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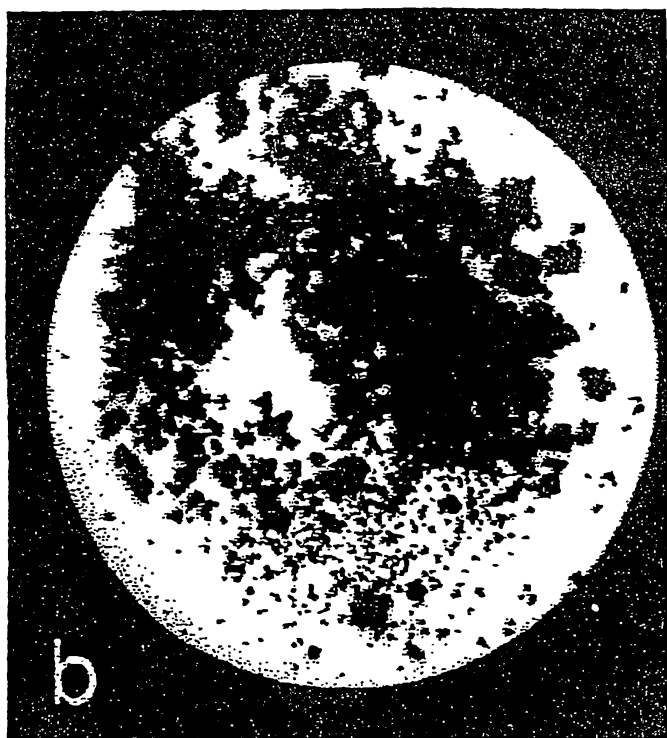
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(54) Title: CIGARETTE COMPONENTS HAVING ENCAPSULATED CATALYST PARTICLES AND METHODS OF MAK-  
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(57) Abstract: Encapsulated catalyst particles  
can be incorporated in tobacco cut filler and/or  
cigarette paper used to form a cigarette. The  
encapsulated catalyst particles, which can  
decrease carbon monoxide and/or nitric oxide in  
mainstream tobacco smoke, comprise catalyst  
particles that are encapsulated with a volatile  
coating. During the smoking of a cigarette  
comprising the encapsulated catalyst particles,  
the volatile coating is volatilized to expose an  
active surface of the catalyst particles .



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**CIGARETTE COMPONENTS HAVING ENCAPSULATED CATALYST PARTICLES AND  
METHODS OF MAKING AND USE THEREOF**

**BACKGROUND**

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). The reduction of carbon monoxide and/or nitric oxide in smoke is desirable.

**SUMMARY**

Disclosed are cigarettes and components of cigarettes (e.g., tobacco cut filler and cigarette paper) comprising encapsulated catalyst particles capable of decreasing carbon monoxide and/or nitric oxide in mainstream tobacco smoke, wherein the encapsulated catalyst particles comprise catalyst particles that are at least partially coated with a volatile encapsulant. Preferably, the catalyst particles are fully coated with the volatile encapsulant.

The catalyst particles, which can comprise nanoscale particles, preferably comprise an elemental metal, alloy, oxide and/or oxyhydroxide of at least one element selected from the group consisting of Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Ag, Sn, Ce, Pr, La, Hf, Ta, W, Re, Os, Ir and Au.

Preferred catalyst particles can decrease tobacco smoke constituents, e.g., catalyze the conversion of carbon monoxide to carbon dioxide and/or nitric oxide to nitrogen, oxidize carbon monoxide to carbon dioxide and reduce nitric oxide to nitrogen.

The volatile encapsulant is preferably a wax, a water-soluble polymer or a water insoluble polymer. The volatile encapsulant can comprise a flavor-bearing compound such as menthol, a menthol derivative or a menthol precursor. Preferred volatile encapsulants have a volatilization temperature of between about 40°C and about 350°C or volatilize upon exposure to an atmosphere having a relative humidity of greater than about 5%.

In an embodiment, the volatile encapsulant comprises a first layer (e.g., a flavor-bearing layer) in contact with the catalyst particles and a second layer formed over the first layer.

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In a cigarette comprising the encapsulated catalyst particles, the volatile encapsulant is adapted to volatilize (e.g., thermally or chemically degrade) during the smoking of a cigarette to expose an active surface of the catalyst particles.

In one embodiment, the encapsulated catalyst particles can be incorporated homogeneously or non-homogeneously along the tobacco rod of a cigarette. In a further embodiment, the encapsulated catalyst particles can be incorporated into the paper wrapper or filter of a cigarette. For example, the encapsulated catalyst particles can be incorporated into the first (i.e., inner) layer of a multi-layer wrapper. The encapsulated catalyst particles can be distributed throughout the paper wrapper or printed on a surface of the paper wrapper. A cigarette can comprise a mixture of different encapsulated catalyst particles.

A method of making a cigarette comprises (i) incorporating encapsulated catalyst particles in and/or on at least one of tobacco cut filler and a cigarette wrapper; (ii) providing the tobacco cut filler to a cigarette making machine to form a tobacco column; and (iii) placing the cigarette wrapper around the tobacco column to form a tobacco rod of a cigarette; and (iv) optionally attaching the cigarette filter to the tobacco column using tipping paper. The encapsulated catalyst particles can be incorporated by spraying, dusting or immersion. For example, encapsulated catalyst particles can be incorporated in cigarette paper by spraying or coating the encapsulated catalyst particles onto a wet base web, intermediate web or finished web.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1(a) shows an optical microscope image of as-received NANOCAT iron oxide catalyst particles. Figures 1(b) and 1(c) show optical microscope images of alginate encapsulated NANOCAT iron oxide in the form of particles and fibers, respectively.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Disclosed are cigarette components, cigarettes, and methods for smoking cigarettes having incorporated therein encapsulated catalyst particles. The encapsulated catalyst particles comprise a core of one

or more catalyst particles and a volatile encapsulating layer (*i.e.*, coating) formed around the core. A volatile encapsulating layer can be a protective layer for the catalyst particles at near-ambient temperatures (*e.g.*, during cigarette storage and downstream of the combustion/pyrolysis zone in a lit cigarette), but upon exposure to an elevated temperature, humidity or gas-phase constituents of cigarette smoke the volatile material can volatilize (*e.g.*, thermally or chemically degrade) to expose the underlying catalyst particles.

Encapsulated catalyst particles can be incorporated into one or more components of a cigarette such as tobacco cut filler, cigarette paper and cigarette filter of the cigarette. In cigarettes comprising the encapsulated catalyst particles, the amount of carbon monoxide and/or nitric oxide in mainstream smoke can be reduced. Methods for providing cigarettes comprising encapsulated catalyst particles include encapsulation of the catalyst particles and incorporation of the encapsulated catalyst particles into one or more components used to form a cigarette.

The incorporation of catalyst particles into one or more components of a cigarette has been disclosed in commonly-owned U.S. Patent Publication Nos. 2004/0131859; 2004/0040566 and 2004/0110633, the contents of which are hereby incorporated by reference. Catalyst particles can be incorporated into a cigarette in order to reduce the concentration in mainstream smoke and/or in sidestream smoke of one or more gas-phase constituents (*e.g.*, CO or NO). However, during smoking of a cigarette comprising catalyst particles, semi-volatile or non-volatile combustion products such as tar can form on the catalyst particles. Early deposition of semi-volatile and non-volatile deposits can effectively deactivate the catalyst particles (*e.g.*, by forming a barrier between the catalyst particles and gas-phase constituents and/or by chemically interacting with the catalyst particles). For example, a layer of semi-volatile or non-volatile material can be effectively impervious to gas phase constituents found in mainstream smoke. Furthermore, at elevated temperatures, semi-volatile or non-volatile materials can react with the catalyst particles and diminish their catalytic activity.

Disclosed are encapsulated catalyst particles comprising a volatile coating that is formed directly on an exposed surface (*e.g.*,

a catalytic surface) of the catalyst particles. By volatile is meant that the encapsulating layer preferably has a volatilization temperature that is less than the volatilization temperature of tar or other solid-phase byproducts of tobacco combustion/pyrolysis. Prior to smoking a cigarette comprising the encapsulated catalyst particles, the volatile coating preferably at least partially encapsulates, more preferably fully encapsulates, the catalyst particles. Preferred volatile coatings are volatilized during smoking of a cigarette.

In a cigarette comprising the encapsulated catalyst particles, when the encapsulated catalyst particles are exposed to a temperature that is less than the volatilization temperature of the coating, the volatile coating forms a protective layer upon which semi-volatile and non-volatile materials (e.g., tar) can deposit. Semi-volatile or non-volatile materials can form and deposit on the volatile coating and not on the catalyst particles. When the temperature reaches or exceeds the volatilization temperature of the encapsulant, the volatile coating - as well as any materials formed thereon - can be removed to expose an active surface of the catalyst particles. Thus, an active surface of the catalyst particles can be exposed under smoking conditions (i.e., in advance of the combustion zone) to catalyze and/or oxidize gaseous constituents of mainstream and/or sidestream smoke. Applicants have unexpectedly found that encapsulated catalyst particles that are incorporated into a cigarette have a higher catalytic efficiency during smoking of the cigarette than catalyst particles that are not encapsulated.

In an embodiment, a cigarette comprises encapsulated catalyst particles wherein during smoking of the cigarette the volatile encapsulant is volatilized at a distance of from about 0.1 mm to about 10 mm, preferably from about 0.5 mm to about 2 mm in advance of the charline. As used herein, the "charline" is the line created in a cigarette paper wrapper at the edge of the combustion zone of the cigarette, produced during smoking of the cigarette.

The encapsulating layer is formed from a volatile material that can thermally or chemically degrade. In a first embodiment, the encapsulant material can thermally degrade (e.g., melt, sublime or pyrolyze) upon exposure to a temperature above an ambient temperature, but below about 350°C, preferably below about 200°C to expose a

surface of the catalyst particles to mainstream smoke, sidestream smoke or both. Preferred encapsulant materials thermally degrade at a temperature between about 40°C and about 200°C. In a further embodiment, the encapsulant material can chemically degrade (e.g., dissolve) upon exposure to components of cigarette smoke that are generated during smoking. For example, moisture in mainstream smoke can interact with the encapsulating layer to volatilize the encapsulant material and expose the catalyst particles. Preferred encapsulating layers chemically degrade upon exposure to mainstream smoke or sidestream smoke having a relative humidity of greater than about 5%, more preferably greater than about 20%.

By providing a volatile encapsulating layer, an active catalytic surface of particles that are incorporated into a cigarette (e.g., into tobacco cut filler) can be exposed in advance of the combustion region of a cigarette. The volatile encapsulating layer can minimize physical interaction and chemical reaction between the catalyst particles and non-volatile or semi-volatile combustion and/or pyrolysis products (e.g., tar). For example, high temperature cracking of tar molecules via reaction with the catalyst particles can be minimized.

The catalyst particles, which comprise the core of the encapsulated catalyst particles, can comprise an elemental metal, alloy, oxide and/or an oxyhydroxide of at least one element selected from the group consisting of Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Ag, Sn, Ce, Pr, La, Hf, Ta, W, Re, Os, Ir and Au.

The catalyst particles preferably comprise nanoscale particles. By "nanoscale" is meant that the catalyst particles have an average particle diameter of less than a micron. Preferably, the nanoscale particles have an average particle size of less than about 100 nm, more preferably less than about 50 nm, and most preferably less than about 10 nm.

Preferred catalyst particles comprise oxides and/or oxyhydroxides of iron. For instance, MACH I, Inc., King of Prussia, Pennsylvania, U.S.A. markets Fe<sub>2</sub>O<sub>3</sub> nanoscale particles under the trade names NANOCAT<sup>®</sup> Superfine Iron Oxide (SFIO) and NANOCAT<sup>®</sup> Magnetic Iron Oxide. The NANOCAT<sup>®</sup> Superfine Iron Oxide (SFIO) is amorphous ferric oxide in the

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form of a free flowing powder, with a particle size of about 3 nm, a specific surface area of about 250 m<sup>2</sup>/g, and a bulk density of about 0.05 g/ml. The NANOCAT<sup>®</sup> Superfine Iron Oxide (SFIO) 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<sup>®</sup> Magnetic Iron Oxide is a free flowing powder with a particle size of about 25 nm and a surface area of about 40 m<sup>2</sup>/g. Further preferred catalyst particles comprise oxides and/or oxyhydroxides of manganese, copper or cerium.

The encapsulant, which forms a coating that encapsulates the catalyst particles, can comprise a wax, a water-soluble polymer, a water insoluble polymer or other material capable of volatilizing during the smoking of a cigarette to expose the underlying catalyst particles. Preferred encapsulating materials are non-toxic, easily coated onto catalyst particles, and stable (*e.g.*, thermally and chemically stable) under typical cigarette storage conditions. A preferred encapsulant comprises one or more flavor-bearing compounds.

The encapsulant can comprise a wax. Preferable waxes include thermomelttable materials having a melting temperature of from about 40°C to about 350°C. Exemplary waxes include beeswax, coconut wax, candelilla wax, carnauba wax, montan wax, ouricury wax, paraffin wax, rice wax, or mixtures thereof.

The encapsulant can comprise a water-soluble polymer. Exemplary water-soluble polymers include polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxides, water-soluble polyamides, water soluble polyesters, water soluble celluloses, acrylic acid polymers, or mixtures thereof. Natural and modified water-soluble polymers include starches, dextrans, gums, gelatins, pectin, alginates, gum arabic, or mixtures thereof.

Preferred encapsulants are alginates. Alginates are salts of the long-chain, carbohydrate biopolymer alginic acid, and include sodium alginate, calcium alginate, potassium alginate, and propylene glycol alginate. Though alginic acid is insoluble in water, the salts are hydrocolloids (*i.e.*, they bind or absorb water) and can be formed into a coating.

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Alginates are generally acid stable and heat resistant. Adjusting the concentration of calcium ions, which cause cross-linking, controls gel strength. Combining alginate with other gums, such as pectin, can increase the viscosity.

Alginates can be dispersed in ambient temperature water, though the solubility is typically less as the water temperature decreases. Alginate concentrations above 2 wt.% can be dispersed using high shear mixing to eliminate clumps. High-speed mixers combine high flow with high shear to increase mixing efficiency. A preferred method of forming encapsulated catalyst particles comprising a calcium alginate coating is discussed below.

The encapsulant can comprise a water-insoluble polymer. Exemplary water-insoluble polymers include polyethylene, polypropylene, polyacrylates, polymethacrylates, polymethylmethacrylates, polyvinyl chloride, polyvinylidene chloride, polysaccharides, or mixtures thereof.

The encapsulant can comprise a flavor-bearing compound. Preferred flavor compounds include menthol, menthol derivatives, and menthol precursors. Other suitable flavor compounds include synthetic and natural fragrances, essential oils, alcohols, aldehydes, esters, ethers, ketones, phenols, and mixtures thereof. The flavor compound can be an aromatic compound or a non-aromatic compound.

Catalyst particles can be coated with one or more layers of the same or different volatile encapsulants. For example, multiple coating steps can be used to achieve the desired thickness and/or coverage of a desired encapsulant. In a further example, catalyst particles can be coated with a first volatile coating, and then with a second volatile coating. In a preferred embodiment, the first volatile coating comprises a flavor-bearing compound.

A variety of methods can be used to form the encapsulated catalyst particles. Suitable methods include providing the catalyst particles and forming at least one volatile encapsulating layer over the catalyst particles. The methods include gas phase techniques and liquid phase techniques.

In an exemplary gas phase technique, catalyst particles can be mixed with a liquid phase encapsulant (e.g., solution or neat liquid of a volatile compound) to form a mixture. During the mixing, the

temperature and the amount of agitation can be controlled. For example, catalyst particles and a solution of an encapsulant can be mixed at room temperature and ultrasonicated to form a homogeneous mixture.

A catalyst particle-encapsulant mixture can be dried to form the encapsulated catalyst particles. According to a preferred method, the mixture can be aspirated to form an aerosol comprising catalyst particles coated with the encapsulant. The aerosolization temperature and dispensation rate can be controlled to form solid phase encapsulated catalyst particles (*i.e.*, wherein the encapsulant layer dries to form a solid coating on the catalyst particles).

By way of example, encapsulated catalyst particles comprising 50 wt.% NANOCAT<sup>®</sup> iron oxide particles coated with gum arabic can be prepared by first mixing iron oxide particles (~ 1 g) with gum arabic (~ 1 g) in about 30 ml of de-ionized water under constant agitation to form a uniform suspension of the iron oxide particles. The suspension is aerosolized using a 0.5 mm nozzle at about 170°C whereby the water present in the mixture is evaporated and gum arabic-coated iron oxide particles are formed. Depending on the processing conditions, the encapsulated catalyst particles can be in the form of a powder, granulate or agglomerate. The encapsulated catalyst particles can be in the shape of spheres, spheroids, threads, fibrils, and the like.

In an exemplary liquid phase technique, catalyst particles can be immersed in a liquid phase encapsulant or encapsulant precursor (*e.g.*, solution or neat liquid of a volatile compound) to form a mixture wherein a coating is formed on the catalyst particles. The temperature during the immersion can be controlled and the mixture can optionally be agitated (*e.g.*, stirred). Catalyst particles and an encapsulant can be mixed at room temperature to form the coating. After immersing, the coated catalyst particles can be dried and optionally processed further to form encapsulated catalyst particles. Further processing can comprise cross-linking the encapsulating polymer, such as via an ion exchange reaction.

A method of forming alginate-encapsulated catalyst particles comprises immersing catalyst particles in a solution of an alginate salt to form coated catalyst particles, and then treating the coated catalyst particles to form a cross-linked polymeric alginate coating.

By way of example, encapsulated catalyst particles comprising 50 wt.% NANOCAT<sup>®</sup> iron oxide particles coated with calcium and/or sodium alginate can be prepared by first mixing iron oxide particles (~ 1 g) with a solution of sodium alginate (1 g of sodium alginate in 100 ml of de-ionized water) under constant agitation to form sodium alginate coated iron oxide particles. The mixture is preferably homogenized (e.g., for 30-130 seconds), allowed to sit in air (e.g., for 10-60 minutes), and then re-homogenized (e.g., for 30-130 seconds).

The sodium alginate coating can be at least partially and preferably fully converted (e.g., polymerized) to a calcium alginate coating via an ion exchange reaction. A known volume of the sodium alginate coated iron oxide particles is preferably contacted with a solution comprising a multivalent cation. The solution can comprise an aqueous or a non-aqueous (e.g., alcoholic) solution. In a preferred method, the solution comprises calcium chloride (e.g., 0.1 M aqueous solution of calcium chloride) whereby  $\text{Ca}^{2+}$  is exchanged for  $\text{Na}^{+}$  via an ion exchange reaction that forms a cross-linked volatile calcium alginate shell around the iron oxide particles. Other multivalent cation solutions suitable for forming a cross-linked encapsulating layer can comprise aluminum, manganese, iron, copper, zinc, strontium, silver and barium. The hardness of a cross-linked polymer encapsulant can be controlled by varying the degree of cross-linking. The amount of cross-linking is proportional to the reaction time (i.e., cure time) between the encapsulant and the multivalent cation solution. Other polymers that can be cross-linked via ion exchange include polysaccharides.

In a preferred method, a known volume of the sodium alginate coated iron oxide particles is dispersed drop-wise (e.g., through a syringe such as a 26.5 gauge needle) into a calcium chloride solution. The height and rate of dispensation can be controlled to control the size of the encapsulated particles. Excess calcium chloride solution can be removed (e.g., filtered or decanted) after a pre-set cure time (e.g., up to about 2 hours) and the calcium alginate-coated particles can be washed and dried. Encapsulated catalyst particles comprising at least about 10, 20, 30, 40, 50, 60, 70, 80 or  $90 \pm 5$  wt.% catalyst particles (e.g., iron oxide particles) can be prepared.

Optical micrographs of iron oxide/calcium alginate samples are shown in Figure 1. Figure 1(a) shows an optical micrograph of as-received NANOCAT<sup>®</sup> iron oxide particles. Figure 1(b) shows an optical micrograph of calcium alginate encapsulated iron oxide particles in the form of irregular and spherical particles. Figure 1(c) shows an optical micrograph of calcium alginate encapsulated iron oxide particles in the form of fibrils.

Additional methods for forming encapsulated catalyst particles include polymer-polymer incompatibility (wherein catalyst particles are coated via preferential adsorption of one polymer from a solution of incompatible polymers that are dissolved in a common solvent); fluidized-bed encapsulation and gas phase polymerization.

Encapsulated micron sized catalyst particles can have an average particle size of from about 1 micron or less to about 1000 microns or more. The encapsulated catalyst particles can have an average particle size of 10, 20, 30, 40, 50, 60, 70, 80 or 90 microns  $\pm$  5 microns up to about 100, 200, 300, 400, 500, 600, 700, 800 or 900 microns  $\pm$  50 microns. The encapsulated catalyst particles can comprise individual particles or an agglomerate of coated catalyst particles. Preferred encapsulated catalyst particles have an average particle size of less than 1 micron. Submicron and nanoscale catalyst particles can be encapsulated to form encapsulated catalyst particles having an average particle size of 10, 20, 30, 40, 50, 60, 70, 80 or 90 nm  $\pm$  5 nm up to about 100, 200, 300, 400, 500, 600, 700, 800 or 900 nm  $\pm$  50 nm, depending on the average thickness of the encapsulant.

According to a preferred method, the encapsulated catalyst particles are incorporated in at least one of tobacco cut filler, cigarette paper and cigarette filter that are used to form a cigarette. By incorporating the catalyst particles into one or more components of a cigarette, the amount of carbon monoxide and/or nitric oxide in mainstream smoke during smoking can be reduced.

Preferably, the encapsulated catalyst particles are incorporated in tobacco cut filler, cigarette paper and/or cigarette filter in an amount effective to reduce the concentration in mainstream smoke of carbon monoxide and/or nitric oxide by at least 5% (e.g., by at least 10%, 15%, 20%, 25%, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, 90% or 95%). A preferred amount of the catalyst particles

per cigarette is up to about 200 mg (e.g., 1 mg to 200 mg, 1 mg to 50 mg, or 50 mg to 100 mg). The encapsulated catalyst particles can be incorporated into a cigarette in an amount effective to convert at least 5%, more preferably at least 25%, of the carbon monoxide in mainstream tobacco smoke to carbon dioxide at a temperature of less than  
5 about 200°C and/or convert at least 5%, more preferably at least 25%, of the nitric oxide in mainstream tobacco smoke to nitrogen at a temperature of less than about 200°C.

Disclosed is a method of making a cigarette comprising the steps of (i) incorporating encapsulated catalyst particles in and/or on at least one of tobacco cut  
10 filler, cigarette paper and cigarette filter; (ii) providing the tobacco cut filler to a cigarette making machine to form a tobacco column; (iii) placing the cigarette wrapper around the tobacco column to form a tobacco rod of a cigarette; and (iv) optionally attaching the cigarette filter to the tobacco column using tipping paper.

15 While not wishing to be bound by theory, it is believed that during smoking of a cigarette having encapsulated catalyst particles incorporated therein, CO and/or NO can be catalyzed in the presence of oxygen to reduce the level of CO and/or NO in mainstream and/or sidestream smoke. It is also believed that subsequent to the catalytic reaction, the catalyst particles may oxidize CO in the presence or absence of oxygen  
20 and/or reduce NO to decrease the level of CO and/or NO in the mainstream and/or sidestream smoke. Preferably, the encapsulated catalyst particles can catalyze both the conversion of CO to CO<sub>2</sub> and NO to N<sub>2</sub>.

As used herein, a catalyst is capable of affecting the rate of a chemical reaction,  
25 e.g., a catalyst can increase the rate of oxidation of carbon monoxide to carbon dioxide without participating as a reactant or product of the' reaction. An oxidant is capable of oxidizing a reactant, e.g., by donating oxygen to the reactant, such that the oxidant itself is reduced. A reducing agent is capable of reducing a reactant, e.g., by receiving oxygen from the reactant, such that the reducing agent itself is oxidized.

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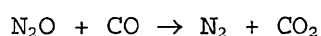
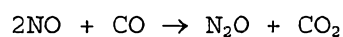
"Smoking" of a cigarette means the heating or combustion of the cigarette to form smoke, which can be drawn through the cigarette. Generally, smoking of a cigarette involves lighting one end of the

cigarette and, while the tobacco contained therein undergoes a combustion reaction, drawing smoke from the combustion through the mouth end of the cigarette. The cigarette may also be smoked by other means. For example, the cigarette may be smoked by heating the cigarette and/or heating using electrical heater means as described in commonly-assigned U.S. Patent Nos. 6,053,176; 5,934,289; 5,591,368 or 5,322,075.

The term "mainstream" smoke refers to the mixture of gases passing down the tobacco rod and issuing through the filter end, *i.e.*, the smoke issuing or drawn from the mouth end of a cigarette during smoking of the cigarette. The mainstream smoke contains smoke that is drawn in through both the lighted region, as well as through the cigarette wrapper. The term "sidestream" smoke refers to smoke produced during static burning.

Several factors contribute to the formation of carbon monoxide and nitric oxide in a cigarette. In addition to the constituents in the tobacco, the temperature and the oxygen concentration in a cigarette during combustion can affect their formation. For example, the total amount of carbon monoxide formed during smoking comes from a combination of three main sources: thermal decomposition (about 30%), combustion (about 36%) and reduction of carbon dioxide with carbonized tobacco (at least 23%). Formation of carbon monoxide from thermal decomposition, which is largely controlled by chemical kinetics, starts at a temperature of about 180°C and finishes at about 1050°C. Formation of carbon monoxide and carbon dioxide during combustion is controlled largely by the diffusion of oxygen to the surface ( $k_a$ ) and via a surface reaction ( $k_b$ ). At 250°C,  $k_a$  and  $k_b$ , are about the same. At 400°C, the reaction becomes diffusion controlled. Finally, the reduction of carbon dioxide with carbonized tobacco or charcoal occurs at temperatures around 390°C and above.

During combustion, nitric oxide is produced in mainstream smoke at a concentration of about 0.5 mg/cigarette. However, nitric oxide can be reduced by carbon monoxide according to the following reactions:



During smoking there are three distinct regions in a cigarette: the combustion zone, the pyrolysis/distillation zone, and the condensation/ filtration zone. The combustion zone is the burning zone of the cigarette produced during smoking of the cigarette, usually at the lighted end of the cigarette. The temperature in the combustion zone ranges from about 700°C to about 950°C, and the heating rate can be as high as 500°C/second. Oxygen is consumed in the combustion of tobacco to produce carbon monoxide, carbon dioxide, nitric oxide, water vapor and other organic compounds (e.g., tar). The combustion zone is highly exothermic and the heat generated is carried to the pyrolysis/distillation zone.

The pyrolysis zone is the region behind the combustion zone, where the temperature ranges from about 200°C to about 600°C. The pyrolysis zone is where most of the carbon monoxide is produced. The major reaction is the pyrolysis (i.e., the thermal degradation) of the tobacco that produces carbon monoxide, carbon dioxide, nitric oxide, charcoal and other smoke components (e.g., tar) using the heat generated in the combustion zone.

In the condensation/filtration zone the temperature ranges from ambient to about 150°C. The major process in this zone is the condensation/filtration of the smoke components. Some amount of carbon monoxide, carbon dioxide, nitric oxide and nitrogen diffuse out of the cigarette and some oxygen (e.g., air) diffuses into the cigarette.

During the smoking of a cigarette, the mainstream smoke flows toward the filter end of the cigarette. As carbon monoxide and nitric oxide travel within the cigarette, oxygen diffuses into and carbon monoxide and nitric oxide diffuse out of the cigarette through the wrapper. After a typical 2-second puff of a cigarette, CO and NO are concentrated in the periphery of the cigarette, i.e., near the cigarette wrapper, in front of the combustion zone. Due to diffusion of O<sub>2</sub> into the cigarette, the oxygen concentration is also high in the peripheral region. Air flow into the tobacco rod is largest near the combustion zone at the periphery of the cigarette and is approximately commensurate with the gradient of temperature, i.e., higher airflow is associated with larger temperature gradients. In a typical cigarette, the highest temperature gradient is from the combustion zone (> 850°C

-900°C) axially toward the filter end of the cigarette. Within a few millimeters behind the combustion zone the temperature drops to near ambient. Further information on air flow 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.

Non-volatile compounds such as tar produced from the combustion and/or pyrolysis of tobacco can coat un-encapsulated catalyst particles and decrease their catalytic efficiency. Non-volatile compounds that form on the surface of encapsulated catalyst particles, however, can be removed by removing the volatile encapsulating layer from the catalyst particles, thereby exposing the catalyst particles to cigarette smoke.

Encapsulated catalyst particles may be provided in the form of a dry powder, paste or dispersion in a liquid. For example, encapsulated catalyst particles can be dusted on, sprayed on, or combined with the cut filler tobacco or cigarette paper. In a further example, tobacco cut filler or cigarette paper material may be rinsed or dip-coated with a liquid containing the encapsulated catalyst particles.

Techniques for cigarette manufacture are known in the art. Any conventional or modified cigarette making technique may be used to incorporate the encapsulated catalyst particles. In production of a cigarette, typically the cut filler composition is optionally combined with other cigarette additives, and provided to a cigarette-making machine to produce a tobacco column, which is then wrapped in cigarette paper to form a tobacco rod that is cut into sections, and optionally tipped with filters. The resulting cigarettes can be manufactured to desired specifications using standard or modified cigarette making techniques and equipment. Cigarettes may range from about 50 mm to about 120 mm in length. The circumference is from about 15 mm to about 30 mm in circumference, and preferably around 25

mm. The tobacco packing density is typically between the range of about 100 mg/cm<sup>3</sup> to about 300 mg/cm<sup>3</sup>, and preferably 150 mg/cm<sup>3</sup> to about 275 mg/cm<sup>3</sup>.

One embodiment provides a method for forming the encapsulated catalyst particles and then depositing the catalyst particles on and/or incorporating them in tobacco cut filler, which is then used to form a cigarette. Tobacco cut filler is normally in the form of shreds or strands cut into widths ranging from about 1/4 cm to about 1/8 cm (about 1/10 inch to about 1/20 inch) or even 1/16 cm (1/40 inch). The lengths of the strands range from between about 0.65 cm to about 7.6 cm (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.).

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.

The encapsulated catalyst particles may be added to cut filler tobacco stock (e.g., loose cut filler) supplied to a cigarette-making machine or incorporated directly on a tobacco rod prior to wrapping a cigarette wrapper around the cigarette rod to form a tobacco column. Preferably the encapsulated catalyst particles are provided continuously along the length of a tobacco rod, though the encapsulated catalyst particles can be provided at discrete locations along the length of a tobacco rod. Thus, the encapsulated catalyst particles may be homogeneously or non-homogeneously distributed along the length of a tobacco rod. For example, a tobacco rod can comprise a first loading of encapsulated catalyst particles at one location along the tobacco rod and a second loading of encapsulated particles at a second location along the tobacco rod. A preferred tobacco rod comprising encapsulated catalyst particles has a first loading of encapsulated catalyst particles at the filter end of the tobacco rod

and a second loading of encapsulated catalyst particles at the distal end of the tobacco rod, wherein the first loading is greater than the second loading.

The encapsulated catalyst particles and tobacco cut filler can be provided in any desired ratio, e.g., 1 wt.% to 90 wt.% encapsulated catalyst particles and 99 wt.% to 10 wt.% tobacco cut filler, more preferably from about 1 wt.% to about 50 wt.% encapsulated catalyst particles, most preferably from about 1 wt.% to about 20 wt.% encapsulated catalyst particles.

In addition to or instead of incorporating the encapsulated catalysts in the tobacco rod, the encapsulated catalyst particles may be incorporated in cigarette paper before or after the cigarette paper is incorporated into a cigarette. The encapsulated catalyst particles can be incorporated into the cellulosic web of the paper by depositing the particles directly on the cellulosic web or on web-filler material that is incorporated in the paper. Encapsulated catalyst particles can be incorporated into cigarette paper and/or into the raw materials used to make cigarette paper (e.g., incorporated into the paper stock of a cigarette paper making machine).

The encapsulated catalyst particles can be incorporated in cigarette paper by spraying or coating the particles onto a wet base (e.g., cellulosic) web, an intermediate web or a finished web. According to one method, encapsulated catalyst particles in the form of a dry powder are physically admixed with the cigarette paper material during the paper manufacturing process. In another method, slurry (e.g., aqueous slurry) of the encapsulated catalyst particles can be incorporated into the head box of a paper-making machine and the encapsulated catalyst particles can be incorporated into cigarette paper during the paper-making process.

The encapsulated catalyst particles and cigarette paper can be provided in any desired ratio, e.g., 1 wt.% to 90 wt.% catalyst and 99 wt.% to 10 wt.% cigarette paper. In a preferred embodiment, the amount of encapsulated catalyst particles comprise from about 1 wt.% to about 50 wt.%, more preferably from about 1 wt.% to about 20 wt.% of the cigarette paper.

The quantity, location and distribution in a cigarette of the encapsulated catalyst particles can be selected as a function of the

temperature and air flow characteristics exhibited during smoking in order to adjust, e.g., increase or maximize the conversion rate of CO to CO<sub>2</sub> and/or NO to N<sub>2</sub>. The amount of the encapsulated catalyst particles incorporated into a cigarette can be selected such that the amount of carbon monoxide and the amount of nitric oxide in mainstream smoke is reduced during smoking of a cigarette.

The encapsulated catalyst particles can be coated and/or printed on at least one surface of a paper wrapper (e.g., an interior and/or exterior surface) to form text or images on the cigarette wrapper. The amount of printing and/or the amount of catalyst can be varied to adjust the amount of CO and/or NO reduction.

The volatile encapsulating layer can be dyed (e.g., with a food dye) to control the appearance of the encapsulated catalyst particles. For example, the color of the encapsulated catalyst particles can be provided to match or contrast with the color of the cigarette paper (or the tobacco cut filler).

A cigarette can comprise a mixture of different encapsulated catalyst particles. The composition of the encapsulated catalyst particles (i.e., the composition and/or size of the catalyst particles and/or the composition and/or thickness of the encapsulant) can be selected to operate in a given temperature range, and a catalytically effective amount of the catalyst particles can be incorporated into a component of a cigarette (e.g., tobacco cut filler, cigarette filter and/or cigarette paper) to control the conversion efficiency and/or selectivity of the catalyst. For example, first encapsulated catalyst particles can be incorporated in the tobacco cut filler of a cigarette and second encapsulated catalyst particles can be incorporated in the cigarette paper. Cigarette paper having encapsulated catalyst particles incorporated therein can be used as paper wrapper, paper filter and/or paper filler within a cigarette.

A cigarette wrapper can be any wrapping suitable for surrounding the cut filler, including wrappers containing flax, hemp, kenaf, esparto grass, rice straw, cellulose and so forth. Optional filler materials, flavor additives, and burning additives can be included in the cigarette wrapper. The wrapper can have more than one layer in cross-section, such as in a bi-layer wrapper as disclosed in commonly-

owned U.S. Patent No. 5,143,098, the entire content of which is herein incorporated by reference.

The encapsulated catalyst particles can be incorporated into a cigarette wrapper. The paper wrapper, which comprises a web of fibrous cellulosic material, can further comprise particles of web-filler material, such as calcium carbonate ( $\text{CaCO}_3$ ). In practice, the web-filler material serves as an agent for controlling the permeability of the wrapper. The permeability of the wrapper is typically 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 drop of 1.0 kilopascals.

The paper wrapper can comprise one or more layers. A preferred cigarette comprises a first wrapper, a second wrapper formed around the first wrapper, and encapsulated catalyst particles incorporated in the first wrapper.

Encapsulated catalyst particles will preferably be distributed throughout the tobacco rod and/or the cigarette wrapper portions of a cigarette. By providing the encapsulated catalyst throughout one or more components of a cigarette it is possible to reduce the amount of carbon monoxide drawn through the cigarette, particularly at the combustion, pyrolysis, condensation and/or filter regions.

A further embodiment provides a method of treating tobacco smoke comprising lighting a cigarette to form tobacco smoke and drawing the smoke through the cigarette, wherein the volatile encapsulant at least partially volatilizes to expose a surface of the catalyst particles. In a preferred embodiment, the volatile encapsulant is volatilized at a distance of from about 0.1 mm to 10 mm in advance of the charline.

While various embodiments have been described, 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 claims appended hereto.

The claims defining the invention are as follows:

1. A component of a cigarette comprising encapsulated catalyst particles capable of decreasing at least one of carbon monoxide and nitric oxide in mainstream tobacco smoke, wherein the catalyst particles are at least partially coated with a volatile encapsulant, and wherein the component is selected from the group consisting of tobacco cut filler, cigarette paper and cigarette filter.
- 5
2. A component according to claim 1, wherein;
- 10 (a) the catalyst particles are fully coated with the volatile encapsulant;
- (b) the catalyst particles comprise at least one of an elemental metal, alloy, oxide and oxyhydroxide of at least one element selected from the group consisting of Mg, Al, Si, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, Y, Zr, Nb, Mo, Ru, Ag, Sn, Ce, Pr, La, Hf, Ta, W, Re, Os, Ir and Au;
- 15 (c), the catalyst particles comprise at least one of an oxide and U oxyhydroxide of manganese, iron, copper or cerium;
- (d) the catalyst particles comprise nanoscale particles; or
- (e) the catalyst particles have an average particle size of less than about 100 nm or less than about 50 nm.
- 20
3. A component according to claim 1, wherein the volatile encapsulant comprises at least one of:
- (a) a wax, a water-soluble polymer or a water insoluble polymer;
- (b) a wax selected from the group consisting of beeswax, coconut wax, candelilla wax, carnauba wax, montan wax, ouricury wax, paraffin wax, rice wax and mixtures thereof;
- 25
- (c) a water-soluble polymer selected from the group consisting of polyvinyl alcohol, polyvinyl pyrrolidone, polyethylene oxides, water-soluble polyamides, water soluble polyesters, water soluble celluloses, acrylic acid polymers, starches, dextrans, gums, gelatins, pectin, alginates, gum arabic and mixtures thereof;
- 30
- (d) a water insoluble polymer selected from the group consisting of polyethylene, polypropylene, polyacrylates, polymethacrylates,

polymethyl-methacrylates, polyvinyl chloride, polyvinylidene chloride, polysaccharides and mixtures thereof.

(e) a first layer in contact with the catalyst particles and a second layer formed over the first layer; and

(f) a first layer comprising a flavor-bearing compound and a second layer formed over the first layer.

4. A component according to claim 1, wherein:

(a) the volatile encapsulant has a volatilization temperature of between about 40°C and about 350°C;

(b) the volatile encapsulant is adapted to volatilize in an atmosphere having a relative humidity of greater than about 5%; or

(c) the volatile encapsulant has a volatilization temperature of between about 40°C and about 350°C and is adapted to volatilize in an atmosphere having a relative humidity of greater than about 5%

5. A component according to claim 1, wherein the volatile encapsulant comprises a flavor-bearing compound.

6. A component according to claim 5, wherein the flavor-bearing compound comprises menthol, a menthol derivative, a menthol precursor, or a mixture thereof.

7. A component according to claim 5, wherein the flavor-bearing compound comprises a synthetic fragrance, a natural fragrance, an essential oil, an aldehyde, an alcohol, an ester, a ketone, a phenol or mixture thereof.

8. A component according to claim 1, wherein the catalyst particles are capable of acting as an oxidant for the conversion of carbon monoxide to carbon dioxide a reducing agent for the conversion of nitric oxide to nitrogen and as a catalyst for the conversion of at least one of carbon monoxide to carbon dioxide and nitric oxide to nitrogen.

9. A cigarette comprising a tobacco rod, cigarette paper and an optional filter, wherein at least one of the tobacco rod, cigarette

paper and filter comprise encapsulated catalyst particles capable of decreasing at least one of carbon monoxide and nitric oxide in mainstream tobacco smoke, wherein the catalyst particles are at least partially coated with a volatile encapsulant.

10. A cigarette according to claim 9, wherein:

(a) the volatile encapsulant is adapted to volatilize during the smoking of a cigarette to expose an active surface of the catalyst particles;

(b) the volatile encapsulant is adapted to thermally or chemically degrade during the smoking of the cigarette to expose a surface of the catalyst particles; or

(c) the volatile encapsulant is adapted to volatilize and thermally or chemically degrade during the smoking of the cigarette to expose a surface of the catalyst particles.

11. A cigarette according to claim 9, wherein the catalyst particles are fully coated with the volatile encapsulant.

12. A cigarette according to claim 9, wherein the encapsulated catalyst particles are at least one of:

(a) incorporated in an amount effective to convert at least 5% of the carbon monoxide in mainstream tobacco smoke to carbon dioxide or at least 5% of the nitric oxide in mainstream tobacco smoke to nitrogen or in an amount effective to convert at least 5% of the carbon monoxide in mainstream tobacco smoke to carbon dioxide and at least 5% of the nitric oxide in mainstream tobacco smoke to nitrogen;

(b) incorporated in a total amount of up to about 200 mg per cigarette; and

(c) homogeneously or non-homogeneously distributed along the length of a tobacco rod.

13. A cigarette according to claim 9, wherein the cigarette paper comprises at least one of:

(a) a wrapper having a first layer and a second layer formed around the first layer, and wherein the encapsulated catalyst particles are incorporated in the first layer; and

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(b) a wrapper and the encapsulated catalyst particles are coated, printed or coated and printed on at least one surface of the wrapper.

14. A cigarette according to claim 9, wherein the cigarette comprises a mixture of different encapsulated catalyst particles.

15. A method of making a cigarette comprising:

(i) incorporating encapsulated catalyst particles in, on, or in and on at least one of tobacco cut filler, cigarette filter and a cigarette wrapper;

(ii) providing the tobacco cut filler to a cigarette making machine to form a tobacco column;

(iii) placing the cigarette wrapper around the tobacco column to form a tobacco rod of a cigarette; and

(iv) optionally attaching the cigarette filter to the tobacco column using tipping paper.

16. A method according to claim 15, wherein the incorporating comprises spraying, dusting or immersion.

17. A method according to claim 15, wherein the encapsulated catalyst particles are incorporated in the cigarette paper by spraying or coating the encapsulated catalyst particles onto a wet base web, intermediate web or finished web.

18. A method according to claim 15, wherein the step of incorporating comprises combining the encapsulated catalyst particles and at least one of the tobacco cut filler and cigarette wrapper in the absence of a liquid.

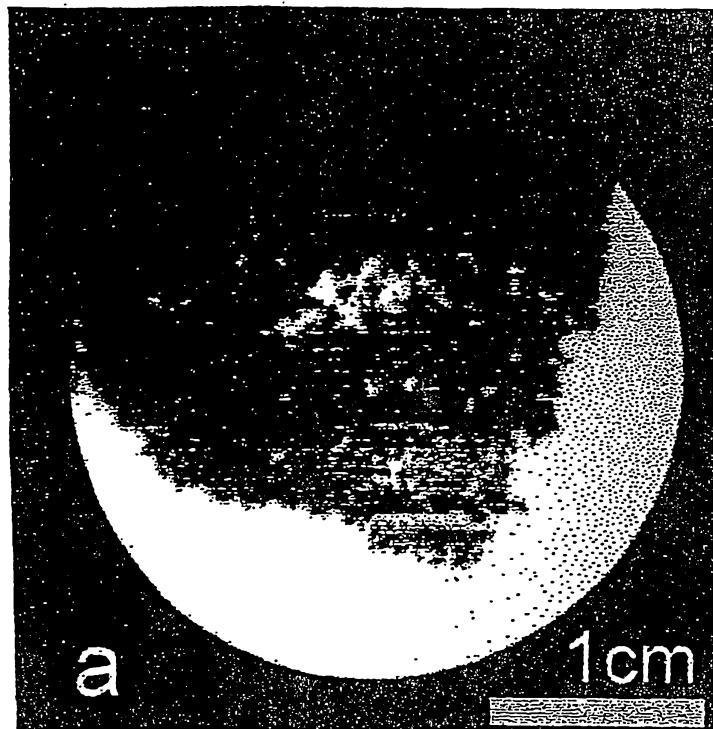


FIG. 1A

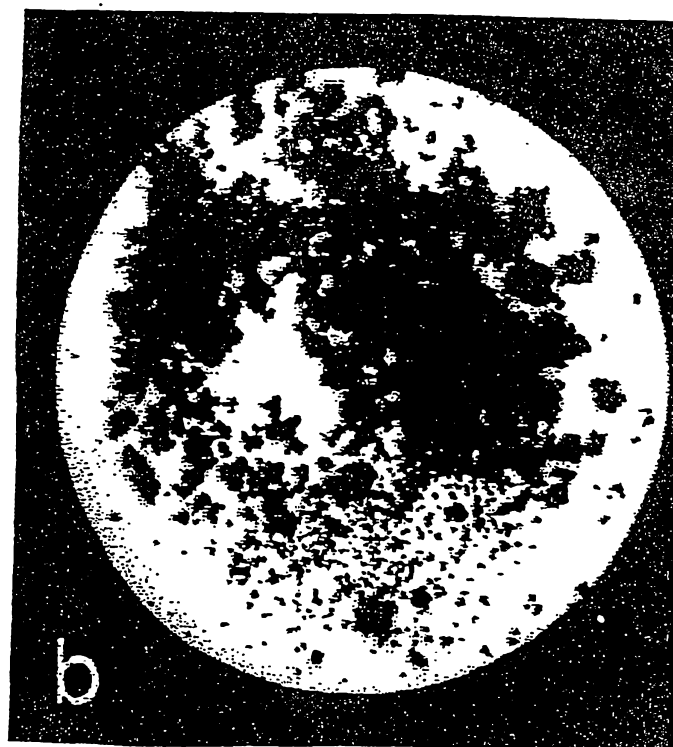


FIG.1B

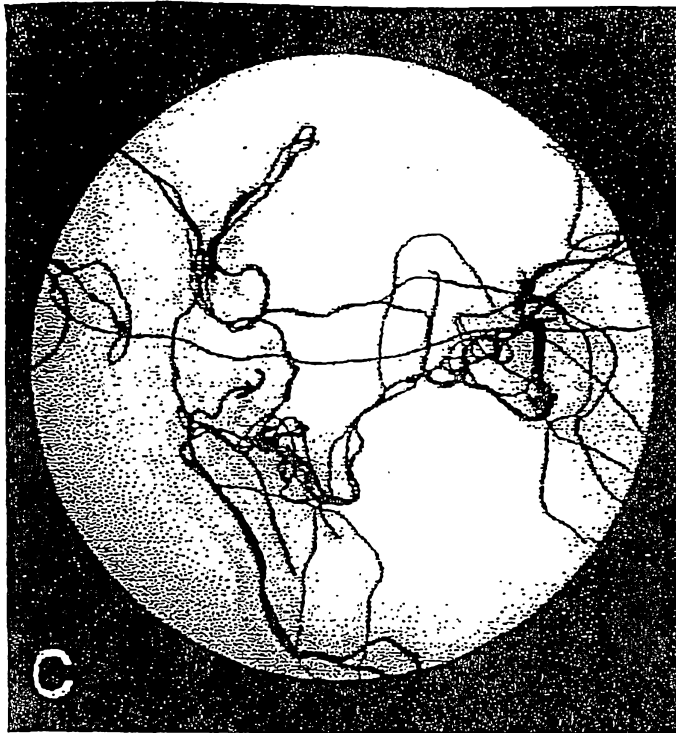


FIG. 1C