sulfury, cold smoke, less off-notes                           |
|                                               | B       | sulfury, cold smoke, less off-notes                           |
| Glutathione                                   | A       | sulfury, cold smoke, less off-notes                           |
|                                               | B       | sulfury, cold smoke, less off-notes                           |
| Methionine                                    | A       | cooked potato and sulfury vegetable are dominating            |
|                                               | B       | cooked potato, sulfury vegetable, less off-notes              |
| 2-Hydroxy-4-(methylthio) butyric acid Ca salt | A       | increased sulfury notes; direction sulfury green & smoked ham |
|                                               | B       | increased sulfury smoked perception with less off-notes       |
| DL-Methionine methylsulfonium chloride        | A       | cooked potato, cabbage notes, untypical aroma                 |
|                                               | B       | no significant difference                                     |

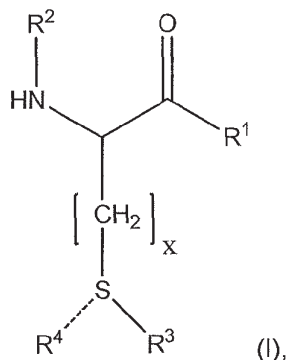
|                     |   |                                                                  |
|---------------------|---|------------------------------------------------------------------|
| S-Methyl-L-Cysteine | A | increase of sulfury notes; green, bell pepper-like & meaty notes |
|                     | B | close to reference with increased hay-like, greenish notes       |

The addition of sulfur containing compounds, especially with free thiol groups, improves the flavor perception of non-combustible products and addresses issues, such as off-notes, complexity and mouth fullness. In particular, addition of the thiol-containing precursors Cysteine and Glutathione contributes positively to the global flavor of aerosols formed upon heating by adding smokiness, mouth fullness, harshness, bitterness and complexity.

In summary the addition of sulfur containing precursors was shown to have a positive effect on the overall sensory perception of prototypes by increasing smoky dark attributes, reducing non-combustible product off-notes and increasing mouth and throat sensations, like bitterness and mouth fullness.

## CLAIMS

1. A smoking article comprising:  
 an aerosol forming substrate;  
 a heating element configured to heat, but not combust, the aerosol forming substrate;  
 a flavour precursor compound added to the aerosol forming substrate, wherein the  
 flavour precursor compound releases at thiol-containing flavour compound  
 upon heating of the aerosol forming substrate by the heating element.
2. A smoking article according to claim 1, wherein the thiol-containing flavour compound  
 is hydrogen sulphide or methanethiol.
3. A smoking article according to claim 1 or 2, wherein the flavour precursor compound  
 has the following structure:

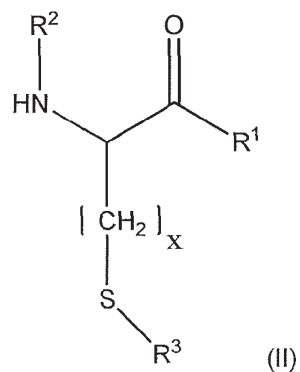


where:

- $\text{R}^1$  is OH or an amino acid residue,
- $\text{R}^2$  is H,  $\text{C}(\text{O})\text{CH}_3$ , or an amino acid residue,
- $\text{R}^3$  is H or C1-C3 unsubstituted alkyl,
- $\text{R}^4$  is optional and, if present, is C1-C3 unsubstituted alkyl, and
- $x$  is an integer from 1 to 3.

4. A smoking article according to claim 3, wherein  $\text{R}^1$  is OH or a glycine residue,  $\text{R}^2$  is H,  $\text{C}(\text{O})\text{CH}_3$ , or a glutamate residue,  $\text{R}^3$  is H or  $\text{CH}_3$ ,  $\text{R}^4$  is not present; and  $x$  is 1 or 2.

5. A smoking article according to claim 1 or 2, wherein the flavour precursor compound has the following structure:



where:

$\text{R}^1$  is OH or an amino acid residue,

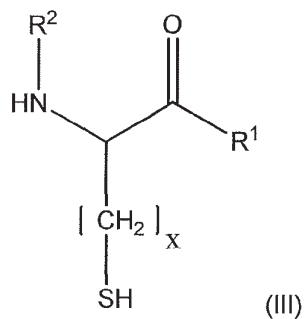
$\text{R}^2$  is H,  $\text{C}(\text{O})\text{CH}_3$ , or an amino acid residue,

$\text{R}^3$  is H, C1-C3 unsubstituted alkyl or a cysteine residue, and

$x$  is an integer from 1 to 3.

6. A smoking article according to claim 5, wherein  $\text{R}^1$  is OH or a glycine residue,  $\text{R}^2$  is H,  $\text{C}(\text{O})\text{CH}_3$ , or a glutamate residue,  $\text{R}^3$  is H or  $\text{CH}_3$ , and  $x$  is 1 or 2.

7. A smoking article according to claim 1 or 2, wherein the flavour precursor compound has the following structure:



where:

$R^1$  is OH or an amino acid residue,

$R^2$  is H,  $C(O)CH_3$ , or an amino acid residue, and

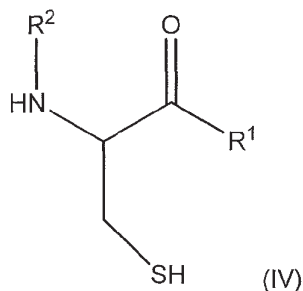
x is an integer from 1 to 3.

5

8. A smoking article according to claim 7, wherein  $R^1$  is OH or a glycine residue,  $R^2$  is H,  $C(O)CH_3$ , or a glutamate residue, and x is 1 or 2.

9. A smoking article according to claim 1 or 2, wherein the flavour precursor compound has the following structure:

10



where:

$R^1$  is OH or an amino acid residue, and

15

$R^2$  is H,  $C(O)CH_3$ , or an amino acid residue.

10. A smoking article according to claim 9, wherein  $R^1$  is OH or a glycine residue and  $R^2$  is H,  $C(O)CH_3$ , or a glutamate residue.

11. A smoking article according to claim 1 or 2, wherein the flavour precursor compound comprises a cysteine residue.

20

12. A smoking article according to claim 11, wherein the flavour precursor compound is selected from the group consisting of cysteine, glutathione, N-acetyl cysteine, S-methyl cysteine, and cystine.

25

13. A smoking article according to claim 1 or 2, wherein the flavour precursor compound is selected from the group consisting of cysteine, cystine, glutathione, methionine, DL

methionine methylsulfonium, N-acetyl cysteine, S-methyl cysteine, DL-homocysteine, N-acetyl methionine, Farnesyl-Met-Ome, Albumin and 2-hydroxy-4-(methylthio)butyric acid.

- 5 14. A smoking article according to claim 13, wherein the flavour precursor compound is cysteine or glutathione.
15. A smoking article according to claim 1 or 2, wherein flavour precursor compound is cysteine.
- 10 16. A smoking article according to any of the preceding claims wherein the aerosol forming substrate comprises tobacco.
17. A smoking article according to claim 16, wherein heating of the tobacco and the  
15 flavour precursor compound results in the production of furfurylthiol.
18. A smoking article according to any of the preceding claims, wherein the flavour precursor compound is configured to release hydrogen sulfide or methanethiol at a temperature of from about 200°C to about 450°C.
- 20 19. A smoking article according to any of the preceding claims, further comprising nicotine or a source of nicotine.