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(54) **CORRUGATED CATALYTIC CIGARETTE PAPER AND CIGARETTES COMPRISING THE SAME**

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(57) **ABSTRACT**

A catalyst-modified corrugated cigarette paper wrapper comprises a fibrous web, an optional web-filler material supported by the web, and catalyst particles supported by the web and/or the web-filler material. In cigarettes comprising the catalyst-modified corrugated cigarette paper, the corrugations define axially-extending channels that can run the length of a tobacco rod. The corrugations can increase the catalytic efficiency of catalyst particles that are incorporated within the catalyst-modified corrugated cigarette paper wrapper.

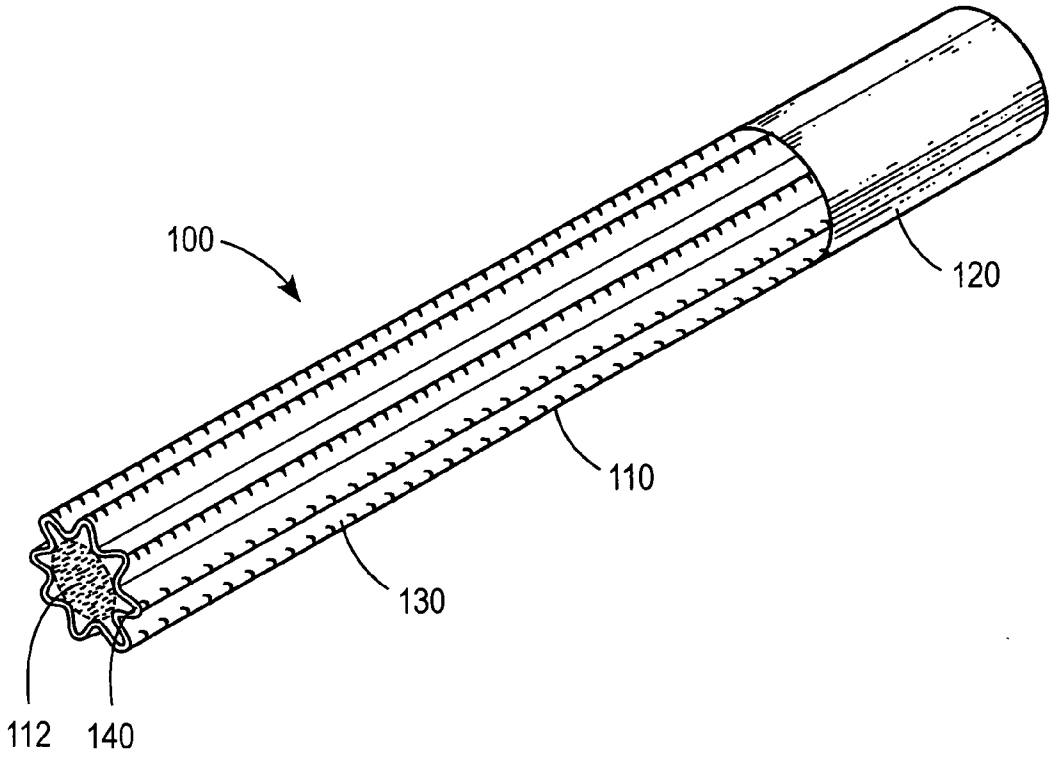

FIG. 1

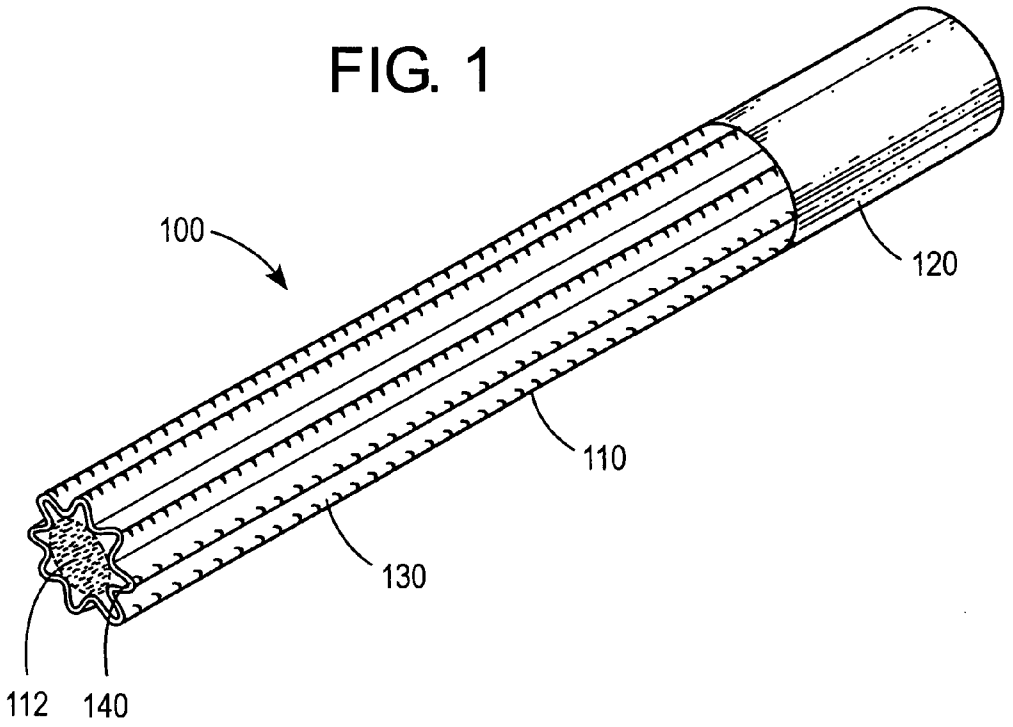

FIG. 2A

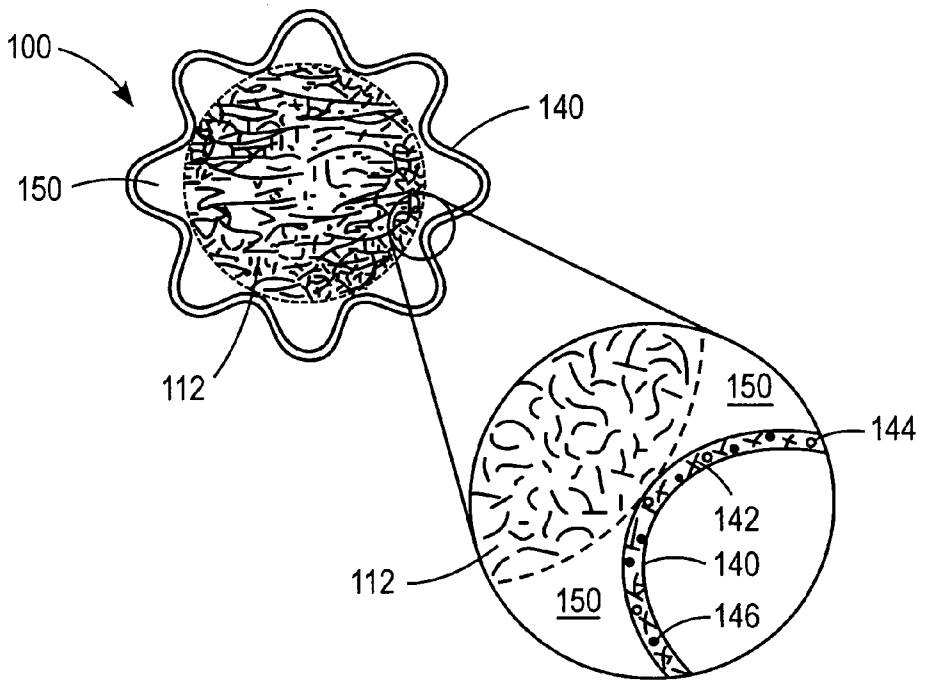

FIG. 2B

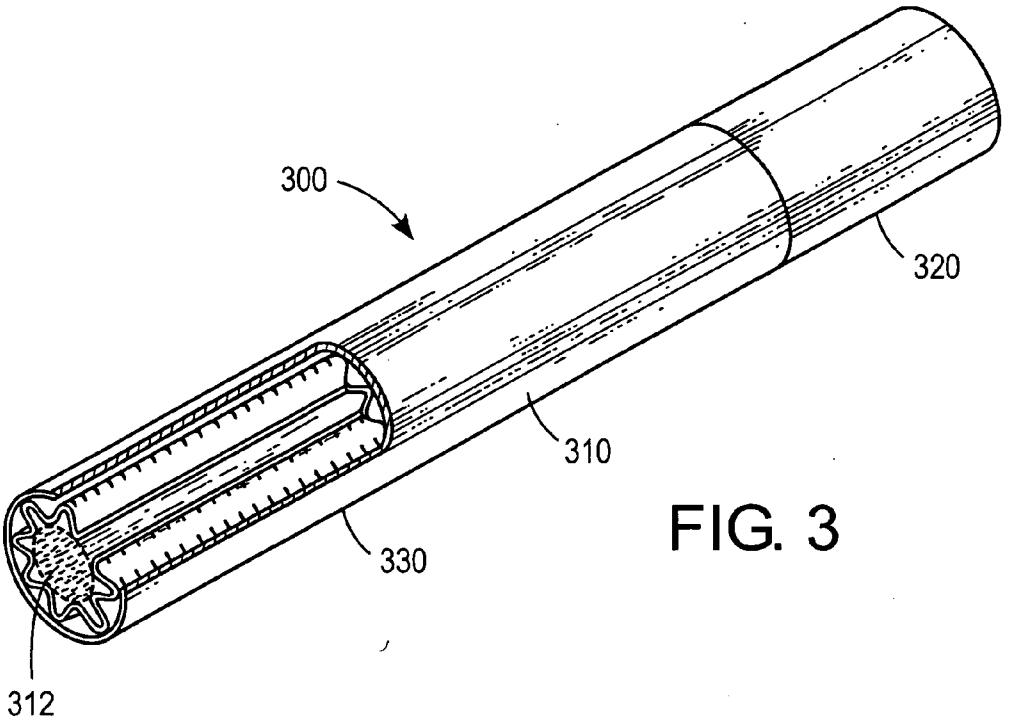

FIG. 3

FIG. 4A

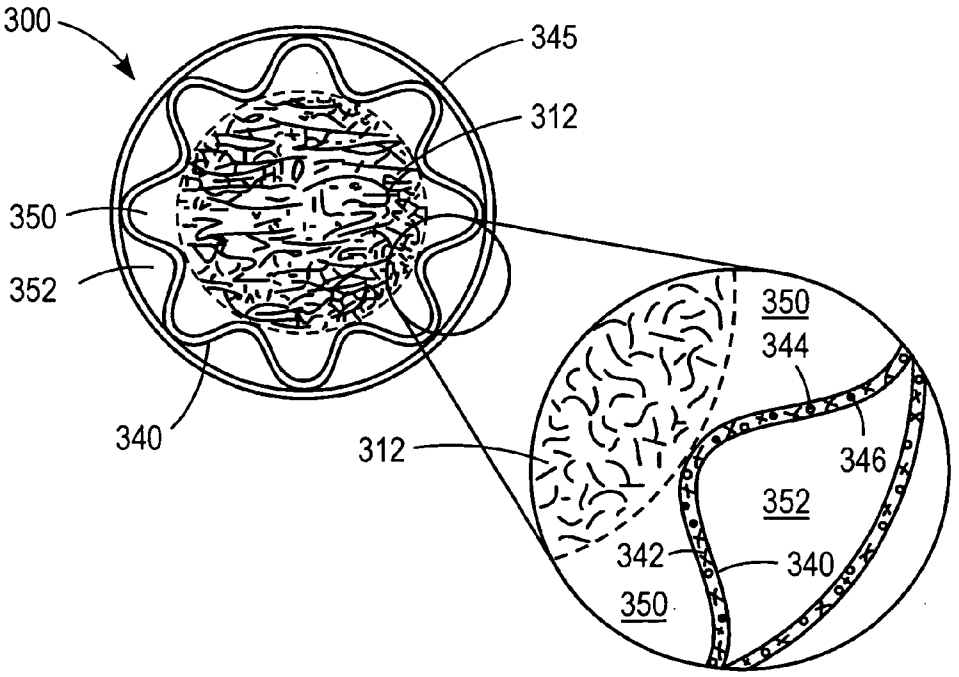

FIG. 4B

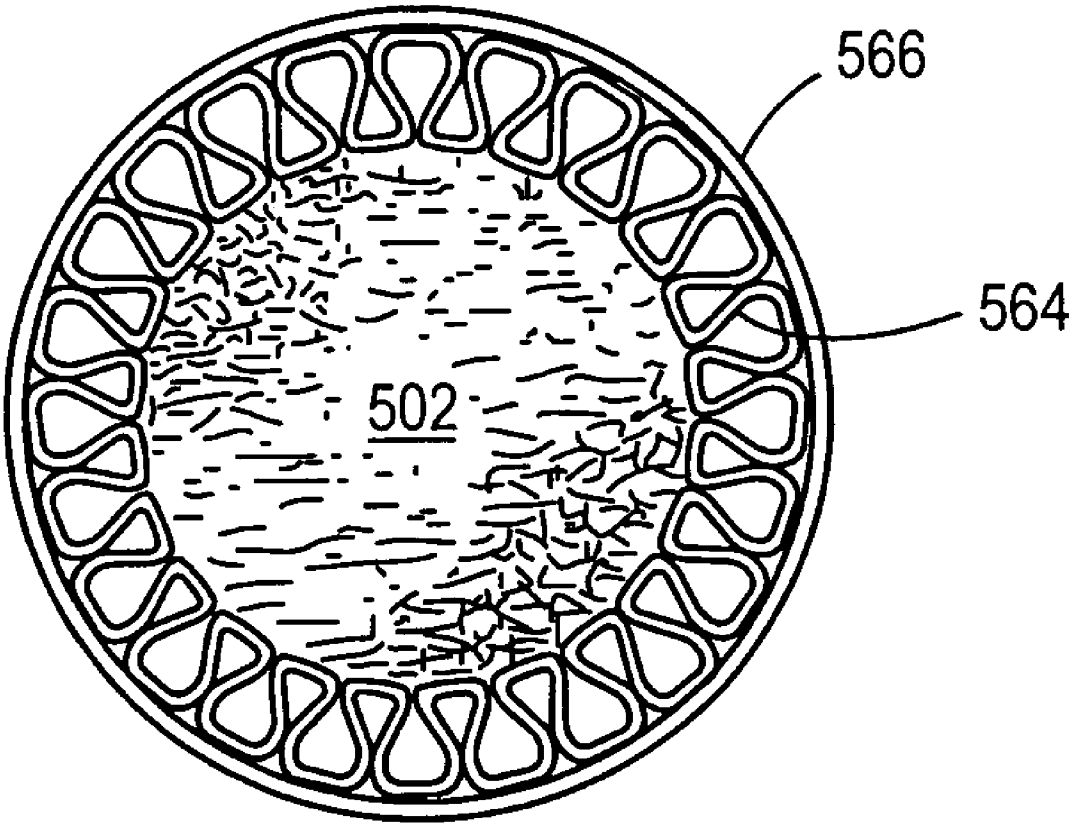

FIG. 5

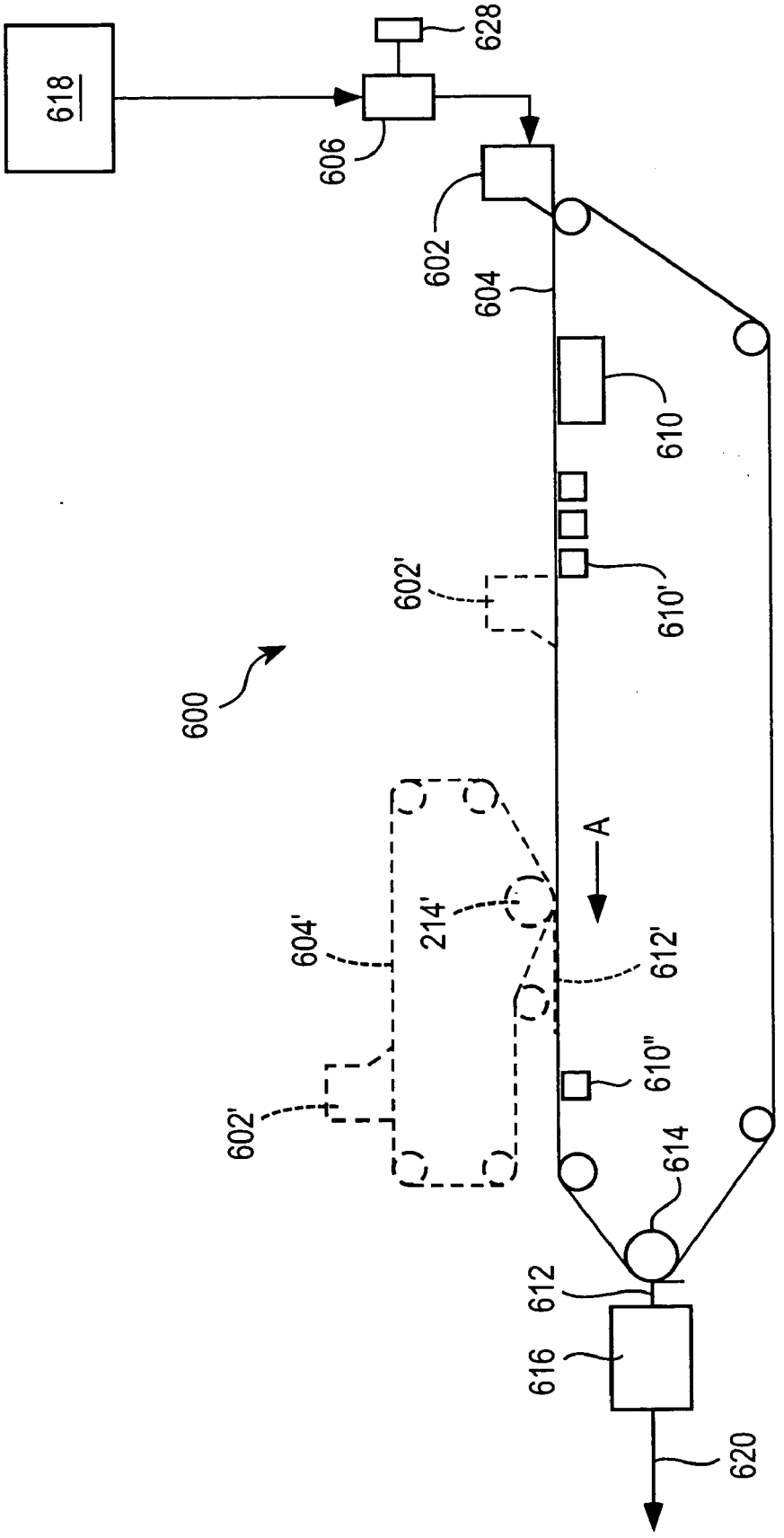
618
628
606
602
604
610
602'
610'
600
A
214'
604'
612'
610"
602'
614
612
616
620

FIG. 6

CORRUGATED CATALYTIC CIGARETTE PAPER AND CIGARETTES COMPRISING THE SAME

CROSS REFERENCE TO RELATED APPLICATION

[0001] This application claims priority under 35 U.S.C. §119(e) to U.S. provisional Application No. 60/754,897, filed on Dec. 30, 2005, the entire content of which is incorporated herein by reference.

BACKGROUND

[0002] In the description that follows reference is made to certain structures and methods, however, such references should not necessarily be construed as an admission that these structures and methods qualify as prior art under the applicable statutory provisions. Applicants reserve the right to demonstrate that any of the referenced subject matter does not constitute prior art.

[0003] Cigarettes produce both mainstream smoke during a puff and sidestream smoke during static burning. Constituents of both mainstream smoke and sidestream smoke are carbon monoxide (CO) and nitric oxide (NO). There is an interest in reducing the concentration of carbon monoxide and nitric oxide in mainstream and sidestream smoke.

SUMMARY

[0004] A cigarette comprises a tobacco rod wrapped in a cigarette wrapper, wherein the cigarette wrapper comprises a catalyst-modified corrugated cigarette paper wrapper having a fibrous web, an optional web-filler material supported by the web, and catalyst particles supported by the web and/or the web-filler material. Catalyst-modified corrugated cigarette paper comprises a fibrous web, an optional web-filler material supported by the web, and catalyst particles supported by the web and/or the web-filler material.

[0005] The catalyst-modified corrugated cigarette paper wrapper defines a plurality of channels that run axially along the length of the cigarette. The corrugations are preferably sized such that their spacing, peak to valley, is less than their height. A preferred catalyst-modified corrugated cigarette paper wrapper is a composite wrapper further comprising a non-corrugated paper wrapper wrapped around the catalyst-modified corrugated paper wrapper. The non-corrugated outer wrapper can be substantially free of catalyst particles or can comprise catalyst particles on an inner surface thereof. A further preferred composite wrapper comprises a gas permeable inner wrapper.

[0006] The catalyst particles (e.g., nanoscale catalyst particles) can be incorporated in the catalyst-modified corrugated cigarette paper wrapper in an amount effective to reduce the concentration in mainstream smoke of carbon monoxide and/or nitric oxide during smoking of a cigarette comprising the wrapper.

[0007] Preferred catalyst particles, which can be coated on an exposed surface of the paper or supported within the fibrous web of the paper (e.g., supported on web-filler material such as calcium carbonate), comprise a transition metal oxide and/or a transition metal hydroxide such as oxides and/or hydroxides of iron. Preferred catalyst-modified corrugated cigarette paper has a permeability of between about 5 and 80 Coresta units.

[0008] A method of making a cigarette comprising a catalyst-modified corrugated cigarette paper wrapper comprises (i) optionally supporting catalyst particles on a web-filler material to form a catalyst-modified web-filler, (ii) incorporating catalyst particles and/or catalyst-modified web-filler in cigarette paper to form catalytic cigarette paper, (iii) forming corrugations in cigarette paper to form a corrugated cigarette paper, (iv) providing cut filler comprising tobacco to a cigarette making machine, and (v) placing the corrugated cigarette paper around the cut filler to form a tobacco rod portion of the cigarette. Optionally, a non-corrugated second wrapper can be placed around the catalyst-modified corrugated cigarette paper wrapper. The non-corrugated second wrapper can be free of catalyst particles or can have catalyst particles incorporated on an inner surface thereof. In a further embodiment, a gas permeable inner wrapper can be formed around the cut filler prior to forming the catalyst-modified corrugated cigarette paper wrapper around the cut filler.

[0009] A method of manufacturing catalyst-modified corrugated cigarette paper comprises (i) forming cigarette paper, (ii) forming corrugations in the cigarette paper, and (iii) incorporating catalyst particles in the cigarette paper. The steps of forming corrugations in the paper and incorporating catalyst particles in the paper can be performed in either order.

[0010] A first preferred method of manufacturing catalyst-modified corrugated cigarette paper comprises supplying cellulosic material and catalyst particles to a head box in a forming section of a papermaking machine, the catalyst particles comprising unsupported catalyst particles and/or catalyst modified web-filler; depositing an aqueous slurry including the cellulosic material and the catalyst particles onto the forming section of the papermaking machine to form a base web with the catalyst particles distributed therein; and removing water from the base web so as to form a sheet of catalytic paper.

[0011] A second preferred method of manufacturing catalyst-modified corrugated cigarette paper comprises supplying cellulosic material to a head box in a forming section of a papermaking machine; depositing an aqueous slurry including the cellulosic material onto the forming section of the papermaking machine to form a base web; distributing catalyst particles on the base web; and removing water from the base web so as to form a sheet paper.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. **1** shows a perspective view of a cigarette comprising a catalyst-modified corrugated cigarette paper wrapper according to one embodiment.

[0013] FIG. **2**(*a*) is an axial view of the cigarette of FIG. **1**, and FIG. **2**(*b*) shows a magnified view.

[0014] FIG. **3** shows a cigarette comprising a catalyst-modified corrugated cigarette paper wrapper and a second outer wrapper.

[0015] FIG. **4**(*a*) shows an axial view of the cigarette of FIG. **3**, and FIG. **4**(*b*) shows a magnified view.

[0016] FIG. **5** shows an axial view of a cigarette comprising a catalyst-modified corrugated cigarette paper wrapper according to a further embodiment.

[0017] FIG. **6** is a schematic illustration of a papermaking machine for making a catalytic cigarette paper.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0018] A catalyst-modified corrugated cigarette paper wrapper comprises a fibrous web, an optional web-filler material supported by the web, and catalyst particles supported by the web and/or the web-filler material. Catalyst-modified corrugated cigarette paper can be used to manufacture a cigarette and is typically consumed during smoking of the cigarette. In cigarettes comprising a catalyst-modified corrugated paper wrapper, the concentration in mainstream and sidestream smoke of carbon monoxide and/or nitric oxide can be reduced.

[0019] In cigarettes comprising catalyst-modified corrugated cigarette paper wrappers, the catalyst particles can promote the conversion of carbon monoxide (CO) to carbon dioxide (CO_2) via catalysis and/or oxidation mechanisms. As an example, the catalyst particles can promote the oxidation of carbon monoxide by a gaseous source of oxygen according to the reaction $MO_x+2CO+O_2=MO_x+2CO_2$, where MO_x represents a transition metal oxide catalyst, or a mixture of transition metal oxide catalysts (M=a transition metal such as Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Ce, Ta, W, Re, Os, Ir, Pt or Au), and x is a positive real number. Further, it is believed that subsequent to the catalytic reaction, the catalyst particles can oxidize carbon monoxide by donating an oxygen atom to a carbon monoxide molecule according to the equation $MO_x+CO=MO_{x-1}+CO_2$. The oxidation of CO can proceed in the presence or absence of a gaseous source of oxygen. In addition to converting CO to CO_2, the catalyst particles can promote the conversion of nitric oxide to nitrogen via catalysis and/or reduction mechanisms.

[0020] The catalyst particles can comprise transition metal oxides and/or transition metal hydroxides. Exemplary catalyst particles comprise iron oxide, iron hydroxide and/or iron oxyhydroxide. Preferred catalyst particles include α-Fe_2O_3, γ-Fe_2O_3, FeOOH, and mixtures thereof. For instance, MACH I, Inc., King of Prussia, PA markets nanoscale particles under the trade names NANOCAT® Superfine Iron Oxide (SFIO) and NANOCAT® Magnetic Iron Oxide. The NANOCAT® Superfine Iron Oxide comprises amorphous ferric oxide (e.g., Fe_2O_3) in the form of a free-flowing powder with an average particle size of about 3 nm, a specific surface area of about 250 m^2/g, and a bulk density of about 0.05 g/cm^3. The Superfine Iron Oxide is synthesized by a vapor-phase process, which renders it substantially free of impurities that may be present in conventional catalysts, and is suitable for use in food, drugs, and cosmetics. The NANOCAT® Magnetic Iron Oxide is a free-flowing powder with a particle size of about 25 nm and a surface area of about 40 m^2/g. The catalyst particles can have a shape that is spherical, cubical, and/or acicular.

[0021] Other exemplary catalyst particles comprise ceria-based catalyst particles. Ceria-based catalyst particles can oxidize CO at near ambient (i.e., room) temperatures. Suitable ceria-based catalyst particles are disclosed in commonly-owned U.S. Pat. No. 6,857,431, the entire content of which is herein incorporated by reference. Still further exemplary catalyst particles comprise doped metal oxides such as yttria doped with zirconium, manganese oxide doped with palladium, or mixtures of metal oxides, doped metal oxides, etc., which are disclosed in commonly-owned U.S. Patent Publication No. 2003/0131859, the entire content of which is herein incorporated by reference.

[0022] In a preferred embodiment, the catalyst particles can comprise nanoscale particles. By "nanoscale" is meant that the catalyst particles have an average particle size of less than about 500 nanometers, preferably less than about 100 nanometers, most preferably less than about 10 nanometers. A bulk density of the catalyst particles is preferably less than about 0.3 g/cm^3, more preferably less than 0.1 g/cm^3. The Brunauer, Emmett, and Teller (BET) surface area of preferred catalyst particles is greater than about 10 m^2/g (e.g., greater than 50,100 or 200 m^2/g).

[0023] The ratio, in weight percent, of web-filler material to catalyst particles can be any suitable ratio ranging from 0% to 99%. The web-filler material, if provided, can include an oxide, carbonate or hydroxide of a Group II, Group III or Group IV metal, or the web-filler material can be selected from the group consisting of $CaCO_3$, TiO_2, SiO_2, Al_2O_3, $MgCO_3$, MgO, and/or $Mg(OH)_2$. A preferred average particle size of the web-filler material is from about 0.1 to 10 micrometers, more preferably less than about 2 micrometers.

[0024] A catalyst-modified corrugated cigarette paper wrapper can increase the firmness and rigidity of a cigarette. Furthermore, a catalyst-modified corrugated cigarette paper wrapper can increase the catalytic efficiency of catalyst particles incorporated in the wrapper.

[0025] An embodiment of a cigarette having a catalyst-modified corrugated cigarette paper wrapper is shown in FIG. **1**. Cigarette **100** has a tobacco rod portion **110** and a filtering tip portion **120**. Optionally, embodiments of the cigarette **100** can be practiced without a filtering tip. The tobacco rod portion **110** comprises a column of tobacco **112** that is wrapped with a cigarette paper wrapper **130**. The cigarette paper wrapper **130** preferably comprises a thin, flexible corrugated layer **140**.

[0026] An axial view of cigarette **100** is shown in FIG. **2**(*a*). As shown in the expanded view in FIG. **2**(*b*), the catalyst-modified corrugated cigarette paper wrapper **140** includes a web **142** of fibrous cellulosic material in which is preferably dispersed particles of web-filler material **144** such as calcium carbonate ($CaCO_3$). Incorporated in the catalyst-modified corrugated paper wrapper **140** are catalyst particles **146**. The catalyst particles **146** can be supported directly on the paper web **142**, or in an alternate embodiment, the catalyst particles can be supported on particles of the web-filler material **144**. The terms "incorporated in" means that the catalyst particles can be surrounded by the matrix of cellulosic material (i.e., embedded between fibers of cellulosic material), or coated on at least one exposed surface of the paper web.

[0027] The corrugations provide a plurality of channels **150** adjacent to the tobacco column that run axially along the length of the cigarette. Thus, smoke (e.g., mainstream and/or sidestream smoke) flowing down the channels can pass over a relatively large area of the corrugated paper wrapper, and when compared to non-corrugated wrappers, the smoke can be in contact with a larger volume of catalyst particles that are incorporated in the wrapper.

[0028] In practice, the gas permeability (i.e., porosity) of cigarette paper can be controlled using the web-filler material **144**. The permeability is measured in units of Coresta, which is defined as the volume of air, measured in cubic centimeters, that passes through one square centimeter of material in one minute at a pressure gradient of 1 kilopascal.

[0029] The permeability of the catalyst-modified corrugated cigarette paper wrapper is preferably from about 5 Coresta units to about 80 Coresta units, and more preferably from about 30 to 35 Coresta units. Other permeabilities of the wrapper can be selected based on the application and location of the wrapper. Further, the catalyst-modified corrugated cigarette paper wrapper can have a basis weight of from about 18 g/m^2 to 60 g/m^2, more preferably from about 30 g/m^2 to about 45 g/m^2. However, any suitable basis weight for the corrugated wrapper can be selected. The paper wrapper can have a thickness of from about 15 to 100 micrometers, more preferably from 20 to 50 micrometers.

[0030] Optionally, the catalyst-modified corrugated cigarette paper wrapper can comprise a multi-layer (e.g., composite) wrapper. Additional layers in a multilayer wrapper can be from 0.1 to 10 times the permeability of the first layer, and can have a thickness of from 0.1 to 2 times the thickness of the first layer. In embodiments where a composite wrapper is provided (e.g., a conventional wrapper formed around a catalyst-modified corrugated cigarette paper wrapper), both the permeability and the thickness of the inner layer and the outer layer can be selected to achieve a desired total air permeability and total thickness for the cigarette.

[0031] A preferred cigarette comprises a composite catalyst-modified corrugated cigarette paper wrapper. An embodiment of a cigarette having a composite cigarette paper wrapper is shown in FIGS. **3** and **4**(*a*)-(*b*). Cigarette **300** includes a tobacco rod portion **310** including a tobacco column **312** and a filtering tip portion **320**. Embodiments of the cigarette **300** can be practiced without a filtering tip. The tobacco rod portion **310** comprises a column of tobacco **312** wrapped with a composite cigarette paper wrapper **330**. The composite cigarette paper wrapper **330** comprises a thin, flexible corrugated layer **340** and an outer layer **345** of sheet material that surrounds the catalyst-modified corrugated cigarette paper wrapper **340**.

[0032] An axial view of the cigarette **300** is shown in FIG. **4**(*a*). Inner channels **350** are formed between the tobacco column **312** and the catalyst-modified corrugated cigarette paper **340**, and outer channels **352** are formed between the catalyst-modified corrugated cigarette paper **340** and the outer layer of sheet material **345**. As in the previous embodiment, compared to a non-corrugated wrapper, the plurality of channels in the catalyst-modified corrugated cigarette paper wrapper can increase the contact area between mainstream and/or sidestream smoke and the catalyst particles incorporated in the wrapper.

[0033] Because the addition of catalyst particles can discolor cigarette paper, e.g., a paper wrapper becomes non-white or brown, in a preferred embodiment, an outer wrapper that is a conventional color, e.g., white, can be placed around an inner corrugated wrapper having catalyst particles incorporated therein. The outer wrapper is preferably not a corrugated wrapper and can be free of catalyst particles so as to provide a smooth outward appearance to the cigarette that is not affected by any coloration from the catalyst particles. Alternatively, catalyst particles can be incorporated in the outer wrapper. For example, catalyst particles can be coated on an inner surface of the outer wrapper in order to minimize discoloration of the outer surface of the outer wrapper.

[0034] FIG. **4**(*b*) shows an expanded view of the cigarette shown in FIG. **4**(*a*). The catalyst-modified corrugated cigarette paper wrapper **340** includes a web of fibrous cellulosic material **342** in which is optionally dispersed particles of web-filler material **344**. Catalyst particles **346** are incorporated in the corrugated wrapper **340**, and the catalyst particles can be supported directly on the paper web **342** or on particles of web-filler material **344**, if provided.

[0035] In the embodiment illustrated in FIGS. **3** and **4**(*a*)-(*b*), the inner corrugated wrapper and the outer wrapper are preferably individual wrappers formed in separate papermaking processes and later wrapped around a column of tobacco cut filler to from a cigarette tobacco rod. The corrugated inner wrapper, the outer wrapper or both wrappers can include catalyst particles (or catalyst-modified web-filler). In examples where catalyst particles are incorporated in both wrappers, the catalyst composition, particle shape, size and loading in each wrapper can be the same or different. Both the inner corrugated wrapper and the outer wrapper can be selected to give a desired performance with respect to cigarette properties, such as puff count, tar, burn rate, and ash appearance. As shown and described, for example, in FIGS. **3** and **4**(*a*)-(*b*), the preferred embodiments of cigarettes and methods of making cigarettes include a tobacco rod portion of a cigarette with a composite wrapper. A preferred composite wrapper comprises an inner catalyst-modified corrugated cigarette paper wrapper and an outer wrapper that is substantially free of catalyst particles.

[0036] A composite catalyst-modified corrugated cigarette paper wrapper can optionally further comprise an inner layer of sheet material adapted to be formed between the tobacco column and the corrugated layer. The inner layer, if provided, is preferably permeable to smoke either by virtue of a relatively porous structure or by the formation of perforations therethrough. When an inner layer of sheet material is provided, inner channels are formed between the inner layer of sheet material and the catalyst-modified corrugated cigarette paper.

[0037] FIG. **5** shows a cigarette comprising a catalyst-modified corrugated cigarette paper wrapper having a higher density of corrugations than the previous embodiments illustrated in FIGS. **1-4**. In the embodiment illustrated in FIG. **5**, the catalyst-modified corrugated cigarette paper wrapper **564** comprises corrugations that bend back upon themselves and form loops, each of which touches the preceding and the following loop of the corrugation near the optional outer layer **566** and again near the tobacco column **502**. In this embodiment, the corrugations can be glued or otherwise attached at least at those points where they contact each other near the outer and inner circumference of the wrapper. Such a corrugated wrapper can be made sufficiently flexible for use with cigarette making machines. By omitting the outer layer **566** of sheet material, the cigarette can have an outward appearance different from that of a standard cigarette.

[0038] In each of the aforementioned embodiments, it is particularly preferred that the catalyst-modified corrugated

cigarette paper wrapper have a thickness that is less than a radius of the tobacco rod (i.e., such that the wrapper represents 50% or less of the diameter of a cigarette comprising the wrapper). It is further preferred that the corrugations be uniformly spaced, peak to valley, at a distance less than their height, so that a tangent to their sloping portions, assuming a regular sinusoidal waveform, makes an angle of less than about 45° (e.g., less than about 40°, 35° or 30°) with respect to a radial axis line of a cigarette comprising the wrapper.

[0039] The axially extending channels defined by the corrugations in the various embodiments may be either opened or closed and, if closed, may be closed at the mouth end of the cigarette, filter end of the cigarette, or both. If the channels are closed, it may be desirable to perforate the wrapper when dilution is desired. Closing either the inner channels or the outer channels while leaving the others open can be accomplished prior to manufacturing the cigarette.

[0040] In preferred embodiments, the channels are open. If, for example, flavoring is added to the catalyst-modified corrugated cigarette paper, smoke and air may be drawn along the open channels toward the mouth end.

[0041] Catalyst-modified corrugated cigarette paper can be made by incorporating catalyst particles in corrugated cigarette paper. For example, a liquid dispersion of catalyst particles can be spray coated on at least one surface of corrugated paper. Alternatively, catalyst-modified corrugated cigarette paper can be made by forming corrugations in catalytic cigarette paper. Catalytic paper comprises catalyst particles that are incorporated in the paper. Preferred methods of forming catalytic paper are described herein below.

[0042] One method of forming the corrugations comprises passing a sheet of cigarette paper between two grooved or threaded rollers. The depth and pitch of the corrugations in the paper can be controlled by the geometry of the forming rollers and the pressure applied to them. When threaded rollers are used, one such roller preferably has a right-handed thread and the other such roller preferably has a left-handed thread, and they are rotated in an opposite sense so that the paper can be fed between the two rollers. The number of corrugations can be controlled by varying the number of grooves or threads on the forming rollers and may range from about 10 to about 60 per inch. The depth of the corrugations may range from about 0.01 to 0.1 inch.

[0043] According to preferred methods of forming catalytic cigarette paper, the catalyst particles can be incorporated into cigarette paper before, during, or after the papermaking/corrugation processes. According to a first embodiment, the catalyst particles can be incorporated within the fibrous web of the paper by first supporting the catalyst particles on web-filler material to form a catalyst-modified web-filler and then incorporating the catalyst-modified web-filler in the paper. In a preferred example, the catalyst-modified corrugated cigarette paper can comprise $CaCO_3$ web-filler or other filler material used in cigarette paper manufacture and nanoscale iron oxide catalyst particles that are supported on the web-filler material.

[0044] A catalyst-modified web-filler can be prepared by forming an aqueous slurry of catalyst particles and web-filler material and drying the slurry. Other techniques for forming a catalyst-modified web-filler include precipitating catalyst particles from a solution onto a web-filler material, or depositing (e.g., via vapor phase deposition) catalyst particles onto a web-filler material. A catalyst-modified web filler can be used as all or part of the web-filler material in the paper-making process.

[0045] Advantageously, the web-filler-supported catalyst particles such as supported nanoscale catalyst particles can exhibit a reduced tendency to agglomerate with each other during processing and a reduced tendency to leech out of the catalytic paper during or after cigarette paper manufacture.

[0046] According to a second embodiment, the catalyst particles can be incorporated in a cigarette paper by supporting the catalyst particles directly on the cellulosic fibers of the paper web. Catalyst particles can be coated (e.g., curtain coated), sprayed, or printed on a wet or dry base web. A retention aid can be used to improve the distribution and adhesion of the catalyst particles. In a further example, the catalyst-modified corrugated cigarette paper wrapper comprises nanoscale iron oxide particles that are supported directly on the paper web.

[0047] The catalyst particles and web-filler material, if provided, can be incorporated in a cigarette paper using conventional papermaking processes. Catalyst particles and/or catalyst-modified web filler can be supplied to the papermaking process as an aqueous slurry or as a dry powder to be slurried. For example, an aqueous slurry ("furnish") including the catalyst particles and cellulosic material can be supplied to a head box of a forming section of a Fourdrinier papermaking machine. The aqueous slurry can be supplied to the head box by one or more conduits in fluid communication with a source, such as a storage tank. Optionally, an aqueous slurry containing catalyst particles and an aqueous slurry of cellulosic material without catalyst particles or with a different concentration or type of catalyst particles can be supplied to separate head boxes.

[0048] An exemplary method deposits aqueous slurry from a head box onto a forming section so as to form a base web of cellulosic material. In a typical Fourdrinier machine, the forming section is a Fourdrinier wire arranged as an endless forming wire immediately below the head box. An opening defined in a lower portion of the head box adjacent to the endless wire permits the aqueous slurry to flow onto the top surface of the endless wire to form a wet base web.

[0049] Optionally, the aqueous slurry can be deposited onto a pre-formed support web that is retained within the paper. For example, a pre-formed support web can be transported through the forming section of a papermaking machine and can be a foundation on which the aqueous slurry is deposited. The aqueous slurry dries and the paper sheet (e.g., finished web) is formed with catalyst-modified web-filler or catalyst particles embedded therein. The support web can be a conventional web, such as a flax support web, or can include a web with an incorporated catalytic component. If the support web includes a catalytic component, the incorporated catalytic component can be supported on a web-filler material, or can be directly supported on the support web without a web-filler material.

[0050] After depositing the aqueous slurry onto the forming section, water is removed from the wet base web, and with additional processing such as further drying and pressing, if necessary, forms a sheet of catalytic paper (e.g., finished web). The catalytic paper can be corrugated in an additional processing step.

[0051] Referring to FIG. **6**, a cigarette papermaking machine **600** includes a head box **602** operatively located at one end of a Fourdrinier wire **604**, and source of feed stock slurry such as a run tank **606** in communication with the head box **602**. The head box **602** can be one typically utilized in the papermaking industry for laying down cellulosic pulp upon the Fourdrinier wire **604**. In the usual context, the head box **602** is communicated to the run tank **606** through a plurality of conduits. The run tank **606** receives furnish from a furnish supply **618**. Preferably, the feed stock from the run tank **606** is a refined cellulosic pulp such as a refined flax or a wood pulp commonly practiced in the cigarette papermaking industry. Preferably, a chalk tank **628** (containing the catalyst modified filler described above) is communicated with the run tank **606** so as to establish a desired "chalk" level in the slurry supplied to the head box **602**.

[0052] The Fourdrinier wire **604** carries the laid slurry pulp (e.g., base web) from the head box **602** along a path in the general direction of arrow A in FIG. **6**, whereupon water is allowed to drain from the pulp through the wire **604** by the influence of gravity and at some locations with the assistance of vacuum boxes **610**, **610'**, **610"** at various locations along the Fourdrinier wire **604**. At some point along the Fourdrinier wire **604**, sufficient water is removed from the base web to establish what is commonly referred to as a dry line where the texture of the slurry transforms from one of a glossy, watery appearance to a surface appearance more approximating that of the finished base web (but in a wetted condition, e.g., an intermediate web). At and about the dry line, the moisture content of the pulp material is approximately 85 to 90%, which may vary depending upon operating conditions and the like.

[0053] Downstream of the dry line, the intermediate web **612** separates from the Fourdrinier wire **604** at a couch roll **614**. From there, the Fourdrinier wire **604** continues on the return loop of its endless path. Beyond the couch roll **614**, the intermediate web **612** continues on through the remainder of the papermaking system which further dries and presses the intermediate web **612**, and surface conditions it to a desired final moisture content and texture to form a paper **620** (e.g., finished web). Such drying apparatus is well known in the art of papermaking, and may include drying section **616** including drying felts, vacuum devices, rolls, and/or presses, applied thermal energy, and the like.

[0054] The cigarette making machine **600** can optionally include more than one head box and/or more than one Fourdrinier wire with either separate or common furnish supply. The optional second head box **602'**, suitably integrated with a run-tank and furnish supply, can lay slurry pulp onto the slurry pulp laid from the first head box **602** and carried along Fourdrinier wire **604**. The second and/or additional head box can be supplied with catalyst modified web filler to a desired "chalk" level or can be free of catalyst modified web-filler, as desired based on the number of layers of slurry pulp to be deposited and/or the use of the wrapper formed from the papermaking process.

[0055] The optional second Fourdrinier wire **604'**, suitably integrated with a head box **602'** laying slurry pulp on the Fourdrinier wire **604'** and draining and drying equipment, can form a second intermediate web **612'**. The second intermediate web **612'** can be separated from the second Fourdrinier wire **604'** at a second couch roll **214'** and laid on the first intermediate web **612** from the Fourdrinier wire **604** to be processed into double layer paper. Multiple optional Fourdrinier wires can be employed to form multiple layer paper having any desired number of layers, such as three, four and so forth, up to ten to twelve layers.

[0056] A method of manufacturing catalyst-modified corrugated cigarette paper comprises forming cigarette paper, forming corrugations in the cigarette paper, and incorporating catalyst particles in the cigarette paper. The step of forming corrugations in the cigarette paper can precede or follow the step of incorporating catalyst particles in the cigarette paper.

[0057] A first preferred method of manufacturing catalyst-modified corrugated cigarette paper comprises supplying cellulosic material and catalyst particles to a head box in a forming section of a papermaking machine, the catalyst particles comprising unsupported catalyst particles and/or catalyst modified web-filler; depositing an aqueous slurry including the cellulosic material and the catalyst particles onto the forming section of the papermaking machine to form a base web with the catalyst particles distributed therein; and removing water from the base web so as to form a sheet of catalytic paper.

[0058] A second preferred method of manufacturing catalyst-modified corrugated cigarette paper comprises supplying cellulosic material to a head box in a forming section of a papermaking machine; depositing an aqueous slurry including the cellulosic material onto the forming section of the papermaking machine to form a base web; distributing catalyst particles on the base web; and removing water from the base web so as to form a sheet paper.

[0059] The catalyst-modified corrugated cigarette paper can comprise a laminated, bi-layer or multilayer catalytic paper. Examples of bi-layer and multilayer paper are disclosed in commonly-owned U.S. Pat. No. 5,143,098, the entire content of which is herein incorporated by reference. In an embodiment of a bi-layer or multilayer catalytic paper, at least one of a first layer and a second layer can include the catalyst particles described in embodiments herein.

[0060] Single layer, bi-layer or multilayer catalyst-modified corrugated cigarette paper may be made using ordinary paper furnish such as pulped wood, flax fibers, or any standard cellulosic fiber. Preferably, flax fibers are used. Different fillers, including different catalytic fillers such as the catalyst modified web-filler described herein, or different fibers may be used for each layer and may be contained in different head boxes. For example, a first head box can hold the materials for a catalytic paper and a second head box can hold the materials for a conventional paper wrapper.

[0061] Additional methods of forming catalyst-modified web-filler material and methods of incorporating web-filler material and catalyst-modified web-filler material in cigarette paper are disclosed in commonly-owned U.S. Patent Publication No. 2005/0051185 and U.S. patent application Ser. No. 10/870,449, the contents of which are hereby incorporated by reference. Additional examples of papermaking processes include the method for making banded smoking article wrappers disclosed in commonly-owned U.S. Pat. No. 5,342,484, the entire content of which is herein incorporated by reference, and the method for producing

paper having a plurality of regions of variable basis weight in the cross direction disclosed in commonly-owned U.S. Pat. Nos. 5,474,095 and 5,997,691, the entire contents of which are herein incorporated by reference.

[0062] Catalyst-modified corrugated cigarette paper can be used as a wrapper for conventional cigarettes or non-conventional cigarettes such as cigarettes for electrical smoking systems described in commonly-assigned U.S. Pat. Nos. 6,026,820; 5,988,176; 5,915,387; 5,692,526; 5,692,525; 5,666,976; 5,499,636 and 5,388,594 or non-traditional types of cigarettes having a fuel rod such as are described in commonly-assigned U.S. Pat. No. 5,345,951, the entire contents of which are herein incorporated by reference.

[0063] The catalyst-modified corrugated cigarette paper wrapper is preferably adapted to surround the cut filler to form a tobacco rod. In addition to cellulose, the wrapper material can comprise hemp, kenaf, esparto grass, rice straw and mixtures thereof. Optional filler materials such as flavor additives and burning additives can be included.

[0064] In cigarette manufacture, the tobacco is normally employed in the form of cut filler, i.e., in the form of shreds or strands cut into widths ranging from about 1/10inch to about 1/20inch or even 1/40inch. The lengths of the strands typically range from between about 0.25 inches to about 3.0 inches. The cigarettes may further comprise one or more flavorants or other additives (e.g., burn additives, combustion modifying agents, coloring agents, binders, etc.).

[0065] Any suitable tobacco mixture may be used for the cut filler. Examples of suitable types of tobacco materials include flue cured, Burley, Bright, Maryland or Oriental tobaccos, the rare or specialty tobaccos, and blends thereof. The tobacco material can be provided in the form of tobacco lamina, processed tobacco materials such as volume expanded or puffed tobacco, processed tobacco stems such as cut-rolled or cut-puffed stems, reconstituted tobacco materials, or blends thereof. The tobacco can also include tobacco substitutes.

[0066] A method of making a cigarette comprising a catalyst-modified corrugated cigarette paper wrapper comprises (i) optionally supporting catalyst particles on a web-filler material to form a catalyst-modified web-filler, (ii) incorporating catalyst particles and/or catalyst-modified web-filler in cigarette paper to form catalytic cigarette paper, (iii) forming corrugations in cigarette paper to form a corrugated cigarette paper, (iv) providing cut filler comprising tobacco to a cigarette making machine; and (v) placing the corrugated cigarette paper around the cut filler to form a tobacco rod portion of the cigarette.

[0067] During the smoking of a cigarette, oxygen diffuses into the cigarette through the lit end and through the paper wrapper, and CO and NO in mainstream smoke flow axially toward the filter end and radially out of the cigarette through the paper wrapper. After a typical 2-second puff, CO and NO are concentrated in the periphery of the cigarette, i.e., proximate to the cigarette wrapper, in front of the burn zone. The oxygen concentration is high in the same region as high CO and NO concentrations due to diffusion of O_2 into the cigarette. Airflow into the tobacco rod is largest near the burn zone at the periphery of the cigarette and is approximately proportional to the gradient of temperature, e.g., larger airflow is associated with higher temperature gradients.

[0068] In a typical cigarette, the temperature varies from about 850-900° C. near the periphery of the cigarette at the burn zone to about 300° C. near the center of the cigarette. The temperature drops further to near ambient temperature at the filter end. The temperature gradient at the lit end is very large and within a few of mm in the axial direction of the burn zone, the temperature drops from about 900° C. to about 200° C. Further information on airflow patterns, the formation of constituents in cigarettes during smoking and smoke formation and delivery can be found in Richard R. Baker, "Mechanism of Smoke Formation and Delivery", Recent Advances in Tobacco Science, vol. 6, pp. 184-224, (1980) and Richard R. Baker, "Variation of the Gas Formation Regions within a Cigarette Combustion Coal during the Smoking Cycle", Beiträge zur Tabakforschung International, vol. 11, no. 1, pp. 1-17, (1981), the contents of both are incorporated herein by reference.

[0069] The loading (e.g., amount), type (e.g., composition, size, shape, etc.) and distribution (e.g., homogeneous or heterogeneous) of catalyst particles in the catalyst-modified corrugated cigarette paper wrapper can be selected as a function of the temperature and airflow characteristics exhibited in a burning cigarette in order to adjust, i.e., increase, decrease, minimize or maximize, the conversion rate of CO to CO_2 and/or the conversion rate of NO to N_2.

[0070] The catalyst-modified corrugated cigarette paper wrapper can comprise one or more different kinds of catalyst particles. Low temperature and even room temperature catalysts can extend the effective region of the reaction zone for CO to $C0_2$ and/or NO to N_2 conversion to any desired length along the cigarette.

[0071] Catalyst-modified corrugated cigarette paper wrappers can be selected to operate in a given temperature range or in a plurality of temperature ranges, and the wrapper can be manufactured such that certain catalyst particles are incorporated into those portions of the wrapper that are predicted to coincide with the appropriate temperature for operation of the catalyst. Methods for selectively incorporating catalyst particles in different regions of a cigarette paper web and for incorporating different catalyst particles in a cigarette paper web are disclosed in co-pending, commonly-owned U.S. Patent Publication No. 2005/0051185, the content of which is hereby incorporated by reference.

[0072] Although the catalyst is described as having an operating temperature, the terminology operating temperature refers to the preferred temperature for conversion of CO to $C0_2$ and/or NO to N_2. The catalyst may convert CO and/or NO outside the described temperature range, but the conversion rate may be affected.

[0073] In any of the examples described herein, the catalyst particles can be distributed homogeneously or non-homogeneously within a catalyst-modified corrugated cigarette paper wrapper.

[0074] In a preferred embodiment, the catalyst particles are incorporated in the catalyst paper in an amount effective to convert at least 25% of carbon monoxide to carbon dioxide and at least 25% of nitric oxide to nitrogen at a temperature of less than 400° C. More preferably, the catalyst particles can convert at least 50% of carbon monoxide and at least 50% of nitric oxide at a temperature of less than 400° C.

[0075] Any of the wrappers, cigarettes or methods described herein can include additional additives conventionally used in wrappers for cigarettes. These additives can include, for example, additives to control the appearance, e.g., color, of the wrapper, additives to control the burn rate of the wrapper, and/or additives to result in a desired ash appearance.

[0076] The catalyst-modified corrugated cigarette paper wrapper can be effective to (1) reduce the concentration in mainstream smoke and/or sidestream smoke of carbon monoxide and/or nitric oxide; (2) decrease particle entrainment in mainstream smoke because the catalyst particles are embedded in or adhered to the wrapper and/or web-filler; (3) increase the catalytic, oxidative and/or reduction efficiency of the catalyst particles; and/or (4) increase the mechanical integrity of the wrapper.

[0077] The terminology "mainstream" smoke refers to the mixture of gases and particles passing down a tobacco rod and issuing through the filter end, i.e., the amount of smoke issuing or drawn from the mouth end of a cigarette during smoking of the cigarette. Mainstream smoke contains smoke drawn in through both the lighted region and through the cigarette paper wrapper. "Sidestream" smoke is the smoke given off by a cigarette between puffs (i.e., during static burning).

[0078] The terms "comprises" and "comprising" as used herein are taken to specify the presence of stated features, steps, or components; but the use of these terms does not preclude the presence or addition of one or more other features, steps, components, or groups thereof.

[0079] All of the above-mentioned references are herein incorporated by reference in their entirety to the same extent as if each individual reference was specifically and individually indicated to be incorporated herein by reference in its entirety.

[0080] While the invention has been described with reference to preferred embodiments, it is to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the invention as defined by the claims appended hereto.

We claim:

1. A cigarette comprising:

a tobacco rod wrapped in a cigarette wrapper, wherein the cigarette wrapper comprises

a catalyst-modified corrugated cigarette paper wrapper comprises a fibrous web,

an optional web-filler material supported by the fibrous web, and

catalyst particles supported by the fibrous web and/or the web-filler material.

2. The cigarette of claim 1, wherein the catalyst-modified corrugated cigarette paper wrapper

comprises a plurality of channels that run axially along the length of the cigarette; and/or

is formed around a gas permeable inner wrapper.

3. The cigarette of claim 1, wherein the catalyst-modified corrugated cigarette paper wrapper is wrapped by a non-corrugated paper wrapper together forming a composite wrapper.

4. The cigarette of claim 3, wherein the non-corrugated paper wrapper

is substantially free of catalyst particles; or

incorporates catalyst particles on an inner surface of the non-corrugated paper wrapper in an amount effective for reducing the concentration of carbon monoxide and/or nitric oxide in mainstream smoke during smoking of the cigarette.

5. The cigarette of claim 1, wherein the catalyst particles

have an average particle size of less than about 500 nanometer; and/or

comprise a transition metal oxide, a transition metal hydroxide, and/or a transition metal oxyhydroxide.

6. A catalyst-modified corrugated cigarette paper comprising:

a fibrous web;

an optional web-filler material supported by the fibrous web; and

catalyst particles supported by the fibrous web and/or the web-filler material.

7. The catalyst-modified corrugated cigarette paper of claim 6, wherein the catalyst particles

are coated on an exposed surface of the catalyst-modified corrugated cigarette paper; and/or

are supported within the fibrous web of the catalyst-modified corrugated cigarette paper.

8. The catalyst-modified corrugated cigarette paper of claim 6, wherein the catalyst particles have an average particle size of less than about 500 nanometers; or less than about 50 nanometers.

9. The catalyst-modified corrugated cigarette paper of claim 6, wherein the catalyst particles comprise a transition metal oxide, a transition metal hydroxide, a transition metal oxyhydroxide, iron oxide, and/or iron hydroxide.

10. The catalyst-modified corrugated cigarette paper of claim 6, wherein the web filler material is not optional and comprises calcium carbonate.

11. The catalyst-modified corrugated cigarette paper of claim 6 having corrugations that are uniformly spaced at a distance less than their height, from peak to valley.

12. The catalyst-modified corrugated cigarette paper of claim 6, wherein the paper has a permeability of between about 5 and 80 Coresta units.

13. A method of making a cigarette containing a catalyst-modified corrugated cigarette paper wrapper, the method comprising:

(i) optionally supporting catalyst particles on a web-filler material to form a catalyst-modified web-filler;

(ii) incorporating catalyst particles and/or catalyst-modified web-filler in the cigarette paper to form a catalytic cigarette paper;

(iii) forming corrugations in the cigarette paper to form a corrugated cigarette paper;

(iv) providing a cut filler comprising tobacco to a cigarette-making machine; and

(v) placing the corrugated cigarette paper around the cut filler to form a tobacco rod portion of the cigarette.

14. The method of claim 13, wherein the corrugated cigarette paper is a first wrapper and the method further comprises (vi) placing a non-corrugated second wrapper around the first wrapper; or

the corrugated cigarette paper is a second wrapper and the method further comprises (vi) placing a first gas permeable wrapper around the cut filler prior to step (v).

15. The method of claim 14, wherein the second wrapper

is free of catalyst particles; or

incorporates catalyst particles on an inner surface of the second wrapper.

16. The method of claim 13, wherein the catalyst particles comprise nanoscale particles.

17. A method of manufacturing catalyst-modified corrugated cigarette paper, the method comprising:

(i) forming cigarette paper;

(ii) forming corrugations in the cigarette paper; and

(iii) incorporating catalyst particles with the cigarette paper.

18. The method of claim 17, wherein step (ii) precedes step (iii); or step (iii) precedes step (ii).

19. The method of claim 17, wherein the incorporating comprises spraying or printing the catalyst particles on the cigarette paper.

20. The method of claim 17, wherein the steps of forming cigarette paper and incorporating catalyst particles in the cigarette paper comprise:

supplying cellulosic material and catalyst particles to a head box in a forming section of a papermaking machine, the catalyst particles comprising unsupported catalyst particles and/or catalyst modified web-filler;

depositing an aqueous slurry including the cellulosic material and the catalyst particles onto the forming section of the paper-making machine to form a base web with the catalyst particles distributed therein; and

removing water from the base web so as to form a sheet of catalytic paper.

21. The method of claim 17, wherein the steps of forming cigarette paper and incorporating catalyst,particles in the cigarette paper comprise:

supplying cellulosic material to a head box in a forming section of a papermaking machine;

depositing an aqueous slurry including the cellulosic material onto the forming section of the papermaking machine to form a base web;

distributing catalyst particles on the base web; and

removing water from the base web so as to form a sheet of catalyst-modified paper.

22. The method of claim 17, wherein the catalyst particles are supported directly on the paper cigarette.

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