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(54) **METHOD AND COMPOSITIONS FOR
IMPARTING COOLING EFFECT TO
TOBACCO PRODUCTS**

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(57) **ABSTRACT**

(21) Appl. No.: **10/838,872**

The present invention relates to smoking articles such as
cigarettes, and in particular to a method and composition for
providing a cooling effect to cigarettes. The tobacco rod of
the cigarette contains a compound that imparts a cooling
effect and sensation of freshness to tobacco smoke.

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METHOD AND COMPOSITIONS FOR IMPARTING COOLING EFFECT TO TOBACCO PRODUCTS

RELATED APPLICATIONS

[0001] This application is a continuation, under 35 U.S.C. § 120, of International Patent Application No. PCTUS02/40835, filed on Dec. 18, 2002 under the Patent Cooperation Treaty (PCT), which was published by the International Bureau in English on Jul. 3, 2003, which designates the United States and which claims the benefit of U.S. Provisional Patent Application No. 60/343,122, filed Dec. 19, 2001.

FIELD OF THE INVENTION

[0002] The present invention relates to smoking articles such as cigarettes, and in particular to a method and composition for providing a cooling effect to cigarettes. The tobacco rod of the cigarette contains a compound that imparts a cooling effect and sensation of freshness to tobacco smoke.

BACKGROUND OF THE INVENTION

[0003] Menthol, or 2-isopropyl-5-methyl-cyclohexanol, is a cyclic monoterpene. It is a major constituent of peppermint oil, which has a minty taste and odor and which produces a cooling sensation when inhaled or consumed. Menthol is used as a flavorant in a variety of products, including toothpastes, mouthwashes, oral sprays, drugs, cough drops, cough lozenges, analgesic balms, inhalers, chewing gums, hard candies, chocolates, beverages, liquors, lotions, after-shave lotions, shampoos, moist towelettes, perfumes, deodorants, and the like.

[0004] Menthol is also a popular flavorant for use in cigarettes, pipe tobacco, chewing tobacco, and other smoking materials. It is used extensively because of the refreshing cooling effect it imparts to tobacco smoke. Menthol, however, has a number of potential drawbacks associated with its use as a flavorant for smoking materials. Menthol has a minty flavor that may not appeal to all tobacco users. The cooling effect exhibited by menthol may be insufficient for certain applications. Menthol also possesses a high degree of volatility at room temperature. This volatility makes it difficult to control the concentration of menthol in cigarettes and can result in problems in packaging and handling. Smoking products containing menthol may also have a short shelf life due to loss of menthol from the product during storage. This problem is especially acute for menthol-flavored cigarettes that also incorporate a charcoal filter. Menthol is irreversibly bound to charcoal and other adsorbents commonly used in filter cigarettes, and over time a substantial and unacceptable decrease in the available menthol results. Adsorption of menthol may also adversely affect the performance of the cigarette filter in removing undesirable components from the smoke generated during combustion of the tobacco product.

[0005] Accordingly, considerable time and expense has been spent on development of a satisfactory method for producing cigarettes exhibiting a satisfactory level of cooling effect. Methods for mentholating unfiltered cigarettes and filtered cigarettes not incorporating an adsorbent are generally unsatisfactory for use on charcoal-filtered cigarettes. For example, the classic method of mentholation

using mentholated strips sealed in a cigarette pack is unsatisfactory because the charcoal will simply absorb the menthol during storage, resulting in what is essentially a non-mentholated cigarette.

[0006] Other methods for producing mentholated smoking products that have been investigated include providing menthol adsorbed on a support, for example, diatomaceous earth, from which the menthol is later released. Such methods suffer from low menthol yields, and may result in unacceptable taste or appearance of the smoking product.

[0007] Other methods have focused on the preparation of menthol derivatives or similar compounds that release menthol or menthol-like flavorants upon pyrolysis or hydrolysis. Such derivatives include ester and carbonate derivatives of menthol, for example, the derivatives disclosed in U.S. Pat. Nos. 3,312,226, 3,332,428, 3,419,543, 4,119,106, 4,092,988, 4,171,702, 4,177,339, 4,212,310, 4,532,944 and 4,578,486. However, such derivatives may suffer from one or more drawbacks. For example, they may have a degree of volatility that makes them unsuited for use with adsorbents, they may not yield a sufficient quantity of free menthol upon decomposition, they may exhibit only a minimal cooling effect, they may be unstable or difficult to process, or the pyrolysis or hydrolysis products may be toxic, carcinogenic, or may result in an unacceptable taste.

SUMMARY OF THE INVENTION

[0008] While various methods have been provided for imparting a cooling effect to cigarettes, no satisfactory and practical substitutes for menthol have heretofore been available. There is, therefore, a need for compounds that are capable of delivering an acceptable feeling of freshness and coolness to the smoke stream of a cigarette.

[0009] Accordingly, in a first embodiment a smoking article is provided, the smoking article including a smokable material and a compound including a cyclic α -keto enamine, wherein the compound is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article.

[0010] In an aspect of the first embodiment, the compound is deposited on the smokable material.

[0011] In an aspect of the first embodiment, the cyclic α -keto enamine is selected from the group consisting of 3-methyl-2-(1-piperidinyl)-2-cyclopenten-1-one, 3-methyl-2-diethylamino-2-cyclopenten-1-one, 5-methyl-2-(1-piperidinyl)-2-cyclopenten-1-one, 5-methyl-2-diethylamino-2-cyclopenten-1-one, 5-methyl-2-dibutylamino-2-cyclopenten-1-one, 5-methyl-2-dihexylamino-2-cyclopenten-1-one, 5-ethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, 3-(4-dimethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, 3-(1-pyrrolidinyl)-2-cyclopenten-1-one, 2-methyl-3-(1-pyrrolidinyl)-2-cyclopenten-1-one, 2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 3-methyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 3,5,5-trimethyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 6-methyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 4,4,6-trimethyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 5-methyl-2-(1-morpholino)-2-cyclopenten-1-one, (S)-5-methyl-2-(2-methoxycarbonyl-1-pyrrolidinyl)-2-cyclopenten-1-one, (S)-3-methyl-2-(2-carboxy-1-pyrrolidinyl)-2-cyclopenten-1-one, 2,5-

dimethyl-4-(1-pyrrolidinyl)-3-(2H)-furanone, 4,5-dimethyl-3-(1-pyrrolidinyl)-2-(5H)-furanone, and mixtures thereof.

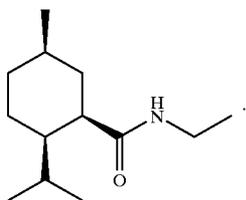
[0012] In an aspect of the first embodiment, the cyclic α -keto enamine comprises 3-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, or 5-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, or 5-methyl-4-(1-pyrrolidinyl)-3-(2H)-furanone, or 4-methyl-3-(1-pyrrolidinyl)-2-(5H)-furanone.

[0013] In an aspect of the first embodiment, the smoking article is a cigarette.

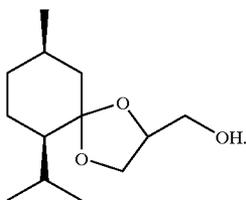
[0014] In an aspect of the first embodiment, the smoking material further includes a filter, and the filter can include charcoal.

[0015] In a second embodiment, a method of providing a smoke stream from a cigarette is provided, wherein the smoke stream is capable of imparting a cooling sensation to the oral cavity, the method comprising the steps of providing a cigarette, the cigarette including a tobacco charge and a compound including a cyclic α -keto enamine; combusting the tobacco charge, whereby a smoke stream is produced; and inhaling the smoke stream from the cigarette, whereby a cooling sensation is imparted to an oral cavity.

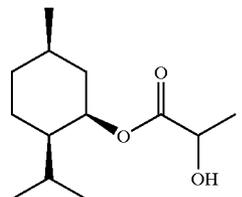
[0016] In a third embodiment, a smoking article is provided, the smoking article including a smokable material and a compound including a carboxamide, wherein the carboxamide is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article, the smoke stream comprising the carboxamide. The carboxamide can have a chemical formula corresponding to:



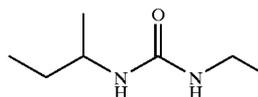
[0017] In a fourth embodiment, a smoking article is provided, the smoking article including a smokable material and a compound including a mentane glycerol ketal, wherein the mentane glycerol ketal is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article, the smoke stream including the mentane glycerol ketal. The mentane glycerol ketal can have a chemical formula corresponding to:



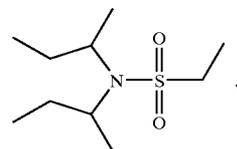
[0018] In a fifth embodiment, a smoking article is provided, the smoking article including a smokable material and a compound including a menthyl ester, wherein the menthyl ester is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article, the smoke stream including the menthyl ester. The menthyl ester can have a chemical formula corresponding to:



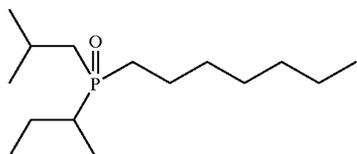
[0019] In a sixth embodiment, a smoking article is provided, the smoking article including a smokable material and a compound including an alkyl-substituted urea, wherein the alkyl-substituted urea is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article, the smoke stream including the alkyl-substituted urea. The alkyl-substituted urea can have a chemical formula corresponding to:



[0020] In a seventh embodiment, a smoking article is provided, the smoking article including a smokable material and a compound including a sulfonamide, wherein the sulfonamide is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article, the smoke stream including the sulfonamide. The sulfonamide can have a chemical formula corresponding to:



[0021] In an eighth embodiment, a smoking article is provided, the smoking article including a smokable material and a compound including a phosphine oxide, wherein the phosphine oxide is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article, the smoke stream including the phosphine oxide. The phosphine oxide can have a chemical formula corresponding to:



[0022] In a ninth embodiment, a finished tobacco product is provided, the finished tobacco product including a tobacco and a compound including a carboxamide, a mentane glycerol ketal, a menthyl ester, an alkyl-substituted urea, a sulfonamide, and a phosphine oxide, wherein the compound is deposited on the tobacco, and wherein the compound is capable of imparting a cooling sensation to an oral cavity.

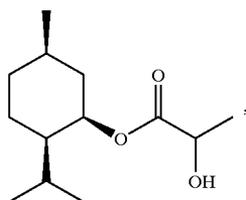
[0023] In a tenth embodiment, a finished tobacco product is provided, the finished tobacco product including a tobacco and a compound including a cyclic α -keto enamine, wherein the compound is deposited on the tobacco, and wherein the compound is capable of imparting a cooling sensation to an oral cavity.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0024] Introduction

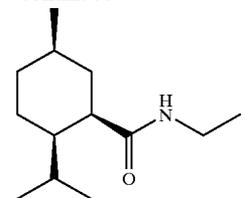
[0025] The following description and examples further illustrate the preferred embodiments of the present invention. Those of skill in the art will recognize that there are numerous variations and modifications of this invention that are encompassed by its scope. Accordingly, the description of preferred embodiments should not be deemed to limit the scope of the present invention.

[0026] In preferred embodiments, methods and compositions for imparting a feeling of freshness and coolness to the smoke stream of a smoking article, such as a cigarette, are provided. The methods and compositions utilize compounds of the class of cyclic α -keto enamines. The compositions do not adversely affect the taste of the cigarette while impart a sensation of "cooling" to the oral cavity, however most impart such a sensation without the "minty" odor characteristic of menthol. Compounds from the class of cyclic α -keto enamines exhibiting a cooling effect have been reported in the literature. See Ottinger, et al., *J. Agric. Food Chem.*, 2000, 49, 5383-5390. Other compounds that may exhibit a cooling effect rendering them suitable for use as flavorants in tobacco products include menthyl esters, for example:

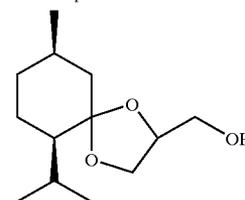


carboxamides, for example:

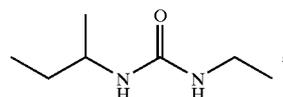
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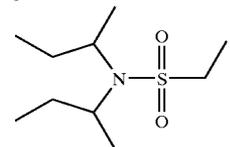
mentane glycerol ketals, for example:



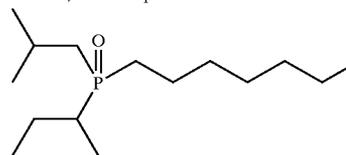
alkyl-substituted ureas, for example:



sulfonamides, for example:



and phosphine oxides, for example:



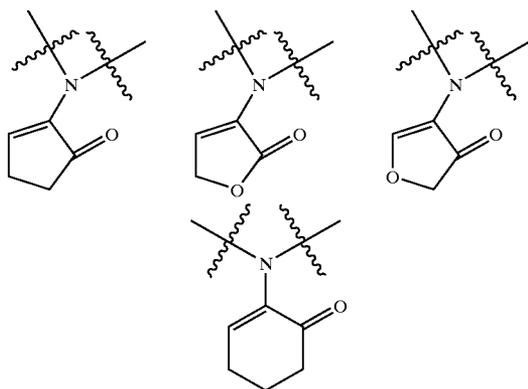
[0027] The preferred embodiments relate to smoking articles such as cigarettes, cigars, and pipe tobacco, and in particular to cigarettes having a reduced content of various polyaromatic hydrocarbons (PAHs), tobacco specific nitrosamines (TSNAs), phenolic compounds, and certain other undesired components in cigarette smoke, including both mainstream and sidestream smoke, or cigarettes having a reduced content of TSNAs, nicotine, or other undesired components in the uncombusted smoking product. The tobacco products of preferred smoking articles may also include a catalytic system including metallic or carbonaceous particles and a source of nitrate or nitrite, as described in copending application Ser. No. 10/007,724 filed on Nov. 9, 2001. The preferred smoking articles typically incorporate activated charcoal filters, however the compounds of preferred embodiments are also suitable for use with unfiltered smoking articles.

[0028] While the compositions and methods of preferred embodiments generally refer to tobacco, particularly in the form of cigarettes, it is to be understood that such compo-

sitions and methods encompass any smokable material or smokable composition, as will be apparent to one skilled in the art.

[0029] Cyclic α -Keto Enamines

[0030] In a preferred embodiment, the cooling agent is selected from the class of compounds including cyclic α -keto enamines. The class of cyclic α -keto enamines includes compounds characterized by the presence of the following moieties:



[0031] Although compounds containing five- and six-membered ketone rings are generally preferred, rings containing additional carbon atoms, e.g., 7, 8, 9, 10, or more carbon atoms, may also be suitable. The hydrogen substituents on the ring may be replaced by other substituents. Preferred substituents include alkyl groups, particularly methyl and ethyl groups. Typically, from one to three of the carbon atoms on the ring may be substituted with alkyl substituents, and a particular carbon atom on the ring may include up to two alkyl substituents. The nitrogen atom preferably is a part of a piperidine, diethylamine, dibutylamine, dihexylamine, morpholine, 1-proline methylester, or 1-proline group.

[0032] While alkyl groups are generally preferred as substituents on the cyclopentenone or cyclohexanone ring, in certain embodiments other hydrocarbyl substituents may also be suitable, including, but not limited to, aryl, alkenyl, cycloalkyl, cycloalkenyl, bicyclic or multicyclic hydrocarbyl groups, branched chains, straight chains, combinations of any of the foregoing, and the like. The hydrocarbyl groups may be substituted or unsubstituted, for example, by one or more heteroatoms. In addition to one or two carbon atom-containing hydrocarbyl groups, suitable hydrocarbyl groups may also include a greater number of carbon atoms, for example, 3, 4, 5, 6, 7, 8, 9, 10, or more carbon atoms. Examples of such hydrocarbyl groups include, but are not limited to propyl, isopropyl, n-butyl, tert-butyl, pentyl, hexyl, heptyl, and higher. In certain embodiments, it may be preferred to substitute one or more hydrogen atoms on the cyclopentenone or cyclohexanone ring with a heteroatom or heteroatom-containing moiety, for example, a halogen such as fluorine, or an ester or ether group. From none to all of the available hydrogens on the cyclopentenone or cyclohexanone ring may be substituted.

[0033] While the nitrogen atom generally forms a part of one of the above-mentioned functional groups (i.e., piperidine, diethylamine, dibutylamine, dihexylamine, morpholine, 1-proline methylester, and 1-proline groups), in certain embodiments it may be desirable for the nitrogen atom to form a part of other substituent groups. For example, the nitrogen atom may be substituted by two or more of the substituent groups described above as suitable substituents on the cyclopentenone or cyclohexanone ring.

[0034] The chemical composition, number, and placement of substituents or alteration(s) in ring size or constituents may have an affect on cooling activity and/or odor, as discussed below. Table 1 lists a number of cyclic keto enamines, including numerous α -keto enamines, that may be suitable for use as cooling agents in tobacco products. The cooling and odor threshold, as determined in tap water using a triangle test, the odor quality, and the ratio of cooling threshold to odor threshold are reported.

TABLE 1

Cyclic Keto Enamine Flavoring Agents					
Cmpd.	Cyclic Keto Enamines	Cooling Threshold (mg/kg)	Odor Threshold (mg/kg)	Odor Quality	Ratio (cool/odor)
1	3-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one	29.0-43.5	43.5-72.5	faintly amine-like	0.8
2	5-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one	4.5-9.0	2.6-5.2	faintly mint-like	1.7
3	3-methyl-2-(1-piperidinyl)-2-cyclopenten-1-one	60.0-100.0	80.0-120.0	faintly amine-like	0.8
4	3-methyl-2-diethylamino-2-cyclopenten-1-one	30.0-50.0	2.0-3.0	carvone-like	10.0
5	5-methyl-2-(1-piperidinyl)-2-cyclopenten-1-one	16.0-24.0	12.0-20.0	faintly mint-like	2.7
6	5-methyl-2-diethylamino-2-cyclopenten-1-one	12.0-20.0	6.0-9.0	curcuma-like	2.1
7	5-methyl-2-dibutylamino-2-cyclopenten-1-one	48.4-67.8	2.4-2.8	mint-like	16.0
8	5-methyl-2-dihexylamino-2-cyclopenten-1-one	—	—	—	—
9	5-ethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one	26.7-42.5	13.4-22.4	faintly mint-like	2.0
10	(E)-4,5-dimethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one	68.0-113.3	136.0-226.6	faintly mint-like	0.5
11	3,5-dimethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one	32.5-53.5	16.0-27.0	rubber-like	2.0
12	3,4-dimethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one	51.3-85.5	25.7-42.8	rubber-like	2.0
13	3-(1-pyrrolidinyl)-2-cyclopenten-1-one	—	234.0-390.0	odorless, bitter	—
14	2-methyl-3-(1-pyrrolidinyl)-2-cyclopenten-1-one	—	92.0-138.0	odorless, bitter	8.0
15	2-(1-pyrrolidinyl)-2-cyclohexen-1-one	495.0-830.0	62.0-106.0	rubber-like	2.0

TABLE 1-continued

Cyclic Keto Enamine Flavoring Agents					
Cmpd.	Cyclic Keto Enamines	Cooling Threshold (mg/kg)	Odor Threshold (mg/kg)	Odor Quality	Ratio (cool/odor)
16	3-methyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one	90.5–150.8	45.2–75.4	faintly mint-like	32.0
17	3,5,5-trimethyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one	1605.0–2675.0	50.2–83.6	amine-like	8.0
18	6-methyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one	26.9–44.8	3.4–5.6	rubber-like	4.0
19	4,4,6-trimethyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one	2213.0–3688.0	553.0–922.0	mint-like	4.0
20	5-methyl-2-(1-morpholino)-2-cyclopenten-1-one	467.0–700.8	935.0–1558.0	rubber-like	0.5
21	(S)-5-methyl-2-(2-methoxycarbonyl-1-pyrrolidinyl)-2-cyclopenten-1-one	112.0–188.0	—	odorless	<1
22	(S)-3-methyl-2-(2-carboxy-1-pyrrolidinyl)-2-cyclopenten-1-one	490.0–735.0	—	odorless	<1
23	5-methyl-4-(1-pyrrolidinyl)-3-(2H)-furanone	1.5–3.0	—	odorless	<0.1
24	2,5-dimethyl-4-(1-pyrrolidinyl)-3-(2H)-furanone	100.0–140.0	30.0–60.0	nutty, roasty	2.7
25	4-methyl-3-(1-pyrrolidinyl)-2-(5H)-furanone	0.05–0.06	—	odorless	<0.1
26	4,5-dimethyl-3-(1-pyrrolidinyl)-2-(5H)-furanone	2.0–4.0	32.0–64.0	faintly mint-like	<0.1

[0035] Compounds 1 and 2 have been identified as active cooling agents found in the dark malt formed from glucose and 1-proline in Maillard reactions. The compounds have virtually no odor or taste, but impart a long lasting sensation of coolness to the oral cavity. Taste testing of Compounds 3-7 indicates that enlargement of the pyrrolidine ring by one methylene group leads to a significant decrease in cooling activity compared to Compounds 1 and 2. Opening the pyrrolidine ring does not substantially decrease the cooling activity (Compound 6). However, increasing the size of the aliphatic amino moiety by two methylene groups drastically decreases the cooling activity of the compound (Compound 7), and increasing the chain length of the amino moiety to six carbon atoms completely diminishes the cooling activity (Compound 8). Insertion of an additional methyl group or substitution of the methyl group by an ethyl group on the cyclopentenone ring results in a significant increase in cooling activity (Compounds 9 and 10 compared to Compound 2). Changing the position of the methyl substituent has a small effect on cooling activity (compare Compound 11 to Compounds 10 and 12). Changing the position of the methyl group and the amino moiety (as in β -keto enamines) results in a loss of cooling activity (see Compounds 13 and 14). Enlargement of the cyclopentenone ring leads to a significant decrease in cooling activity (compare Compounds 16 and 18 to Compounds 1 and 2). Subtraction of or insertion of additional methyl groups significantly decreases cooling activity (compare Compound 18 to Compounds 15 and 19). Incorporation of an oxygen atom into the pyridine moiety substantially decreases the cooling effect (see Compounds 20, 21, and 22). Substitution of the methylene group at C(4) in Compound 1 results in a strong increase in cooling activity (see Compound 23), and yields a compound with no odor. Adding a second methyl group, however, produces a significant decrease in cooling activity (compare Compound 24 to Compounds 1 and 23). Changing the position of the oxygen atom in the cyclopentenone ring, as in a γ -lactone, dramatically increases cooling activity (see Compounds 25-26) to a level substantially higher than that observed for either Compound 1 or (-)-menthol.

[0036] On the basis of the ratio of cooling to odor, Compounds 23, 25, and 26 are suitable for use as odorless cooling agents (i.e., they possess a ratio of cooling to odor of <0.1). The data reveal no clear association between a minty odor and cooling. Compounds 1, 2, 23, and 25 demonstrate a high degree of cooling effect, and have been identified as particularly preferred for use in flavoring smoking articles.

[0037] Synthesis

[0038] The cooling agents of preferred embodiments may be synthesized according to methods published in the literature. See, e.g., Ottinger, et al., *J. Agric. Food Chem.*, 2000, 49, 5383-5390.

[0039] Compounds 1-12 and 15-26 may be synthesized as follows. A solution of the cyclic enolone (100 mmol) and the corresponding amino compound (400 mmol) are refluxed in ethanol (600 mL) and acetic acid (400 mmol) for 3 h. The cyclic enolone is selected as follows: (E)-2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one (to prepare Compound 10), (E)-2-hydroxy-3,4-dimethyl-2-cyclopenten-1-one (to prepare Compound 12), 2,5-dimethyl-4-hydroxy-3-(2H)-furanone (to prepare Compound 24), 2-hydroxy-2-cyclohexen-1-one (to prepare Compound 15), 2-hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one (to prepare Compound 17), 2-hydroxy-3,5,5-trimethyl-2-cyclohexen-1-one (to prepare Compound 19), 2-hydroxy-3,5-dimethyl-2-cyclopenten-1-one (to prepare Compound 11), 2-hydroxy-3-ethyl-2-cyclopenten-1-one (to prepare Compound 9), 2-hydroxy-3-methyl-2-cyclohexen-1-one (to prepare Compounds 16 and 18), 2-hydroxy-3-methyl-2-cyclopenten-1-one (to prepare Compounds 3-8, and 20-21), and 4-hydroxy-5-methyl-3-(2H)-furanone (to prepare Compound 23). The amine is selected as follows: pyrrolidine (to prepare Compounds 1, 2, 9, 12, 15-20, 23, and 24), piperidine (to prepare Compounds 3 and 5), diethylamine (to prepare Compounds 4 and 6), dibutylamine (to prepare Compound 7), dihexylamine (to prepare Compound 8), morpholine (to prepare Compound 20), 1-proline methylester (to prepare Compound 21).

[0040] After cooling the solution to room temperature, the solvent is removed under vacuum, the residue is taken up in

water (300 mL), and the pH is adjusted to 9 with sodium hydroxide solution (30% in water). The solution is then extracted with diethyl ether (5×150 mL), the combined organic layers are washed with an aqueous solution of Na₂CO₃ (200 mL; 0.5 mol/L), dried over Na₂SO₄, and then solvent is removed under vacuum. The residual oil is dissolved in pentane/diethyl ether (8/2, v/v; 10 mL) and then injected into a column (30×500 mm) packed with a slurry of Al₂O₃ (basic activity III-IV, Merck, Darmstadt, Germany) in pentane. Fractionation of the reaction products is performed by chromatography using pentane/diethyl ether mixtures with increasing diethyl ether content. Solvent is removed from the fractions collected under vacuum to yield the target compounds as colorless oils. The fractions may be identified by their spectroscopic data. See Ottinger, et al., *J. Agric. Food Chem.*, 2000, 49, at 5384-5386.

[0041] To obtain Compounds 13 and 14, additional processing steps are necessary. A solution of 3-hydroxy-2-cyclopenten-1-one (100 mmol) or 3-hydroxy-2-methyl-2-cyclopenten-1-one (100 mmol), respectively, is refluxed in the presence of pyrrolidine (400 mmol), acetic acid (400 mmol), and ethanol (600 mL) for 4 h. After cooling the solution to room temperature, the solvent is removed under vacuum, the residue is taken up in water (300 mL), and the pH is adjusted to 14 with concentrated sodium hydroxide solution. The solution is then extracted with diethyl ether (5×150 mL) and solvent is removed from the combined organic layers under vacuum. The residual solid is recrystallized from diethyl ether, yielding the target compounds as yellow crystals.

[0042] Compound 22 may be obtained as follows. A mixture of 2-hydroxy-3-methyl-2-cyclopenten-1-one (50 mmol) and 1-proline (80 mmol) are refluxed in ethanol (400 mL) for 4 h. After cooling the sample to room temperature, the reaction mixture is taken up in water (500 mL), filtered, and the pH is adjusted to 9 by adding an aqueous sodium hydroxide solution (1 mol/L). The solution is extracted with dichloromethane (5×200 mL), the aqueous layer is freeze-dried, the residue is taken up in a mixture of methanol and aqueous ammonium formate (15 mL; 5/95, v/v; pH 7.0; 0.1 mol/L), and then fractionated by flash chromatography on RP-18 material (15.0 g; Lichroprep 25-40 μm, Merck, Darmstadt, Germany) using the same solvent mixture as the mobile phase. After injection of the crude material into the column and chromatography with an eluent flow of 1.5 mL/min, the effluent of a peak detected at λ=300 nm after 5 h is collected. After evaporation of the solvent and freeze-drying, the material is purified by RP-HPLC using the following solvent gradient: after isocratic chromatography with a mixture of methanol and aqueous ammonium formate buffer (10/90, v/v; pH 7.0; 0.1 mol/L) for 10 min, the methanol content is increased to 100% within 10 min. Monitoring the effluent at 322 nm gives a peak at 9 min, which is collected in several runs. The combined eluents are freeze-dried, yielding the product (3.5 mmol; 7% in yield).

[0043] Compound 25 is prepared as follows. Diethyl oxalate (1.03 mol) and ethyl propionate (1.03 mol) are added dropwise to a suspension of sodium ethoxide (1.00 mol) in diethyl ether (300 mL). After refluxing the sample for 3 h, the reaction mixture is cooled to room temperature, the solvent is removed under vacuum (45 mbar), and the residue is taken up in water (160 mL). Formaldehyde (1.0 mol, 35% in solution) is added in small portions while the mixture is

cooled in a water bath. The reaction mixture is then heated for 1 h at 50° C., the ethanol generated is removed under vacuum, the solution is acidified with concentrated hydrochloric acid (225 mL), water (60 mL) and hydroquinone (100 mg) are added, and the mixture is refluxed for 4 h. The mixture is then cooled to room temperature, extracted with ethyl acetate (5×100 mL), and solvent is removed from the combined organic layers under vacuum. The residue is recrystallized from diethyl ether, yielding the product (38.8 g, 34% in yield) as white crystals.

[0044] Compound 26 may be prepared as follows. 3-hydroxy-4-methyl-2(5h)-furanone (100 mmol), acetic acid (100 mmol), and pyrrolidine (100 mmol) is refluxed in ethanol (225 mL) for 2.5 h., yielding the product.

[0045] Incorporation into Smoking Article

[0046] The cooling agent is typically applied to the smokable material. If the smokable material is tobacco, it is convenient to apply a solution or suspension of cooling agent to cut filler before, during, or after the addition of the top flavor, or before, during, or after application of the casing solution.

[0047] The cooling agent is preferably well dispersed throughout the tobacco so as to provide uniform effectiveness throughout the entire mass of smokable material and throughout the entire period during which the material is smoked. In the case of cigarette tobacco wherein a blend of various tobaccos is preferred, the solution or suspension of cooling agent may be applied to one or more of the blend constituents, or all of the blend constituents, as desired. Preferably, the solution or suspension is applied to all of the blend constituents so as to ensure substantially uniform coverage.

[0048] It is preferred to apply the solution or suspension of cooling agent to the smokable material in the form of a fine mist, such as is produced using an atomizer. In a particularly preferred embodiment, the solution or suspension is applied to tobacco, preferably cut filler, in a rotating tumbler equipped with multiple spray heads. Such a method of application ensures an even coating of cooling agent on the tobacco product. The tobacco may be heated before, during, or after application of the solution so as to facilitate evaporation of excess solvent.

[0049] It is preferred to add a sufficient quantity of the cooling agent to the smokable material to yield a satisfactory level of cooling. Typically, the smokable material contains from about 0.0001 or less, 0.0005, 0.001, 0.005, 0.01, 0.05, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, or 1 mg to about 100 mg or more cooling agent per gram smokable material, preferably from about 2, 3, 4, or 5 mg to about 20, 30, 40, 50, 60, 70, 80, or 90 mg, and more preferably from about 6, 7, 8, 9, or 10 mg to about 11, 12, 13, 14, 15, 16, 17, 18, or 19 mg. The amount of cooling agent preferred may vary depending upon the cooling and odor properties of the compound, including, but not limited to, the cooling threshold, the odor threshold, odor quality, and ratio of cooling threshold to odor threshold. The lower the cooling threshold, the less cooling agent is required to produce an acceptable cooling effect. In a particularly preferred embodiment, a typical full flavored king size cigarette will contain sufficient cooling agent to yield a cooling effect of the same magnitude as that delivered in a typical mentholated full flavored king size cigarette.

[0050] In certain embodiments, it may be preferred to employ a single compound to provide a cooling effect. In other embodiments, it may be preferred to employ a combination of two or more of the compounds of preferred embodiments. Likewise, it may be preferred in certain embodiments to use a combination of (–)menthol and/or another cooling substance, and one or more of the compounds of the preferred embodiments. Combinations of compounds that take advantage of the different cooling and/or odor characteristics of the compounds may be preferred in order to provide a tailored degree of cooling and/or a tailored flavor.

[0051] Once the cooling agent has been applied, the smokable material may be further processed and formed into any desired shape or used loosely, for example, in cigars, cigarettes, and pipe tobacco, in any suitable manner as is well-known to those skilled in the art.

[0052] The Filter

[0053] In preferred embodiments, a filter for tobacco smoke is provided for the smoking article. The filter can be provided in combination with cigarettes or cigars or other smokable devices containing divided tobacco. Preferably, the filter is secured to one end of the smokable device, positioned such that smoke produced from the tobacco passes into the filter before entering the smoker. The filter can also be provided by itself, in a form suitable for attachment to a cigarette, cigar, pipe, or other smokable device.

[0054] The filter according to preferred embodiments advantageously removes at least some amount of an undesired component from tobacco smoke. Undesired components in tobacco smoke may include permanent gases, organic volatiles, semivolatiles, and nonvolatiles. Permanent gases (such as carbon dioxide) make up 80 percent of smoke, and are generally unaffected by filtration or adsorption materials. The levels of organic volatiles, semivolatiles, and nonvolatiles may be reduced by filters of various designs. The filters according to preferred embodiments may advantageously remove undesired components including, but not limited to, tar, nicotine, carbon monoxide, nitrogen oxides, HCN, acrolein, nitrosamines, polyaromatic hydrocarbons, particulates, oils, various carcinogenic substances, and the like.

[0055] The filter preferably permits satisfactory or improved smoke flavor, nicotine content, and draw characteristics. The filter is preferably designed to be acceptable to the user, being neither cumbersome nor unattractive. Filters according to preferred embodiments may be made of inexpensive, safe, and effective components, and may preferably be manufactured with standard cigarette manufacturing machinery.

[0056] The filter may incorporate one or more materials capable of absorbing, adsorbing, or reacting with at least one undesirable component of tobacco smoke. Such absorbing, adsorbing, or reacting materials may be incorporated into the filter using any suitable method or device. In a preferred embodiment, the absorbing, adsorbing, or reacting material may be contained within a smoke-permeable cartridge to be placed within the filter, or contained within a cavity within the filter. In another embodiment, the absorbing, adsorbing, or reacting material is deposited or applied on and/or in the filter material.

[0057] Application methods may include forming a paste of the absorbing, adsorbing, or reacting material in a suitable liquid, applying the paste to the filter material, and allowing the liquid to evaporate. Alternatively, the absorbing, adsorbing, or reacting material may be mixed with an adhesive substance and applied to the filter material. All of the filter material may include the absorbing, adsorbing, or reacting material, or only a portion of the filter material may include the adsorbing or reacting material.

[0058] The cigarette filters of the preferred embodiments preferably include activated carbon (commonly referred to as charcoal) as an adsorbing material. The process by which activated carbon removes compounds is adsorption, which is a different process than absorption. Absorption is the process whereby absorbates are dispersed throughout a porous absorbent, while adsorption is a surface attraction effect. Both adsorption and absorption can be physical or chemical effects. The adsorptive effect associated with activated carbon is mainly a physical effect. In activated carbon filters, smoke compounds in the organic volatile and semivolatile phases diffuse through the carbon particles, move over the surface and then move into the activated carbon pores compelled by a phenomenon known as Van der Waal's forces. Although these forces are generally considered weak, at very short range (one or two molecular diameters), they are strong enough to attract and effectively hold smoke components.

[0059] Activated carbon may be obtained from a variety of sources, including, but not limited to, wood, coconut shells, coal, and peat. Wood generally produces soft and macroporous activated carbon (pores from 50 to 1,000 nm in diameter). Peat and coal materials generally produce activated carbon that is predominantly mesoporous (pores 2 to 50 nm in diameter). Activated carbon derived from coconut shells is generally microporous (pores of less than 2 nm in diameter), has a large surface area, and has a low ash and base metal content when compared to certain other types of activated carbon.

[0060] Preferred activated carbons are microporous and have a high density, which imparts improved structural strength to the activated carbon so that it can resist excessive particle abrasion during handling and packaging.

[0061] The filters of preferred embodiments may also contain various other adsorptive, absorptive, or porous materials in addition to activated carbon as described above. Examples of such materials, include, but are not limited to, cellulosic fiber, for example, cellulose acetate, cotton, wood pulp, and paper; polymeric materials, for example, polyesters and polyolefins; ion exchange materials; natural and synthetic minerals such as activated alumina, silica gel, and magnesium silicate; natural and synthetic zeolites and molecular sieves (see, for example U.S. Pat. No. 3,703,901 to Norman et al.); natural clays such as meerschaum; diatomaceous earth; activated charcoal and other materials as will be understood by those with skill in the art. The adsorptive, absorptive, or porous material may be any nontoxic material suitable for use in filters for smokable devices that are compatible with other substances in the smoking device or smoke to be filtered.

[0062] Typically, the filter element may include as the major component a porous material, for example, cellulose acetate tow or cellulosic paper, referred to below as a "filter

material." The adsorptive or absorptive component, often a granular or particulate substance such as activated carbon, is generally dispersed within the porous filter material of the filter segment or positioned within a cartridge or cavity (for example, within a cavity of a triple filter, as discussed below).

[0063] The filter material may have the form of a non-woven web of fibers or a tow. Alternatively, the filter material may have a sheet-like form, particularly when the material is formed from a mixture of polymeric or natural fibers, such as cotton or wood pulp. Filter material in web or sheet-like form can be gathered, folded, crimped, or otherwise formed into a suitable (for example, cylindrical) configuration using techniques which will be apparent to one skilled in the art. See, for example, U.S. Pat. No. 4,807,809 to Pryor et al.

[0064] In preferred embodiments, the filter material constitutes cellulose acetate tow or cellulose paper. Cellulose acetate tow is the most widely preferred filter material in cigarettes worldwide. Cellulose paper filter materials generally provide better tar and nicotine retention than do acetate filters with a comparable pressure drop, and have the added advantage of superior biodegradability. Cellulose and cellulose acetate reduce the amount of chemicals in the semivolatile phase and the nonvolatile phase, which is composed of solid particulates (commonly referred to as "tar"). These compounds are reduced in direct proportion to the amount of cellulose or cellulose acetate in the filter. Increasing density of the cellulose or cellulose acetate generally means increasing the pressure drop, which increases the filter retention and therefore decreases tar delivery. Filters retain generally less than 10 percent of vapor phase components.

[0065] In certain embodiments, it may be preferred to use a polymeric material such as cellulose acetate as the filter material rather than a material such as cellulose paper. Polymeric materials may be preferred in embodiments wherein superior chemical inertness or structural integrity during use are desired attributes of the filter, for example, when certain smoke-altering components reactive to cellulose paper are present in the filter, or when components reactive to cellulose paper are generated within the filter. Cellulose acetate tow (such as that available from Celanese Acetate of Charlotte, N.C.) is the most commonly preferred polymeric material, however suitable polymeric materials may include other synthetic addition or condensation polymers, such as polyamides, polyesters, polypropylene, and polyethylene.

[0066] The polymeric material may be any nontoxic polymer suitable for use in filters for smokable devices that are compatible with other substances in the smoking device or smoke to be filtered, and which possess the desired degree of inertness. The polymeric material is preferably in fibrous tow form, but may optionally be in other physical forms, for example, crimped sheet. The polymeric material may constitute a single polymer or a mixture of different polymers, for example, two or more of components such as homopolymers, copolymers, terpolymers, functionalized polymers, polymers having different molecular weights, polymers constituting different monomers, polymers constituting two or more of the same monomers in different proportions, oligomers, and nonpolymeric components. The polymer may also

be subjected to suitable pre-treatment or post-treatment steps, for example, functionalization of the polymer, coating with suitable materials, and the like.

[0067] When polymeric fibers are employed as the filter material, they can make up all or a portion of the composition of the filter material of the filter. Alternatively, the filter material can be a mixture or blend of polymer fibers, or a mixture or blend of polymer fibers and nonpolymeric fibers, for example, cellulose fibers obtained from wood pulp, purified cellulose, cotton fibers, and the like. A mixture of filter materials may be preferred in certain embodiments where it is desired to reduce materials costs, as polymeric materials may be more expensive than natural fibers. Any suitable proportion of polymeric material may be present, for example from 100% by weight polymeric material down to 80, 60, 50, 40, 30, 25, 20, 15, or 10% by weight or less polymeric material.

[0068] As discussed above, in certain embodiments it may be desirable to coat the filter material with one or more substances that may react chemically with an undesirable component of the smoke. Such substances may include natural or synthetic polymers, or chemicals known in the art to provide for a treated filter material capable of altering the chemistry of tobacco smoke. One method for coating the filter material is to prepare a solution or dispersion of the substance with a suitable solvent. Suitable solvents may include, for example, water, ethanol, acetone, methyl ethyl ketone, toluene, and the like.

[0069] The solution or dispersion can be applied to the surface of the filter material using gravure techniques, spraying techniques, printing techniques, immersion techniques, injection techniques, and the like. Most preferably, the filter material is essentially insoluble in the preferred solvent, and as such does not substantially affect the general structure of the filter material. After the solution or dispersion is applied to the surface of the filter material, the solvent is removed, typically by air-drying at room temperature or heating, for example, in a convection or forced-air oven. The amount of solution or dispersion which is applied to the filter material is typically sufficient to cover the outer surface of the filter material, but not sufficient to fill the void spaces between the fibers of filter material.

[0070] Typically, the amount of solution or dispersion applied to the filter material is sufficient to deposit at least about 5 percent, preferably at least about 8 percent, more preferably at least about 10 percent, and most preferably at least about 15 percent of the substance, based on the weight of the filter material prior to treatment.

[0071] When the substance is a polymer, the polymer can be synthetic polymer or a natural polymer. Synthetic polymers are derived from the polymerization of monomeric materials (for example, addition or condensation polymers) or are isolated after chemically altering the substituent groups of a polymeric material. Natural polymers are isolated from organisms (for example, plants such as seaweed), usually by extraction.

[0072] Exemplary synthetic polymers that may be applied to filter materials include, but are not limited to, carboxymethylcellulose, hydroxypropylcellulose, cellulose esters such as cellulose acetate, cellulose butyrate and cellulose acetate propionate (for example, from Eastman Chemical

Corporation of Kingsport, Tenn.), polyethylene glycols, water dispersible amorphous polyesters with aromatic dicarboxylic acid functionalities (for example, Eastman AQs from Eastman Chemical Corporation), ethylene vinyl alcohol copolymers (for example, from Mica Corp. of Shelton, Conn.), partially or fully hydrolyzed polyvinyl alcohols (for example, the Airvols from Air Products and Chemicals of Allentown, Pa.), ethylene acrylic acid copolymers (for example, Envelons from Rohm and Haas of Philadelphia, Pa. and Primacors from The Dow Chemical Co. of Wilmington, Del.), polysaccharides (for example, Keltrol from CP Kelco of San Diego, Calif.), alginates (for example, from International Specialty Products of Wayne, N.J.), carrageenans (for example, Viscarin GP109 and Nutricol GP120F konjac flour from FMC) and starches (for example, Nadex 772, K-4484 and N-Oil from National Starch & Chemical Co.).

[0073] Typically, natural or synthetic polymers tend to coat the surface of the filter material very efficiently, and have a high viscosity, making high coating levels unnecessary and sometimes difficult. Typically, certain natural or synthetic polymers can be applied to the filter material at levels of at least about 0.001 percent, preferably at least about 0.01 percent, more preferably at least about 0.1 percent, and most preferably at least about 1 percent, based on the weight of the filter material prior to treatment. Typically, the amount of certain natural or synthetic polymers applied to the filter material does not exceed about 10 percent, and normally does not exceed about 5 percent, based on the weight of the filter material prior to treatment.

[0074] The natural or synthetic polymeric material that is applied to the filter material can vary, depending upon factors such as the chemical functionality, hydrophilicity, or hydrophobicity desired. If desired, more than one type of natural or synthetic polymer can be applied to the filter material in a single dispersion or solution. If desired, the filter material can have at least one type of natural or synthetic polymer dissolved or dispersed in a suitable solvent applied thereto and the solvent removed, after which the resulting coated filter material has at least one other natural or synthetic polymer applied in similar fashion. If multiple applications are conducted in this way, it is desirable that the solvent or solvents do not substantially dissolve any natural or synthetic polymer already coated onto the filter material.

[0075] Filters of preferred embodiments may include more than one segment. One configuration of such filters is the dual filter, wherein the filter constitutes two different segments, with one segment adjacent to the mouth and the other segment of the filter adjacent to the tobacco rod. A common type of dual filter is one wherein a cellulose acetate segment is situated on the mouth side of the filter, and a cellulose paper segment is situated on the side of the filter adjacent to the tobacco rod. Activated charcoal may be incorporated into the cellulose paper segment of the filter to assist in removal of undesired components from tobacco smoke.

[0076] Another filter configuration, referred to as a triple filter, has three segments, including a segment adjacent to the mouth, a segment adjacent to the tobacco rod, and a segment situated between the two other segments. The different segments may be prepared from different materials,

or may be materials having the same composition but different physical form, for example, crimped sheet and tow, or may be materials having the same composition and physical form, but wherein one segment contains an additional component not present in another segment. A common triple filter configuration includes two segments selected from one or both of cellulose acetate and cellulose, one adjacent to the mouth and one adjacent to the filter, with a segment in between containing a smoke-altering component. Examples of smoke-altering components include activated carbon or other absorbents, or components imparting flavor to the smoke.

[0077] One variety of triple filter is the cavity filter. The cavity filter is composed of two segments separated by a cavity containing one or more smoke-altering components. The cavity may contain an adsorbent material as described above, optionally in combination with other suitable components such as activated charcoal.

[0078] Dual and triple filters may be symmetrical (all filter segments are the same length) or asymmetrical (two or more segments are of different lengths). Filters may be recessed, with an open cavity on the mouth side, reinforced by an extra stiff plug wrap paper.

[0079] When the filter element contains a solid material in a form other than tow or sheet, it may be incorporated into the filter element using any suitable method or device, such as those described above for incorporating an absorbing, adsorbing, or reacting material into the filter element. Liquids may be incorporated into the porous filter material by immersing the filter material in the liquid, spraying the liquid onto the filter material, or combining the liquid with another component, for example, a component capable for forming a gel or a solid, then applying the liquid-containing substance to the porous filter material using methods well known to those skilled in the art.

[0080] The form of the filter material and the configuration of the filter material, as well as the filtration efficiency for particulate matter and vapor phase components of each segment of the filter element may be varied so as to yield the desired balance of performance characteristics for the filter element, as will be recognized by those skilled in the art. Filter materials in tow form can be processed and manufactured into filter rods using known techniques. Filter materials in sheet-like or web form can be formed into filter rods using techniques described in U.S. Pat. No. 4,807,809 to Pryor et al., and U.S. Pat. No. 5,074,320 to Jones, Jr. et al. Filter materials also can be formed into rods using a rod-making unit (for example, from Molins Tobacco Machinery, Ltd. of Bucks, United Kingdom).

[0081] The porous filter material may contain various additional minor components. These components may include pigments, dyes, preservatives, antioxidants, defoamers, solvents, lubricants, waxes, oils, resins, adhesives, and other materials, as are known in the art.

[0082] In a preferred embodiment, the smoking article is provided with a cavity filter composed of two cellulose acetate segments separated by a cavity containing activated charcoal, wherein the filter segments are wrapped in a paper plug wrap. The plug wrap may be provided with perforations in the cellulose acetate segment adjacent to the tobacco rod if air dilution is desired, for example, for low or ultra-low tar

cigarettes. The cellulose acetate segment adjacent to the tobacco rod is preferably about 9 mm in length, the mouth end segment is preferably 11 mm in length, and the cavity is preferably 5 mm in length. The cavity is preferably substantially filled. Substantially filled generally refers to a cavity segment wherein more than about 95 vol. % is filled with packed particles, preferably more than about 96, 97, 98, or 99 vol. % is filled with packed particles, and most preferably about 100 vol. % is filled with packed particles. However, in certain embodiments it may be desirable for the cavity to be less than substantially filled, for example, less than about 95, 94, 93, 92, 91, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 vol. % or less. In a preferred embodiment, the cavity is substantially filled with one type of activated charcoal. However, in certain other embodiments the activated charcoal may constitute a mixture of activated charcoals (for example, charcoals of varying particle size or source), or the activated charcoal may be mixed or combined with one or more inert ingredients, such as magnesium silicate (available as CAVIFLEX™ and SEL-X-4™ from Baumgartner, Inc. of Melbane, N.C.), inert carbon, or semolina. Most preferably, the cavity segment contains 0.1 g of a single type of activated charcoal as the sole component in a 5 mm long cavity segment of filter. In various embodiments various types of activated charcoal or carbon prepared from different starting materials, having different surface area and particle size, or having different properties may be preferred. Suitable activated carbons, including specialty activated carbons, may be obtained from Calgon Carbon Corporation of Pittsburgh, Pa.

[0083] Additives

[0084] Additional components, as are known in the art, may also be added to the smokable material, or may be contained within the filter, the tobacco rod, or other components of the smoking articles of preferred embodiments. Nonlimiting examples of such components include tobacco extracts, lubricants, flavorings, and the like. These additional components preferably do not react with the cooling compounds of preferred embodiments in such a way as to substantially reduce its effectiveness in yielding a cooling effect during use of the smoking article. To the extent that such reactions do occur, they can be compensated for by alterations in the concentration or the type of the cooling compound and/or other components present.

[0085] The filter element optionally can include a tobacco or flavor extract in intimate contact with the filter material. If desired, the tobacco or flavor extract can be spray dried and/or subjected to heat treatment. The filter element prior to smoking may include less than about 10% tobacco or flavor extract to more than 50% percent tobacco or flavor extract, based on the total dry weight of the filter element and extract. In some embodiments, the tobacco filter elements typically include a lubricating substance in intimate contact with the filter material. Normally, prior to smoking the cigarette, the filter element includes at least about 0.1 percent lubricating substance, based on the weight of the filter material of that segment. The lubricating substance can be a low molecular weight liquid (for example, glycerine) or a high molecular weight material (for example, an emulsifier).

[0086] Flavorants in addition to the cooling compounds of preferred embodiments, even flavorants such as menthol

itself, can be incorporated into the cigarette using techniques familiar to the skilled artisan. If desired, flavor additives such as organic acids can be incorporated into the cigarette as additives to cut filler. See, for example, U.S. Pat. No. 4,830,028 to Lawson et al. The flavor extract may typically be included at a level of from about 5% or less to about 50% or more of the total dry weight of the filter element and the extract, preferably from about 10% to about 45%, and more preferably from about 15%, 20%, or 25% to about 30%, 35%, or 40%.

[0087] The Smokable Material

[0088] The cooling compounds may be used in conjunction with any suitable smokable material. Examples of preferred smokable materials are the tobaccos that include but are not limited to Oriental, Virginia, Maryland, and Burley tobaccos, as well as the rare and specialty tobaccos. The tobacco plant may be a variety produced through conventional plant breeding methods, or may be a genetically engineered variety. Low nicotine and/or low TSNAs tobacco varieties, including genetically engineered varieties, are especially preferred. The tobacco may be cured using any acceptable method, including, but not limited to, flue-curing, air-curing, sun-curing, and the like, including curing methods resulting in low nitrosamine levels, such as the curing methods disclosed in U.S. Pat. Nos. 6,202,649 and 6,135,121 to Williams.

[0089] Generally, the tobacco material is aged. The cured or uncured tobacco may be subjected to any suitable processing step, including, but not limited to, microwave or other radiation treatment, treatment with ultraviolet light, or extraction with an aqueous or nonaqueous solvent.

[0090] The tobacco can be in the form of tobacco laminae, processed tobacco stems, reconstituted tobacco material, volume expanded tobacco filler, or blends thereof. The type of reconstituted tobacco material can vary. Certain suitable reconstituted tobacco materials are described in U.S. Pat. No. 5,159,942 to Brinkley et al. Certain volume expanded tobacco materials are described in U.S. Pat. No. 5,095,922 to Johnson et al. Blends of the aforementioned materials and tobacco types can be employed. Exemplary blends are described in U.S. Pat. No. 5,074,320 to Jones, Jr. et al. Other smokable materials, such as those smokable materials described in U.S. Pat. No. 5,074,321 to Gentry et al., and U.S. Pat. No. 5,056,537 to Brown et al., also can be employed.

[0091] The smokable materials generally are employed in the form of cut filler as is common in conventional cigarette manufacture. For example, the smokable filler material can be employed in the form of pieces, shreds, and/or strands cut into widths ranging from about $\frac{1}{60}$ inch (0.04 mm) to about $\frac{1}{2}$ inch (5 mm), preferably from about $\frac{1}{40}$ inch (0.6 mm) to about $\frac{1}{20}$ inch (1.3 mm). Generally, such pieces have lengths between about 0.25 inch (6 mm) and about 3 inches (76 mm). In certain embodiments, however, it may be preferred to use cut filler having widths less than about $\frac{1}{60}$ inch (0.04 mm) or more than about $\frac{1}{2}$ inch (5 mm), and lengths less than about 0.25 inch (6 mm) or more than about 3 inches (76 mm).

[0092] The smokable material can have a form (for example, a blend of smokable materials, such as a blend of various types of tobacco in cut filler form) having a rela-

tively high nicotine content. Such a smokable material typically has a dry weight nicotine content above about 2.0%, 2.25%, 2.5%, 2.75%, or 3.0% or more. Such smokable materials are described in U.S. Pat. No. 5,065,775 to Fagg.

[0093] Alternatively, the smokable material can have a form having a relatively low or negligible nicotine content. Such a smokable material typically has a dry weight nicotine content below about 1.5%, 1.25%, 1.0%, 0.75%, 0.5%, 0.1%, 0.05% or less. Tobacco having a relatively low nicotine content is described in U.S. Pat. No. 5,025,812 to Fagg et al.

[0094] As used herein, the term "dry weight nicotine content" in referring to the smokable material refers to the mass of alkaloid nicotine as analyzed and quantitated by spectroscopic techniques divided by the dry weight of the smokable material analyzed. See, for example, Harvey et al., *Tob. Sci.*, Vol. 25, p. 131 (1981).

[0095] In a preferred embodiment, the smokable material constitutes a tobacco product obtained from tobacco plants that are substantially free of nicotine and/or tobacco-specific nitrosamines. Tobaccos that may be substantially free of nicotine or TSNAs may be produced by interrupting the ability of the plant to synthesize nicotine using genetic engineering. Copending PCT Application No. PCTUS02/18040 filed Jun. 6, 2002 and PCT Publication No. WO9856923 to Conkling et al. describe tobacco that is substantially free of nicotine and TSNAs that is made by exposing at least one tobacco cell of a selected variety to an exogenous DNA construct having, in the 5' to 3' direction, a promoter operable in a plant cell and DNA containing a portion of a DNA sequence that encodes an enzyme in the nicotine synthesis pathway. The DNA is operably associated with the promoter, and the tobacco cell is transformed with the DNA construct, the transformed cells are selected, and at least one transgenic tobacco plant is regenerated from the transformed cells. The transgenic tobacco plants contain a reduced amount of nicotine and/or TSNAs as compared to a control tobacco plant of the same variety. In preferred embodiments, DNA constructs having a portion of a DNA sequence that encodes an enzyme in the nicotine synthesis pathway may have the entire coding sequence of the enzyme, or any portion thereof.

[0096] In a preferred embodiment, the smokable material constitutes a tobacco product obtained from tobacco plants that have reduced nicotine content and/or TSNAs such as those described in copending application Ser. No. 09/941,042, filed Aug. 28, 2001.

[0097] Tobacco products having specific amounts of nicotine and/or TSNAs may be created through blending of low nicotine/low TSNAs tobaccos, such as those described above, with conventional tobaccos. Some blending approaches begin with tobacco prepared from varieties that have extremely low amounts of nicotine and/or TSNAs. By blending prepared tobacco from a low nicotine/low TSNAs variety (for example, undetectable levels of nicotine and/or TSNAs) with a conventional tobacco (for example, Burley, which has 30,000 parts per million (ppm) nicotine and 8,000 parts per billion (ppb) TSNAs; Flue-Cured, which has 20,000 ppm nicotine and 300 ppb TSNAs; and Oriental, which has 10,000 ppm nicotine and 100 ppb TSNAs), tobacco products having virtually any desired amount of

nicotine and/or TSNAs can be manufactured. Tobacco products having various amounts of nicotine and/or TSNAs can be incorporated into tobacco use cessation kits and programs to help tobacco users reduce or eliminate their dependence on nicotine and reduce the carcinogenic potential.

[0098] For example, a step 1 tobacco product can constitute approximately 25% low nicotine/low TSNAs tobacco and 75% conventional tobacco; a step 2 tobacco product can constitute approximately 50% low nicotine/low TSNAs tobacco and 50% conventional tobacco; a step 3 tobacco product can constitute approximately 75% low nicotine/low TSNAs tobacco and 25% conventional tobacco; and a step 4 tobacco product can constitute approximately 100% low nicotine/low TSNAs tobacco and 0% conventional tobacco. A tobacco use cessation kit can include an amount of tobacco product from each of the aforementioned blends to satisfy a consumer for a single month program. That is, if the consumer is a one pack a day smoker, for example, a single month kit provides 7 packs from each step, a total of 28 packs of cigarettes. Each tobacco use cessation kit may include a set of instructions that specifically guide the consumer through the step-by-step process. Of course, tobacco products having specific amounts of nicotine and/or TSNAs may be made available in conveniently sized amounts (for example, boxes of cigars, packs of cigarettes, tins of snuff, and pouches or twists of chew) so that consumers could select the amount of nicotine and/or TSNAs they individually desire. There are many ways to obtain various low nicotine/low TSNAs tobacco blends using the teachings described herein and the following is intended merely to guide one of skill in the art to one possible approach.

[0099] To obtain a step 1 tobacco product, which is a 25% low nicotine/low TSNAs blend, prepared tobacco from an approximately 0 ppm nicotine/TSNAs tobacco can be mixed with conventional Burley, flue-cured, or Oriental in a 25%/75% ratio respectively to obtain a Burley tobacco product having 22,500 ppm nicotine and 6,000 ppb TSNAs, a flue-cured product having 15,000 ppm nicotine and 225 ppb TSNAs, and an Oriental product having 7,500 ppm nicotine and 75 ppb TSNAs. Similarly, to obtain a step 2 product, which is 50% low nicotine/low TSNAs blend, prepared tobacco from an approximately 0 ppm nicotine/TSNAs tobacco can be mixed with conventional Burley, flue-cured, or Oriental in a 50%/50% ratio respectively to obtain a Burley tobacco product having 15,000 ppm nicotine and 4,000 ppb TSNAs, a flue-cured product having 10,000 ppm nicotine and 150 ppb TSNAs, and an Oriental product having 5,000 ppm nicotine and 50 ppb TSNAs. Further, a step 3 product, which is a 75%/25% low nicotine/low TSNAs blend, prepared tobacco from an approximately 0 ppm nicotine/TSNAs tobacco can be mixed with conventional Burley, flue-cured, or Oriental in a 75%/25% ratio respectively to obtain a Burley tobacco product having 7,500 ppm nicotine and 2,000 ppb TSNAs, a flue-cured product having 5,000 ppm nicotine and 75 ppb TSNAs, and an Oriental product having 2,500 ppm nicotine and 25 ppb TSNAs.

[0100] It is appreciated that tobacco products are often a blend of many different types of tobaccos, which are grown in many different parts of the world under various growing conditions. As a result, the amount of nicotine and TSNAs may differ from crop to crop. Nevertheless, by using con-

ventional techniques one can easily determine an average amount of nicotine and TSNA's per crop used to create a desired blend. By adjusting the amount of each type of tobacco that makes up the blend one of skill can balance the amount of nicotine and/or TSNA's with other considerations such as appearance, flavor, and smokability. In this manner, a variety of types of tobacco products having varying level of nicotine and/or nitrosamines, as well as appearance, flavor, and smokability can be created. Such types of tobacco products may behave in similar manners when the cooling compounds of preferred embodiments are applied thereto.

[0101] While in the preferred embodiments the cooling compounds are used in conjunction with a smokable material including tobacco, any other smokable materials may be preferred in other embodiments. For example, the smokable plant materials may include various herbal smoking materials. Mullein and Mugwort are commonly preferred base materials in blends of herbal smoking materials. Some other commonly preferred plant materials that are also smokable materials include Willow bark, Dogwood bark, Pipsissewa, Pyrola, Kinnikinnik, Manzanita, Madrone Leaf, Blackberry, Raspberry, Loganberry, Thimbleberry, and Salmonberry.

[0102] The Wrapping Material

[0103] Various wrapping materials that circumscribe the charge of smokable material may be employed. Examples of suitable wrapping materials include cigarette paper wrappers available from Schweitzer-Mauduit International in Alpharetta, Ga. Cigarette paper wraps the column of tobacco in a cigarette and can be made from flax, wood, or a combination of fibers. Certain properties such as basis weight, porosity, opacity, tensile strength, texture, ash appearance, taste, brightness, good gluing, and lack of dust are selected to provide optimal performance in the finished product, as well as to meet runnability standards of the high-speed production processes preferred by cigarette manufacturers.

[0104] A more porous paper is one that allows air to easily pass into a cigarette. Porosity is measured in Coresta units and can be controlled to determine the rate and direction of airflow through the cigarette. The higher the number of Coresta units, the more porous the paper. Tar and nicotine yields are commonly controlled without altering the flavor of the cigarette through the choice of paper. The use of highly porous papers can help create lower tar levels in a cigarette. Higher paper porosity increases the combustibility of a cigarette by adding more air to the process, which increases the heat and the burning rate. A higher burn rate may lower the number of puffs that a smoker takes per cigarette. Papers having porosities up to 200 Coresta units or higher are generally preferred, however different kinds of cigarettes may use papers of different preferred porosities. For example, American-blend cigarettes typically use 40 to 50 Coresta unit papers. Flue-cured tobacco cigarettes, which burn slower, generally use higher porosities, ranging from 60 to 80 Coresta unit papers. Higher porosities may be obtained by electronically perforating (EP) the paper.

[0105] Cigarette papers are available that are prepared from various base fibers. Flax and wood are commonly preferred base fibers. In addition to 100% flax and 100% wood papers, papers are also available with flax and wood fibers mixed in various ratios. Wood based papers are widely

preferred because of their low cost, however certain consumers prefer the taste of flax based papers.

[0106] Suitable cigarette papers may be obtained from RFS (US) Inc., a subsidiary of privately-held PURICO (IOM) Limited of the United Kingdom, which is the current owner of P. H. Glatfelter Company's Ecusta mill which manufactures tobacco papers. In preferred embodiments, a paper having a porosity of about 26 Coresta EP to 90 Coresta EP is preferred. Suitable papers include Number 409 papers having a porosity of 26 Coresta and 0.85% citrate content, and Number 00917 papers having a porosity of 26 Coresta EP. However, in certain embodiments, it may be preferred to use a paper having a lower air permeability, for example, a paper that has not been subjected to electronic perforation and which has a low inherent porosity, for example, less than 26 Coresta.

[0107] In preferred embodiments, the cigarette paper is suitable for use in "self-extinguishing" cigarettes. Examples of cigarette papers suitable for use in self-extinguishing cigarettes include, for example, papers saturated with a citrate or phosphate fire retardant or incorporating one or more fire retardant bands along the length of the paper. Such papers may also include thicker papers of reduced flammability.

[0108] Wrapping materials described in U.S. Pat. No. 5,220,930 to Gentry may be preferred in certain embodiments. More than one layer of circumscribing wrapping material can be employed, if desired. See, for example, U.S. Pat. No. 5,261,425 to Raker et al. Other wrapping material includes plug wrap paper and tipping paper. Plug wrap paper wraps the outer layer of the cigarette filter plug and holds the filter material in cylindrical form. Highly porous plug wrap papers are preferred in the production of filter-ventilated cigarettes.

[0109] Tipping paper joins the filter element with the tobacco rod. Tipping papers are typically made in white or a buff color, or in a cork pattern, and are both printable and glueable at high speeds. Such tipping papers are used to produce cigarettes that are distinctive in appearance, as well as to camouflage the use of activated carbon in the filter element. Pre-perforated tipping papers are commonly preferred in filter-ventilated cigarettes.

[0110] In the case of cigars, reconstituted tobacco wrapper is often wrapped around the outside of machine-made cigars to provide a uniform, finished appearance. The wrapper material can incorporate printed veins to give the look of natural tobacco leaf. Such wrapper material is manufactured utilizing tobacco leaf by-products. Reconstituted tobacco binder holds the "bunch" or leaves of tobacco in a cylindrical shape during the production of machine-made cigars. Reconstituted tobacco binder is also manufactured utilizing tobacco leaf by-products.

[0111] An extremely small amount of a sideseam adhesive is preferred to secure the ends of the cigarette paper wrapper around the tobacco rod (and filter element, if present). Any suitable adhesive may be used. In a preferred embodiment, the sideseam adhesive is an emulsion of ethylene vinyl acetate copolymer in water.

[0112] The cigarette wrapper may include extremely small amounts of inks containing oils, varnishes, pigments, dyes, and processing aids, such as solvents and antioxidants. Ink

components may include such materials as linseed varnish, linseed oil polymers, white mineral oils, clays, silicas, natural and synthetic pigments, and the like, as are known in the art.

[0113] Smoking Articles

[0114] The smoking articles of the preferred embodiments may have various forms. Preferred smoking articles may be typically rod-shaped, including, for example, cigarettes and cigars. In addition, the smoking article may be tobacco for a pipe. For example, the smoking article can have the form of a cigarette having a smokable material (for example, tobacco cut filler) wrapped in a circumscribing paper wrapping material. Exemplary cigarettes are described in U.S. Pat. No. 4,561,454 to Guess. In a preferred embodiment, the smoking article is a cigarette having a smokable filter material or tobacco rod.

[0115] In another preferred embodiment, a cigarette is provided which yields relatively low levels of “tar” per puff on average when smoked under FTC smoking conditions (for example, an “ultra low tar” cigarette).

[0116] In another preferred embodiment, a cigarette is provided having a smokable filler material or tobacco rod having a relatively low or negligible nicotine content, and a filter element.

[0117] In another preferred embodiment, a cigarette is provided having a smokable filler material or tobacco rod having a relatively low TSNA content, and a filter element.

[0118] The amount of smokable material within the tobacco rod can vary, and can be selected as desired. Packing densities for tobacco rods of cigarettes are typically between about 150 and about 300 mg/cm³, and are preferably between about 200 and about 280 mg/cm³, however, higher or lower amounts may be preferred for certain embodiments.

[0119] Typically, a tipping material circumscribes the filter element and an adjacent region of the smokable rod such that the tipping material extends about 3 mm to about 6 mm along the length of the smokable rod. Typically, the tipping material is a conventional paper tipping material. Different tipping materials having different porosities may be preferred. For example, the tipping material can be essentially air impermeable, air permeable, or can be treated (for example, by mechanical or other perforation techniques) so as to have a region of perforations, openings or vents, thereby providing a means for providing air dilution to the cigarette. The total surface area of the perforations and the positioning of the perforations along the periphery of the cigarette can be varied in order to control the performance characteristics of the cigarette.

[0120] The mainstream cigarette smoke may be diluted with air from the atmosphere via the natural porosity of the cigarette wrapper and/or tipping material, or via perforations, openings, or vents in the cigarette wrapper and/or tipping material. Air dilution means may be positioned along the length of the cigarette, typically at a point along the filter element which is at a maximum distance from the extreme mouth-end thereof. The maximum distance is dictated by factors such as manufacturing constraints associated with the type of tipping material employed and the cigarette manufacturing apparatus and process. For example, for a filter element having a 27 mm length, the maximum distance

may be between about 23 mm and about 26 mm from the extreme mouth-end of the filter element. In a preferred aspect, the air dilution means is positioned toward the extreme mouth-end of the cigarette relative to the smoke-altering filter segment. For example, for a filter element having a 27 mm length including a smoke-altering filter segment of 12 mm length and a mouth-end segment of 15 mm, a ring of air dilution perforations can be positioned either 13 mm or 15 mm from the extreme mouth-end of the filter element.

[0121] As used herein, the term “air dilution” is the ratio (generally expressed as a percentage) of the volume of air drawn through the air dilution means to the total volume of air and smoke drawn through the cigarette and exiting the extreme mouth-end portion of the cigarette. For air diluted or ventilated cigarettes, the amount of air dilution can vary. Generally, the amount of air dilution for an air-diluted cigarette is greater than about 10 percent, typically greater than about 20 percent, and often greater than about 30 percent. Typically, for cigarettes of relatively small circumference (namely, about 21 mm or less) the air dilution can be somewhat less than that of cigarettes of larger circumference. The upper limit of air dilution for a cigarette typically is less than about 85 percent, more frequently less than about 75 percent. Certain relatively high air diluted cigarettes have air dilution amounts of about 50 to about 75 percent, often about 55 to about 70 percent.

[0122] Cigarettes of certain embodiments may yield less than about 0.9, often less than about 0.5, and usually between about 0.05 and about 0.3 FTC “tar” per puff on average when smoked under FTC smoking conditions (FTC smoking conditions include 35 ml puffs of 2 second duration separated by 58 seconds of smolder). Such cigarettes are “ultra low tar” cigarettes which yield less than about 7 mg FTC “tar” per cigarette. Typically, such cigarettes yield less than about 9 puffs, and often about 6 to about 8 puffs, when smoked under FTC smoking conditions. While “ultra low tar” cigarettes are generally preferred, in certain embodiments, however, cigarettes providing less than about 0.05 or more than about 0.9 FTC “tar” per puff are contemplated.

[0123] In certain embodiments, cigarettes yielding a low or negligible amount of nicotine are provided. Such cigarettes generally yield less than about 0.1, often less than about 0.05, frequently less than about 0.01, and even less than about 0.005 FTC nicotine per puff on average when smoked under FTC smoking conditions. In other embodiments, a cigarette delivering higher levels of nicotine may be desired. Such cigarettes may deliver about 0.1, 0.2, 0.3, or more FTC nicotine per puff on average when smoked under FTC smoking conditions.

[0124] Cigarettes yielding a low or negligible amount of nicotine may yield between about 1 mg and about 20 mg, often about 2 mg to about 15 mg FTC “tar” per cigarette; and may have relatively high FTC “tar” to FTC nicotine ratios of between about 20 and about 150.

[0125] Cigarettes of the preferred embodiments may exhibit a desirably high resistance to draw, for example, a pressure drop of between about 50 and about 200 mm water pressure at 17.5 cc/sec of air flow. Typically, pressure drop values of cigarettes are measured using instrumentation available from Cerulean (formerly Filtrona Instruments and Automation) of Milton Keynes, United Kingdom. Cigarettes

of preferred embodiments preferably exhibit resistance to draw values of about 70 to about 180, more preferably about 80 to about 150 mm water pressure drop at 17.5 cc/sec of airflow.

[0126] Cigarettes of preferred embodiments may include a smoke-altering filter segment. The smoke-altering filter segment may reduce one or more undesirable components in the smoke, and/or may provide an enhanced tobacco smoke flavor, a richer smoking character, enhanced mouthfeel and increased smoking satisfaction, as well as improvement of the perceived draw characteristics of the cigarette.

[0127] Catalyst System for Reducing Carcinogens in Smoke

[0128] In preferred embodiments, smoking articles incorporating the cooling compounds of preferred embodiments also incorporate a catalyst system including catalytic metallic and/or carbonaceous particles and a nitrate or nitrite source. The catalyst system is incorporated into the smokable material so as to reduce the concentration of certain undesirable components in the resulting smoke. In embodiments wherein the particles are metallic, the particles are preferably prepared by heating an aqueous solution of a metal ion source and a reducing agent, preferably a reducing sugar or a metal ion source, with hydroxide. Preferably, after the metallic particles are formed in solution, the nitrate or nitrite source is added to the solution, and the solution is applied to the smokable material. However, embodiments in which the particles and the nitrate or nitrite source are added separately to the smokable material are also contemplated. The catalyst system and smoking articles incorporating the same are described in detail in copending U.S. application Ser. No. 10/007,724 filed on Nov. 9, 2001 and entitled "METHOD AND PRODUCT FOR REMOVING CARCINOGENS FROM TOBACCO SMOKE."

[0129] Metallic Particles

[0130] In preferred embodiments, particles of a catalytic metallic substance are applied to the smokable materials. The term "metallic", as used herein, is a broad term and is used in its ordinary sense, including without limitation, pure metals, mixtures of two or more metals, mixtures of metals and non-metals, metal oxides, metal alloys, mixtures or combinations of any of the aforementioned materials, and other substances containing at least one metal. Suitable catalytic metals include the transition metals, metals in the main group, and their oxides. Many metals are effective in this process, but preferred metals include, for example, Pd, Pt, Rh, Ag, Au, Ni, Co, and Cu.

[0131] Many transition and main group metal oxides are effective, but preferred metal oxides include, for example, AgO, ZnO, and Fe₂O₃. Zinc oxide and iron oxide are particularly preferred based on physical characteristics, cost, and carcinogenic behavior of the oxide. A single metal or metal oxide may be preferred, or a combination of two or more metals or metal oxides may be preferred. The combination may include a mixture of particles each having different metal or metal oxide compositions. Alternatively, the particles themselves may contain more than one metal or metal oxide. Suitable particles may include alloys of two or more different kinds of metals, or mixtures or alloys of metals and nonmetals. Suitable particles may also include particles having a metal core with a layer of the correspond-

ing metal oxide making up the surface of the particle. The metallic particles may also include metal or metal oxide particles on a suitable support material, for example, a silica or alumina support. Alternatively, the metallic particles may include particles including a core of support material substantially encompassed by a layer of catalytically active metal or metal oxide. In addition to the above-mentioned configurations, the metallic particles may in any other suitable form, provided that the metallic particles have the preferred average particle size.

[0132] The particles may be prepared by any suitable method as is known in the art. When preparing metallic particles, suitable methods include, but are not limited to, wire electrical explosion, high energy ball milling, plasma methods, evaporation and condensation methods, and the like. However, in preferred embodiments, the particles are prepared via reduction of metal ions in aqueous solution, as described below.

[0133] While any suitable metal, metal oxide, or carbonaceous particle (as described below) is preferred, it is particularly preferred to use a metal, metal oxide, or carbonaceous particle that has a relatively low level of transfer to cigarette or other smoke condensate produced upon combustion of the smokable material. For example, palladium has a lower level of transfer than silver. Also, metal oxides tend to have relatively low levels of transfer. However, in certain embodiments it may be preferred to use a metal, metal oxide, or carbonaceous particle having a relatively high level of transfer to smoke condensate. In providing a compound that effectively catalyzes the decomposition of nitrate salts, it is also generally preferred that the metal, metal oxide, or carbonaceous particle have a relatively low specific heat.

[0134] Carbonaceous Particles

[0135] In certain embodiments, particles of a catalytic carbonaceous substance are applied to the smokable materials. The term "carbonaceous", as used herein, is a broad term and is used in its ordinary sense, including without limitation, graphitic carbon, fullerenes, doped fullerenes, carbon nanotubes, doped carbon nanotubes, other suitable carbon-containing substances, and mixtures or combinations of any of the aforementioned substances.

[0136] The carbonaceous particles may be prepared by any suitable method as is known in the art. When preparing graphitic particles suitable methods may include, but are not limited to, milling techniques, and the like.

[0137] Fullerenes include, but are not limited to, buckminster fullerene (C₆₀), as well as C₇₀ and higher fullerenes. The structure of fullerenes and carbon nanotubes may permit them to be doped with other atoms, for example, metals such as the alkali metals, including potassium, rubidium, and cesium. These other atoms may be included within the carbon cage or carbon nanotube, as is observed for certain atoms when enclosed within endohedral fullerene. Atoms may also be incorporated into a crystal structure, e.g., the bct structure of A₄C₆₀ (wherein A=K,Rb,Cs, and C=buckminster fullerene) or the bcc structure of A₆C₆₀ (wherein A=K,Rb,Cs, and C=buckminster fullerene). Fullerenes may also be dimerized or polymerized. Certain fullerenes, such as C₇₀ fullerenes, are known radical traps and as such may be suitable for use in a catalyst system without the presence of nitrate or other radical trap generators.

[0138] Fullerenes are preferably prepared by condensing gaseous carbon in an inert gas. The gaseous carbon is obtained, for example, by directing an intense pulse of laser at a graphite surface. The released carbon atoms are mixed with a stream of helium gas, where they combine to form clusters of carbon atoms. The gas containing clusters is then led into a vacuum chamber where it expands and is cooled to a few degrees above absolute zero. The clusters are then extracted. Other suitable methods for preparing fullerenes as are known in the art may also be used.

[0139] Carbon nanotubes may be prepared by electric arc discharge between two graphite electrodes. In the electric arc discharge method, material evaporates from one electrode and deposits on the other in the form of nanoparticles and nanotubes. Purification is achieved by competitive oxidation in either the gas or liquid phase. Carbon nanotubes may also be catalytically grown. In catalytic methods, filaments containing carbon nanotubes are grown on metal surfaces exposed to hydrocarbon gas at temperatures typically between 500-1100° C. Other techniques for forming carbon nanotubes include laser evaporation techniques, similar to those used to form fullerenes. However, any suitable method for forming carbon nanotubes may be used.

[0140] Particle Size

[0141] The particles of preferred embodiments preferably have an average particle size of greater than about 0.5 micron (0.5 μm), more preferably greater than about 0.6, 0.7, 0.8, 0.9, 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, or 2 μm . The preferred size may depend on the metallic or carbonaceous substance. Particle sizes can be as large as 150 μm or more, more preferably 150, 140, 130, 120, 110, 100, 90, 80, 70, 60, 50, 40, 30, 20, 19, 18, 17, 15, 14, 13, 12, 11, 10, 9, 8, 7, 6, 5, 4, 3 μm or less in diameter. In other embodiments, preferred particle size may be less than or equal to about 0.5 μm (500 nm), or 400, 300, 200, 100, 90, 80, 70, 60, 50, 40, 30, 20, 10, 9, 8, 7, 6, 5, 4, 3, 2, 1 nm or less. In preferred embodiments, the particles are of a substantially uniform size distribution, that is, a majority of the metallic particles present have a diameter generally within about $\pm 50\%$ or less of the average diameter, preferably within about $\pm 45\%$, 40%, 35%, 30% or less of the average diameter, more preferably within $\pm 25\%$ or less of the average diameter, and most preferably within $\pm 20\%$ or less of the average diameter. The term "average" includes both the mean and the mode.

[0142] While a uniform size distribution may be generally preferred, individual particles having diameters above or below the preferred range may be present, and may even constitute the majority of the particles present, provided that a substantial amount of particles having diameters in the preferred range are present. In other embodiments, it may be desirable that the particles constitute a mixture of two or more particle size distributions, for example, a portion of the mixture may include a distribution on nanometer-sized particles, and a portion of the mixture may include a distribution of micron-sized particles. The particles of preferred embodiments may have different forms. For example, a particle may constitute a single, integrated particle not adhered to or physically or chemically attached to another particle. Alternatively, a particle may constitute two or more agglomerated or clustered smaller particles that are held together by physical or chemical attractions or bonds to form a single larger particle. The particles may have different

atomic level structures, including but not limited to, for example, crystalline, amorphous, and combinations thereof. In various embodiments, it may be desirable to include different combinations of particles having various properties, including, but not limited to, particle size, shape or structure, chemical composition, crystallinity, and the like.

[0143] Nitrate or Nitrite Source

[0144] Any suitable source of nitrate or nitrite may be preferred. Preferred nitrate or nitrite sources include the nitrate or nitrite salts, of metals selected from Groups Ia, Ib, Ia, IIb, IIIa, IIIb, IVa, IVb, Va, Vb, and the transition metals of the Periodic Table of Elements.

[0145] In preferred embodiments, the nitrate or nitrite source includes a nitrate of lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, yttrium, lanthanum, cerium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, erbium, scandium, manganese, iron, rhodium, palladium, copper, zinc, aluminum, gallium, tin, bismuth, hydrates thereof and mixtures thereof. Preferably, the nitrate salt may be an alkali or alkaline earth metal nitrate. More preferably, the nitrate or nitrite source may be selected from the group of calcium, magnesium, and zinc with magnesium nitrate being the most preferred salt. In a particularly preferred embodiment, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ may be preferred as a nitrate source. While nitrate and nitrite salts are generally preferred, any suitable metal salt or organometallic compound, or other compound capable of releasing nitric oxide may be preferred.

[0146] While not wishing to be limited to any particular mechanism, it is believed that the nitrate or nitrite source forms nitric oxide radicals and that this reaction process is catalyzed by the metallic or carbonaceous particles in the combustion zone of tobacco. The nitric oxide radicals are believed to act as a trap for other organic radicals that are responsible for formation of PAHs and other carcinogenic compounds.

[0147] The temperature at which a particular nitrate or nitrite source decomposes to form nitric oxide may vary. Since a temperature gradient exists across the combustion zone of a tobacco rod, the choice and concentration of the nitrate or nitrite source may be selected so as to provide optimum production of nitric oxide during combustion. Certain nitrates and nitrites alone, especially those of the Group Ia metals, function as effective combustion promoters, accelerating the burn rate of the smokable material and decreasing the total smoke yield, but not necessarily decreasing the quantity of PAHs within the smoke. The nitric oxide yield of such nitrates may also be relatively low.

[0148] In certain embodiments, it may be preferred that the metal ion source and the nitrate or nitrite source constitute the same compound, for example, palladium(II) nitrate.

[0149] Catalyst Preparation

[0150] In preferred embodiments, metallic particles may be prepared from an aqueous solution. For example, metal particles may be prepared from an ion source containing one or more metal ion sources and one or more reducing sugars. Suitable metal ion sources include any ionic or organometallic compound that is soluble in aqueous solution and is capable of yielding metal ions that may be reduced to particles of a catalytic metal or utilized to form a metal

oxide. In a particularly preferred embodiment, the catalytic source includes a metal such as palladium, and the palladium ion source includes water-soluble palladium salts. Illustrative non-limiting examples of suitable palladium salts include simple salts such as palladium nitrate, palladium halides such as palladium di or tetrachloride diammine complexes such as dichlorodiamminepalladium(II) ($\text{Pd}(\text{NH}_3)_2\text{Cl}_2$), and palladate salts, especially ammonium salts such as ammonium tetrachloropalladate(II) and ammonium hexachloropalladate(IV).

[0151] One form of palladium that may be especially preferred is ammonium tetrachloropalladate(II), $(\text{NH}_4)_2\text{PdCl}_4$. Ammonium tetrachloropalladate is generally preferred over ammonium hexachloropalladate because under typical conditions for preparing the metallic particles, a higher metal ion to metal conversion may be observed for ammonium tetrachloropalladate(II).

[0152] In a preferred embodiment, an aqueous solution of reducing agent is prepared, to which the metal ion source is added. In preferred embodiments, the reducing agent may be a reducing sugar, however other suitable reducing agents may be preferred. Although any compound capable of reducing the metal ion can be employed, as a practical matter the reducing agent is preferably non-toxic and preferably does not form toxic byproducts when pyrolyzed during smoking. In addition, the reducing agent is preferably water-soluble.

[0153] Preferred reducing agents are the reducing sugars. Suitable reducing agents include organic aldehydes, specifically hydroxyl-containing aldehydes such as the sugars glucose, mannose, galactose, xylose, ribose, and arabinose. Other sugars containing hemiacetal or keto groupings may be employed, for example, maltose, sucrose, lactose, fructose, and sorbose. Pure sugars may be employed, but crude sugars and syrups such as honey, corn syrup, invert syrup or sugar, and the like may also be employed. Other reducing agents include alcohols, preferably polyhydric alcohols such as glycerol, sorbitol, glycols, especially ethylene glycol and propylene glycol, and polyglycols such as polyethylene and polypropylene glycols. In alternative embodiments, other reducing agents may be preferred, such as carbon monoxide, hydrogen, or ethylene.

[0154] The solution is preferably heated before the metal ion source is added to the solution, and maintained at an elevated temperature afterwards so as to reduce the time for conversion of the metal ions to metallic particles. In a preferred embodiment, a reducing sugar such as low invert sugar may be preferred as the reducing agent. In certain embodiments, it may be desirable to have an excess or deficiency of reducing agent present in solution. Generally, it is preferred to prepare an aqueous solution containing from about 5 wt. % to about 20 wt. % of the reducing sugar, preferably about 6 wt. % to about 16 or 17 wt. %, more preferably from about 7, 8, 9, 10, or 11 wt. % to about 12, 13, 14, or 15 wt. %. When the reducing agent is invert sugar, it is preferred to prepare an 11 wt. % to about 12 wt. % solution. The amount of reducing agent preferred may vary depending on the type of reducing agent preferred and the amount of metal ion source to be added to the solution.

[0155] It may be preferred to prepare the solution in a glass-lined vessel equipped with a heating jacket. In certain embodiments, however, it may be preferred to prepare the

solution in another kind of vessel constructed of or lined with another type of material, for example, plastic, stainless steel, ceramic, and the like. It is generally preferred to conduct the reaction in a closed vessel. In certain embodiments, it may be desirable to conduct the reaction under reduced pressure or elevated pressure, or under an inert atmosphere, such as nitrogen or argon.

[0156] In preparing the aqueous solution of the reducing sugar, it is preferred to use deionized ultrafiltered water. While in preferred embodiments the metallic particles are prepared from aqueous solution, in other embodiments it may be desirable to use another suitable solvent system, for example, a polar solvent such as ethanol, or a mixture of ethanol and water. Additional components may be present in the solution as well, provided that they do not substantially adversely impact the catalytic activity of the metallic particles.

[0157] After adding the reducing sugar to the deionized ultrafiltered water, the solution is preferably heated with constant mixing so as to avoid hot spots in the solution. Although in certain embodiments it may be desirable to prepare the particles from a room temperature solution, or even a solution cooled below room temperature, it is generally preferred to heat the solution so as to speed the reaction between the reducing sugar and the metal ion source once it is added to the solution. The solution may be heated to any suitable temperature, but boiling of the solution and decomposition of the reducing sugar is preferably avoided. In a preferred embodiment wherein low invert sugar is the reducing sugar, the solution is typically heated up to about 95° C. or more, preferably from above room temperature to about 90° C., more preferably from about 50° C., 55° C., 60° C., or 65° C. 85° C., and most preferably from about 70° C. or 75° C. to about 80° C.

[0158] The metal ion source is added to the heated aqueous solution of reducing agent, which is stirred while the metal ions react with the reducing sugar to produce metallic particles. It is generally preferred to add sufficient metal ion source so as to produce a solution containing from less than about 3000 ppm to more than about 5000 ppm metal. Preferably, sufficient metal ion source is added to produce a solution containing from about 3250, 3500, or 3750 ppm to about 4250, 4500, 4750 ppm metal, more preferably from about 3800, 3850, 3900, or 3950 ppm to about 4050, 4100, 4150, or 4200 ppm metal, and most preferably about 4000 ppm metal.

[0159] The reaction time for conversion of metal ion to metal particles may vary depending upon the reducing agent and metal ion source preferred, but generally ranges from about 30 minutes or less to about 24 hours or more, and typically ranges from about 1 or 2 hours up to about 3, 4, or 5 hours. In a preferred embodiment, wherein ammonium tetrachloropalladate is the metal ion source, a substantial conversion of palladium ion to palladium metal may be achieved after 3 hours for a solution heated to a temperature of about 75° C. Although in certain embodiments a lower conversion may be acceptable, it is generally desirable to achieve a conversion of metal ion to metal of at least 50%, preferably at least 60%, more preferably at least 70%, and most preferably at least 75, 80, 85% or more.

[0160] The metallic particles produced in this manner generally have diameters of about 1 μm or less. In certain

other embodiments metallic particles having individual diameters and average diameters below about 20 nm or above about 1 μm may be produced. The size of the metallic particles may be conveniently determined using conventional methods of X-ray diffraction or other particle size determination methods, for example, laser scattering.

[0161] After a sufficient conversion of metal ion to metal or metal oxide is achieved, and the metallic particles are formed, the nitrate or nitrite source is added to the suspension. Any suitable compound that yields nitrate or nitrite ion in aqueous solution may be preferred. Preferably, the nitrate or nitrite source is an alkali metal or alkaline earth metal nitrate or nitrite. In a particularly preferred embodiment, the nitrate or nitrite source is magnesium nitrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. It is generally preferred to add a sufficient amount of nitrate or nitrite source so as to produce a solution containing from less than about 70 ppm to more than about 100 ppm nitrogen (in the form of nitrate or nitrite). Preferably, sufficient nitrate or nitrite source is added to produce a solution containing from about 75, 80, or 85 ppm to about 90 or 95 ppm nitrogen, more preferably from about 80 ppm nitrogen.

[0162] Generally, it is preferred that the suspension of metallic particles not be excessively concentrated or dilute, so as to facilitate efficient application of the suspension to the smokable material.

[0163] While it is generally preferred to prepare a suspension of particles as described above by reduction of metal ion in solution, followed by addition of the nitrate or nitrite source, in other embodiments it may be preferred to use a different method to prepare the particles. If the metallic or carbonaceous particles are not prepared in solution, the particles may be mixed with an appropriate liquid to form a suspension. Because of their high surface area, it may be difficult to sufficiently wet the surface of the particles so as to form a uniform suspension. In such cases, any suitable method may be preferred to facilitate forming the suspension, including, but not limited to, mechanical methods such as sonication or heating, or chemical methods such as the use of small quantities of surfactants, provided the surfactants do not interfere with the catalytic activity of the particles. Once the suspension is formed, addition of the nitrate or nitrite source may proceed as described above.

[0164] While it is generally preferred to apply the metallic or carbonaceous particles and nitrate or nitrite source to the smokable material in the form of a suspension, other methods of applying the particles and nitrate or nitrite source are also contemplated. For example, if the particles are in dry form, they may be added to the smokable material as a powder. It may be advantageous to moisten the smokable material with a suitable substance, for example, water, prior to application of the powder in order to provide better adhesion of the particles to the smokable material.

[0165] When the carbonaceous or metallic particles are added to the smokable material in powder form, the nitrate or nitrite source in solid form may also be applied to the smokable material in powder form, either in a separate step before or after the addition of the particles, or simultaneously with the particles, for example, in admixture with the particles. Suitable methods as are well known in the art may be used to prepare a suitable solid form of nitrate or nitrite source. In particularly preferred methods, the solid form of nitrate or nitrite source is prepared by freeze drying

or spray drying methods, both of which may yield extremely small particle sizes. It is generally preferred that the nitrate or nitrite source be in the form of particles having an average diameter on the order of the preferred average diameters for the particles. The nitrate or nitrite source may also be provided as a solution applied to the smokable material as a separate step from adding the particle powder, preferably before adding the particle in dry form to the smokable material.

[0166] Optimization of the Catalyst System

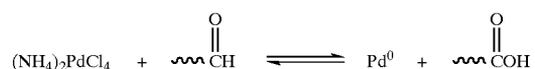
[0167] There are many aspects to consider when attempting to optimize the catalyst system, the first of which is the conversion of the palladium salt to palladium metal in the aqueous reducing solution. This conversion requires a chemical reduction reaction in an aqueous solution. Earlier work was directed to the conversion of the palladium salt to palladium metal in a casing solution. It was suggested in the patent literature that the preferred reducing agent for this reaction in the casing solution is fructose—a known reducing sugar. One origin of fructose in the casing solution is from low invert sugar. In an attempt to repeat this earlier research with casing solutions and produce a more consistent/controllable reaction, all of the components in the casing solution were eliminated that were considered non-essential to the reduction reaction (e.g., propylene glycol, licorice, cocoa, and the like), while the components thought to be essential (e.g., water, palladium salt and low invert sugar) were retained in the same ratios as found in the casing solution, namely 93 g water to 1 g palladium salt to 8 g low invert sugar per pound of tobacco, respectively. Another component that was in the original casing solution but which is now considered non-essential to the reduction reaction is $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. This component was present in early formulations, however nitrate analysis of the treated tobacco verified that $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ decomposes to a certain degree when mixed in aqueous solutions containing palladium metal. It was also found through early testing that carcinogen reduction in cigarettes was not reproducible when the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was allowed to be in contact with palladium metal for extended periods of time. When the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was removed from the reacting solution and instead added to the reacting solution prior to catalyst application on the tobacco, consistent and reproducible carcinogen reductions in experimental cigarettes were obtainable.

[0168] One feature of the preferred reduction reaction is the percent conversion of palladium salt to palladium metal in the aqueous solution containing low invert sugar as a reducing agent. At a temperature of approximately 70-75° C., the percent conversion typically increases steadily with time and after the first three hours of the reaction more than 60-70% of the salt has typically been converted to the metal. Most of the palladium salt is typically converted to metal within the first hour (approximately 50%). Longer reaction times (for example, above three hours) generally only increase the percent conversion modestly. Given the task of balancing maximum conversion with an acceptable production schedule, three hours is generally preferred as the minimum time for this reaction to occur before application of the catalyst solution to the tobacco.

[0169] To increase production rates and lower production costs, it is desirable to increase the percent conversion of

palladium salt to palladium metal. An immediate benefit of increasing the percent conversion is the capacity to use less total palladium salt in the reaction, as an increase in percent conversion with less salt may in fact produce equivalent amounts of palladium metal in the reaction. This results in lower consumption of the most expensive reagent in the reaction.

[0170] Several possibilities exist to increase the percent conversion of this reaction. The reduction reaction is based on an aldehyde being oxidized and releasing electrons to the Pd II nucleus, thereby producing metallic palladium.



[0171] In a particularly preferred catalyst system as described above, it is believed that the aldehyde source is the reducing sugar fructose. In theory, any compound containing an aldehyde functional group can reduce the palladium salt to palladium metal. However to apply the resulting mixture to tobacco it is preferred that the reducing agent is non-toxic. As discussed previously in regard to the particularly preferred catalyst system, low invert sugar is used as the "reducing agent" for this reaction and it is believed that the fructose component of low invert sugar is the active reducing agent. Interestingly, pure fructose when supplied as a reducing agent for the palladium reduction has been shown not to be very effective, even when the fructose is in 10 molar excess. This observation suggests that there is an additional "co-reducing agent" or possibly a catalyst for the reducing agent contained within the low invert sugar solution. Due to the complex mixture associated with low invert sugar it will continue to be a challenge to discover exactly what the reducing agent or agents are when utilizing low invert sugar as a reactant. Nevertheless, the particularly preferred system performs remarkably well given the fact that the mechanism for palladium reduction is not well understood in this system.

[0172] Application of Catalyst to Smokable Material

[0173] After the nitrate or nitrite source has been added to the suspension containing metallic or carbonaceous particles, it is applied to the smokable material. If the smokable material is tobacco, it is preferred to apply the suspension to cut filler prior to addition of the top flavor. If a top flavor is not applied, then it is preferred to apply the suspension to the cut filler as a final step, for example, before it is formed into a tobacco rod. The catalytic particles may be applied before, during, or after application of a casing solution, however in a preferred embodiment the catalytic particles are applied after application of the casing solution. Casing solutions are pre-cutting solutions or sauces added to tobacco and are generally made up of a variety of ingredients, such as sugars and aromatic substances. Such casing solutions are generally added to tobacco in relatively large amounts, for example, one part casing solution to five parts tobacco.

[0174] The particles and nitrate or nitrite source are preferably well dispersed throughout the tobacco so as to provide uniform effectiveness throughout the entire mass of smokable material and throughout the entire period during

which the material is smoked. In the case of cigarette tobacco wherein a blend of various tobaccos is preferred, the suspension may be applied to one or more of the blend constituents, or all of the blend constituents, as desired. Preferably, the suspension is applied to all of the blend constituents so as to ensure substantially uniform coverage of the particles and nitrate or nitrite source.

[0175] For certain types of suspensions of particles, a degradation in performance may be observed if an excessive period of time is allowed to elapse before the suspension is applied to the smokable product. This degradation in performance may be due to various factors, including loss of particles from the suspension due to their accumulation on the interior surfaces of the reaction vessel, or an undesirable increase in particle size over time. When the suspension includes palladium particles, the suspension is generally applied to the cut filler within about ten hours after the desired degree of metal ion conversion is reached and the nitrate or nitrite source is added to the suspension. The suspension is preferably applied within about 9, 8, 7, or fewer hours, more preferably within about 6, 5, or 4 hours, and most preferably within 3, 2, or 1 hours or less. However, in certain embodiments, including those utilizing palladium particles, it may be possible to apply the suspension after a delay of longer than ten hours while maintaining acceptable catalytic performance.

[0176] It is preferred to apply the suspension to the smokable material in the form of a fine mist, such as is produced using an atomizer. In a particularly preferred embodiment, the suspension is applied to tobacco, preferably cut filler, in a rotating tumbler equipped with multiple spray heads. Such a method of application ensures an even coating of the metallic particles on the tobacco product. The tobacco may be heated during or after application of the solution so as to facilitate evaporation of excess solvent.

[0177] It is preferred to add a sufficient quantity of the metallic or carbonaceous particle suspension to the smokable material such that the smokable material contains from about 500 ppm or less to about 1500 ppm or more of the metal or carbon in the form of catalytic particles. Preferably, the smokable material contains from about 500 ppm to about 1000, 1100, 1200, 1300, or 1400 ppm of the metal or carbon in the form of catalytic particles, more preferably 500, 600 or 700 to about 800, 900, or 1000 ppm, and most preferably about 800 ppm. It is generally preferred that the smokable material contains from about 0.4 to about 1.5 wt. % nitrogen (from nitrate or nitrite). Preferably, the smokable material contains from about 0.5 or 0.6 wt. % to about 1.0, 1.1, 1.2, 1.3, or 1.4 wt. % nitrogen, more preferably from about 0.6, 0.7, or 0.8 wt. % to about 0.9 wt. %, and most preferably about 0.9 wt. % nitrogen. In a preferred embodiment, one kilogram of tobacco constitutes 800 milligrams of metal or carbon in the form of catalytic particles, and 9 grams of nitrogen in the form of the nitrate or nitrite source.

[0178] Once the metallic or carbonaceous particles and nitrate or nitrite source have been applied, the smokable material may be further processed and formed into any desired shape or used loosely, for example, in cigars, cigarettes, or pipe tobacco, in any suitable manner as is well-known to those skilled in the art.

[0179] The above description discloses several methods and materials of the present invention. Such modifications

will become apparent to those skilled in the art from a consideration of this disclosure or practice of the invention disclosed herein. Consequently, it is not intended that this invention be limited to the specific embodiments disclosed herein, but that it cover all modifications and alternatives coming within the true scope and spirit of the invention as embodied in the attached claims.

What is claimed is:

1. A smoking article, the smoking article comprising:
 - a smokable material; and
 - a compound comprising a cyclic α -keto enamine, wherein the cyclic α -keto enamine is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article.
2. The smoking article of claim 1, wherein the smokable material comprises a tobacco.
3. The smoking article of claim 1, wherein the cyclic α -keto enamine is deposited on the smokable material.
4. The smoking article of claim 1, wherein the cyclic α -keto enamine is selected from the group consisting of 3-methyl-2-(1-piperidinyl)-2-cyclopenten-1-one, 3-methyl-2-diethylamino-2-cyclopenten-1-one, 5-methyl-2-(1-piperidinyl)-2-cyclopenten-1-one, 5-methyl-2-diethylamino-2-cyclopenten-1-one, 5-methyl-2-dibutylamino-2-cyclopenten-1-one, 5-methyl-2-dihexylamino-2-cyclopenten-1-one, 5-ethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, (E)-4,5-dimethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, 3,5-dimethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, 3,4-dimethyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one, 3-(1-pyrrolidinyl)-2-cyclopenten-1-one, 2-methyl-3-(1-pyrrolidinyl)-2-cyclopenten-1-one, 1-pyrrolidinyl)-2-cyclohexen-1-one, 3-methyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 3,5,5-trimethyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 6-methyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 4,4,6-trimethyl-2-(1-pyrrolidinyl)-2-cyclohexen-1-one, 5-methyl-2-(1-morpholino)-2-cyclopenten-1-one, (S)-5-methyl-2-(2-methoxycarbonyl-1-pyrrolidinyl)-2-cyclopenten-1-one, (S)-3-methyl-2-(2-carboxy-1-pyrrolidinyl)-2-cyclopenten-1-one, 2,5-dimethyl-4-(1-pyrrolidinyl)-3-(2H)-furanone, 4,5-dimethyl-3-(1-pyrrolidinyl)-2-(5H)-furanone, and mixtures thereof.
5. The smoking article of claim 1, wherein the cyclic α -keto enamine comprises 3-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one.
6. The smoking article of claim 1, wherein the cyclic α -keto enamine comprises 5-methyl-2-(1-pyrrolidinyl)-2-cyclopenten-1-one.
7. The smoking article of claim 1, wherein the cyclic α -keto enamine comprises 5-methyl-4-(1-pyrrolidinyl)-3-(2H)-furanone.
8. The smoking article of claim 1, wherein the cyclic α -keto enamine comprises 4-methyl-3-(1-pyrrolidinyl)-2-(5H)-furanone.
9. The smoking article of claim 1, comprising a cigarette.
10. The smoking article of claim 1, further comprising a filter.
11. The smoking article of claim 10, wherein the filter comprises an activated charcoal or an activated carbon.
12. A method of providing a smoke stream from a cigarette, wherein the smoke stream is capable of imparting a cooling sensation to an oral cavity, the method comprising:

providing a cigarette, the cigarette comprising a tobacco charge and a compound comprising a cyclic α -keto enamine;

combusting the tobacco charge, whereby a smoke stream is produced, the smoke stream comprising the cyclic α -keto enamine; and

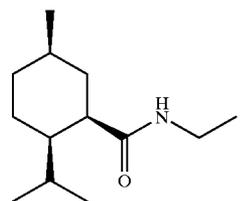
inhaling the smoke stream, whereby a cooling sensation is imparted to an oral cavity.

13. A smoking article, the smoking article comprising:

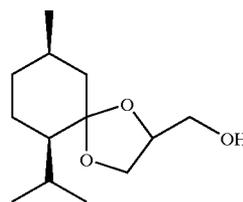
a smokable material; and

a compound selected from the group consisting of a carboxamide, a mentane glycerol ketal, a menthyl ester, an alkyl-substituted urea, a sulfonamide, a phosphine oxide, wherein the compound is capable of imparting a cooling sensation to an oral cavity of a smoker upon inhalation of a smoke stream from the smoking article.

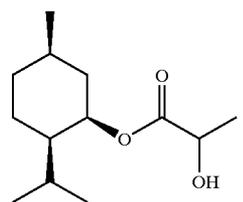
14. The smoking article of claim 13, wherein the carboxamide has a chemical formula corresponding to:



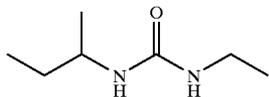
15. The smoking article of claim 13, wherein the mentane glycerol ketal has a chemical formula corresponding to:



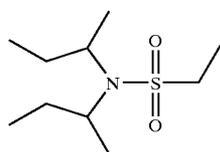
16. The smoking article of claim 13, wherein the menthyl ester has a chemical formula corresponding to:



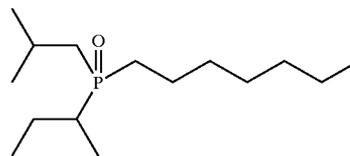
17. The smoking article of claim 13, wherein the alkyl-substituted urea has a chemical formula corresponding to:



18. The smoking article of claim 13, wherein the sulfonamide has a chemical formula corresponding to:



19. The smoking article of claim 13, wherein the phosphine oxide has a chemical formula corresponding to:



20. The smoking article of claim 13, wherein the smoking material comprises a tobacco.

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