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(54) **Low sidestream smoke cigarette with combustible paper having modified ash characteristics**

(57) A low sidestream smoke cigarette comprises a  
conventional tobacco rod (54), and a combustible treat-  
ment paper (56, 58) having a sidestream smoke treat-  
ment composition. The treatment composition comprises  
in combination, an oxygen storage and donor metal oxide  
oxidation catalyst and an essentially non-combustible

particulate adjunct for said catalyst. Improvements are  
made in the treatment composition and/or the addition  
of metal oxides or carbonates thereto to improve ash  
characteristics.

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## Description

### FIELD OF THE INVENTION

**[0001]** The invention relates to sidestream smoke reduction in burning cigarettes and other smoking products. More particularly, the invention relates to cigarette paper, cigarette wrapper, or a wrapper for a cigar or other like tobacco products for reducing visible sidestream smoke while providing a modified ash.

### BACKGROUND OF THE INVENTION

**[0002]** Various attempts have been made to reduce or eliminate sidestream smoke emanating from a burning cigarette. The applicant developed various approaches to cigarette sidestream smoke control systems as described in its Canadian patents 2,054,735 and 2,057,962; U.S. patents 5,462,073 and 5,709,228 and published PCT applications WO 96/22031; WO 98/16125 and WO 99/53778.

**[0003]** Other sidestream smoke control systems have been developed which use filter material or adsorptive material in the tobacco, filter or paper wrapper. Examples of these systems are described in U.S. Patents 2,755,207, 4,108,151 and 4,225,636; EP patent applications 0 740 907 and 0 251 254; and WO 97/27831 and WO 99/53778. U.S. Patent 2,755,207 describes a low sidestream smoke cigarette paper. The cigarette paper on burning yields a smoke substantially free of obnoxious components. The cigarette paper is cellulosic material in fibre form. It has intimately associated therewith a finely divided mineral type siliceous catalyst material. The cigarette paper which is essentially non-combustible and refractory remains substantially unchanged during combustion of the cigarette paper and functions like a catalyst in modifying the combustion of the paper. Suitable siliceous catalysts include acid-treated clays, heat-treated montmorillonite and natural and synthetic silicates containing some hydrogen atoms which are relatively mobile. Suitable mixed silica oxides include silica oxides with alumina, zirconia, titania, chromium oxide and magnesium oxide. Other silicas include the oxides of silicon and aluminum in a weight ratio of 9:1 of silica to alumina.

**[0004]** U.S. Patent 4,108,151 describes the use of a gamma alumina filler for cigarette paper which selectively reduces the organic vapor phase constituents in tobacco smoke. There is at least 50% by weight of alumina filler in the cigarette paper for reducing the organic vapor phase constituents in a tobacco smoke. As a result there is a reduction in the visible sidestream smoke emanating from a burning cigarette. The gamma alumina is most commonly known as activated alumina which is finely pulverized to pass through a 300-mesh screen.

**[0005]** U.S. Patent 4,225,636 describes the use of carbon in the cigarette paper to reduce organic vapour phase components and total particulate matter found in sidestream smoke. In addition, the carbon results in a sub-

stantial reduction in visible sidestream smoke emitting from a burning cigarette. Activated carbon is preferred as the carbon source. The use of the activated carbon results in a slight drop in visible sidestream smoke. Up to 50% of the cigarette paper may be finely divided carbon. The carbon-coated papers may be used as the inner wrap for the tobacco rod in combination with a conventional cigarette.

**[0006]** European patent application 0 740 907 published November 6, 1996 describes the use of zeolites in the tobacco of the cigarette to alter the characteristics of the mainstream smoke and in particular remove various components from the mainstream smoke such as some of the tars. The zeolite as provided in the tobacco, also apparently change the characteristics of the sidestream smoke. The zeolites used were of a particle size between 0.5 mm to 1.2 mm.

**[0007]** European application 0 251 254 describes the use of a high superficial surface area filler in cigarette paper. The fillers are generally crystals and solids having surface areas of at least 20 m<sup>2</sup>/g. The fillers are preferably, peroxides, carbonates, phosphates, sulphates, aluminates and silicates. It is taught that porous fillers such as zeolites are not preferred in cigarette paper and are taught as functioning similarly to conventional chalk.

**[0008]** Published PCT patent application WO 97/27831 describes the use of a dealuminated zeolite for absorbing nonpolar or weakly polar molecules from a polar liquid or gas. Effective amounts of the powdered dealuminated zeolite may be incorporated in cigarette paper to reduce the carbon monoxide in sidestream smoke. The step of dealuminating aluminous zeolite renders the zeolite hydrophobic so as to affect absorption and removal of the nonpolar and weakly polar molecules which even happens in the presence of water.

**[0009]** Published PCT patent application WO 99/53778 describes a non-combustible sheet of treatment material for reducing sidestream smoke emissions. The sheet is used as a wrap and is applied over conventional cigarette paper of a conventional cigarette. The wrap has a very high porosity to allow the cigarette to burn at or close to conventional free-burn rates while at the same time reduce visible sidestream smoke emissions. The non-combustible wrap includes non-combustible ceramic fibres, non-combustible activated carbon fibres as well as other standard materials used in making the wrap. The wrap also includes zeolites or other similar sorptive materials and an oxygen donor/oxygen storage metal oxide oxidation catalyst. The non-combustible wrap provides an acceptable degree of sidestream smoke control, however, due to the non-combustible nature of the wrap, a charred tube remains.

**[0010]** U.S. Patents 4,433,697 and 4,915,117 describe the incorporation of ceramic fibres in a cigarette paper manufacture. U.S. Patent 4,433,697 describes at least 1% by weight of certain ceramic fibres in the paper furnish in combination with magnesium oxide and/or magnesium hydroxide fillers to reduce visible sidestream smoke em-

anating from the burning cigarette. The furnish of fibre pulp, ceramic fibres and fillers are used to make a paper sheet on conventional paper making machines. The ceramic fibres may be selected from the group of polycrystalline alumina, aluminum-silicate and amorphous alumina. A filler of magnesium hydroxide or magnesium oxide is used and is coated on or applied to the fibres of the sheet.

**[0011]** Ito, U.S. Patent 4,915,117 describes a non-combustible sheet for holding tobacco. The thin sheet is formed from ceramic materials which upon burning produces no smoke. The ceramic sheet comprises a woven or non-woven fabric of ceramic fibre or a mixture of paper and ceramics thermally decomposed at high temperature. The ceramic fibre may be selected from inorganic fibres such as silica fibre, silica-alumina fibre, alumina fibre, zirconia fibre, or alumino borosilicate and glass fibre. The ceramic sheet is formed by binding these materials by inorganic binders such as silica gel or alumina gel. The fibres are preferably 1 to 10 micrometers in diameter.

**[0012]** Published PCT patent application WO 01/41590 describes the use of ceramic materials in cigarette wrappers to reduce sidestream smoke. The ceramic filler which is incorporated in the cigarette wrapper using a binder has particle size in range of 2-90  $\mu\text{m}$ . The ceramic filler is of a predefined shape which is spherical or substantially spherical, oval or substantially oval or another irregular shape approximating thereto. The ceramic filler may be alumina, silica, an alumino-silicate, silicon carbide, stabilised or un-stabilised zirconium oxide, zircon, garnet, feldspar and the like. The ceramic filler is provided in the cigarette wrapper at greater than 40% by weight of the dry materials in the slurry that is used to produce the wrapper. The binder may be an alginate, a gum, cellulose, pectin, starch or Group I or II metal salts of these binders. The resultant wrapper has a porosity usually less than 200 Coresta Units and is preferably in the range of 2-100 Coresta Units. The wrapper has a density of 0.5-3.0  $\text{g}/\text{cm}^3$ . The wrapper is preferably used as an overwrap for a porous non-smokeable plugwrap tobacco rod having porosities of about 12,000 Coresta Units.

**[0013]** Sol gels have been applied to conventional cigarette paper in order to reduce sidestream smoke, particularly sol gels made from a magnesium aluminate, calcium aluminate, titania, zirconia and aluminum oxide, as described in Canadian Patent 1,180,968 and Canadian Patent application 2,010,575. Canadian Patent 1,180,968 describes the application of magnesium hydroxide in the form of an amorphous gel as a cigarette paper filler component to improve ash appearance and sidestream smoke reduction. The magnesium hydroxide gel is coated on or applied to the fibres of the sheet of the cigarette paper. Canadian patent application 2,010,575 describes the use of gels produced by a solution gelation or sol-gel process for controlling the combustion of wrappers for smoking articles. The gels may

be applied as coatings to paper fibres before the paper is formed into wrappers. The wrappers are useful for reducing visible sidestream smoke. The metal oxides for the sol gels may be oxides of aluminum, titanium, zirconium, sodium, potassium or calcium.

**[0014]** Published German patent application DE 3508 127 describes a novelty type cigarette which produces a shower of sparks when smoked. This is achieved by incorporating a granular misch metal in the form of cerium ferrite or silico-cerium in the cigarette paper. When the cigarette is smoked particularly in dark spaces the burning cigarette gives off sparks along with a bright light effect. The cerium ferrite particles incorporated in the cigarette paper usually have a particle size of about 20  $\mu\text{m}$ .

**[0015]** Catalysts have also been directly applied to cigarette paper, such as described in Canadian Patent 604,895 and U.S. Patent 5,386,838. Canadian Patent 604,895 describes the use of platinum, osmium, iridium, palladium, rhodium and ruthenium in the cigarette paper. These metals function as oxidation catalysts to treat vapours arising from combustion of the paper wrapper. Optimum catalytic effect has been provided by the metal palladium. The metal particles in a suitable medium are dispersed onto the face of a paper wrapper before it is applied to the cigarette.

**[0016]** U.S. Patent 5,386,838 describes the use of a sol solution comprising a mixture of iron and magnesium as a smoke suppressive composition. The smoke suppressive composition is made by co-precipitating iron and magnesium from an aqueous solution in the presence of a base. The iron magnesium composition demonstrates high surface area of approximately 100  $\text{m}^2/\text{g}$  to approximately 225  $\text{m}^2/\text{g}$  when heated to a temperature between 100°C and approximately 500°C. The iron magnesium composition may be added to paper pulp which is used to make smoke suppressive cigarette paper. The iron magnesium composition apparently functions as an oxidation catalyst and reduces the amount of smoke produced by the burning cigarette. The catalyst may also be applied to the tobacco, for example, as described in U.S. Patent 4,248,251, palladium, either in metallic form or as a salt, may be applied to the tobacco. The presence of palladium in tobacco reduces the polycyclic aromatic hydrocarbons in the mainstream smoke. Palladium is used in combination with an inorganic salt or nitric or nitrous acid. Such nitrates include lithium, sodium, potassium, rubidium, cesium, magnesium, calcium, strontium, lanthanum, cerium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, erbium, scandium, manganese, iron, rhodium, palladium, copper, zinc, aluminum, gallium, tin, bismuth, hydrates thereof and mixtures thereof. Catalysts have also been used in tubes to reduce sidestream smoke such as described in published PCT application WO 98/16125.

**[0017]** U.S. patent 6 228 799 describes a composition comprising cerium oxide and zirconium oxide in particulate form and having a high surface area usually in excess of 35  $\text{m}^2/\text{g}$ . The composition is made by co-precipitating

cerium and zirconium species from a solution at an elevated temperature, which is then separated and dried at temperatures between 80-300° C and then calcined at temperatures between 200 and 1,200° C.

**[0018]** Catalytic materials have been used in aerosol types of cigarettes which do not produce sidestream or mainstream smoke per se, but instead a flavoured aerosol. Examples of these aerosol cigarettes include those described in U.S. patents 5,040,551, 5,137,034 and 5,944,025, which use catalysts to provide the necessary heat generation to develop the aerosol. Such catalyst systems include oxides of cerium, palladium or platinum.

**[0019]** A variety of sidestream smoke control systems have been contemplated in the prior art but none of them contemplate a combustible cigarette paper which burns like a normal cigarette without appreciably affecting cigarette taste and has an acceptable ash.

# STATEMENTS OF INVENTION

**[0020]** According to a first aspect of the invention there is provided, a low sidestream smoke cigarette having a conventional tobacco rod and a combustible treatment paper, said treatment paper having a sidestream smoke treatment composition comprising an oxygen storage and donor metal oxide oxidation catalyst and an essentially non-combustible finely divided particulate adjunct for said catalyst, the improvement comprising the use of a solid solution of particulate mixed metal oxides as said catalyst and said adjunct.

**[0021]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst for the solid solution being selected from the group consisting of lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide and mixtures thereof.

**[0022]** Preferably, said adjunct is selected from the group of metal oxides consisting of zirconium oxide, aluminum oxide, magnesium oxides, titanium oxide and mixtures thereof.

**[0023]** Preferably, said solid solution of mixed metal oxides further comprising an oxidation catalyst selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof.

**[0024]** Preferably, said solid solution of mixed metal oxides being selected from the group consisting of cerium/lanthanum mixed oxide, cerium/zirconium mixed oxide, cerium/zirconium/lanthanum mixed oxide, cerium/zirconium/praseodymium mixed oxide, cerium/zirconium/lanthanum/praseodymium mixed oxide, cerium/zirconium/neodymium mixed oxide and mixtures thereof.

**[0025]** Preferably, said solid solution being a high surface area porous particulate.

**[0026]** Preferably, said solid solution being a low surface area particulate.

**[0027]** Preferably, said catalyst and said adjunct is said high surface area cerium/zirconium mixed oxide.

**[0028]** Preferably, said catalyst selected from the

group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof is either included in said solid solution of cerium/zirconium mixed oxide or is applied to the surface of said high surface area cerium/zirconium mixed oxide.

**[0029]** Preferably, said cerium/zirconium mixed oxide has a particle size greater than about 1  $\mu\text{m}$ .

**[0030]** Preferably, said cerium/zirconium mixed oxide has a particle size less than about 30  $\mu\text{m}$ .

**[0031]** Preferably, said cerium/zirconium mixed oxide have a ratio ranging from about 5: 95 to about 95: 5.

**[0032]** Preferably, said ratio is about 75: 25 and said particle size is about 6  $\mu\text{m}$  to 10  $\mu\text{m}$ .

**[0033]** Preferably, said treatment composition is incorporated within said treatment paper at a loading rate of about 2.5 g/m<sup>2</sup> to about 125 g/m<sup>2</sup>.

**[0034]** Preferably, said treatment composition is coated on said treatment paper.

**[0035]** Preferably, said treatment composition includes particulate zirconium oxide, titanium oxide, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof.

**[0036]** Preferably, said treatment composition includes particulate zeolite.

**[0037]** Preferably, said zeolite is a carrier for an oxidation catalyst selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide, and mixtures thereof.

**[0038]** Preferably, said treatment composition includes zirconium oxide.

**[0039]** According to a second aspect of the invention there is provided a low sidestream smoke cigarette comprising a conventional tobacco rod and a combustible treatment paper having a sidestream smoke treatment composition, said treatment composition comprising an oxygen storage and donor metal oxide oxidation catalyst, an essentially non-combustible particulate adjunct for said catalyst and a metal oxide or carbonate for modifying ash characteristics.

**[0040]** Preferably, said adjunct is a high surface area particulate.

**[0041]** Preferably, said particulate adjunct is a zeolite based material ranging from about 0.1% by weight of total dry weight composition to about 60% by weight of total dry weight composition and preferably less than 25% by weight and most preferably less than 15% by weight.

**[0042]** Preferably, said ash modifying metal oxide or carbonate is selected from the group consisting of zirconium oxide, titanium oxide, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof.

**[0043]** Preferably, said adjunct is a support for a ceria sol to be applied thereto and dried.

**[0044]** Preferably, said adjunct is high surface area ce-

rium oxide.

**[0045]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst is selected from a group consisting of transition metal oxides, rare earth metal oxides and mixtures thereof.

**[0046]** Preferably, said transition metal oxides are selected from the group consisting of oxides of group IVB, VB, VIB, VIIB, VIIIB, IB metals and mixtures thereof.

**[0047]** Preferably, said rare earth metal oxide is selected from the group consisting of oxides consisting of scandium, yttrium and lanthanide metals and mixtures thereof.

**[0048]** Preferably, said lanthanide metals oxide are selected from the group consisting of lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide and mixtures thereof.

**[0049]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst and adjunct therefor is a solid solution of mixed metal oxides where the adjuncts are selected from the group consisting of zirconium oxide, aluminium oxide, magnesium oxide, titanium oxide and mixtures thereof.

**[0050]** Preferably, said solid solution of mixed metal oxides comprises a catalyst selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide.

**[0051]** Preferably, said solid solution of mixed metal oxides includes cerium/lanthanum mixed oxides, cerium/zirconium mixed oxides, cerium/aluminum mixed oxides, cerium/magnesium mixed oxides, cerium/titanium mixed oxides, cerium/zirconium/lanthanum mixed oxides, cerium/lanthanum mixed oxide, cerium/zirconium mixed oxide, cerium/zirconium/lanthanum mixed oxide, cerium/zirconium/praseodymium mixed oxide, cerium/zirconium/lanthanum/praseodymium mixed oxide, cerium/zirconium/neodymium mixed oxide.

**[0052]** Preferably, said adjunct is selected from the group consisting of clays essentially non-combustible mill fibers, monolithic mineral base materials, essentially non-combustible carbon, zeolites and mixtures thereof.

**[0053]** Preferably, said adjuncts are selected from the group consisting of zirconium oxide, titanium oxide, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof, metal oxide fibers and milled porous ceramic fibers and mixtures thereof.

**[0054]** Preferably, said solid solution being a high surface area porous particulate.

**[0055]** Preferably, said solid solution being a low surface area particulate.

**[0056]** Preferably, said ash modifying particulate is zirconium oxide.

**[0057]** Preferably, an oxidation catalyst is used with said oxygen storage and donor metal oxide oxidation catalyst, said oxidation catalyst being selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide, and mix-

tures thereof.

**[0058]** Preferably, said zeolite is a Y-type zeolite, ZSM-5 type zeolite or Beta type zeolite.

**[0059]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst is a porous particulate solid solution of cerium/zirconium which is preferably a mixed oxide high surface area material.

**[0060]** Preferably, zirconium oxide and/or a zeolite are used in combination with said cerium/zirconium mixed oxide.

**[0061]** Preferably, an oxidation catalyst is used with said cerium/zirconium metal oxide, zirconium oxide and/or zeolite.

**[0062]** Preferably, said oxidation catalyst is selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide, and mixtures thereof, said selected oxidation catalyst being either incorporated in said solid solution of cerium/zirconium mixed oxide or applied to surfaces of particulate cerium/zirconium mixed oxide, zirconium oxide and/or zeolite.

**[0063]** Preferably, said zeolite is a Y-type zeolite.

**[0064]** Preferably, said treatment composition is applied as a coating to cigarette paper, said coating composition including a metal oxide or carbonate selected from the group consisting of zirconium oxide, titanium oxide, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof.

**[0065]** Preferably, said combustible treatment paper comprises an inner sheet and an outer sheet, said inner sheet comprises said treatment composition for reducing sidestream smoke, said outer layer comprising a treatment composition for modifying ash characteristics.

**[0066]** Preferably, said inner paper has greater than 35% by weight of a zeolite material.

**[0067]** Preferably, said inner paper and outer paper have said treatment composition coated, incorporated or impregnated thereon or therein.

**[0068]** Preferably, said inner paper has said sidestream smoke reduction composition incorporated therein.

**[0069]** Preferably, said inner paper has said sidestream smoke reduction composition coated thereon.

**[0070]** Preferably, said inner paper has said sidestream smoke reduction composition incorporated and coated thereon.

**[0071]** Preferably, said outer paper has said sidestream smoke reduction composition incorporated thereon.

**[0072]** Preferably, said outer paper has said sidestream smoke reduction composition coated thereon.

**[0073]** Preferably, said outer paper has said sidestream smoke reduction composition incorporated and coated thereon.

**[0074]** Preferably, said inner paper comprising an oxygen storage and donor metal oxide oxidation catalyst

with adjunct and a high surface area adsorptive material, the outer layer comprising an oxygen storage and donor metal oxide oxidation catalyst with adjunct and metal oxide for modifying ash characteristics.

**[0075]** Preferably, said treatment composition for reducing sidestream smoke and said treatment composition for modifying ash are applied as a coatings respectively to said inner sheet and said outer sheet.

**[0076]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst is a porous particulate high surface area solid solution cerium/zirconium mixed oxide.

**[0077]** Preferably, said cerium oxide and said zirconium oxide in said solid solution are in a ratio of about 5: 95 to about 95: 5.

**[0078]** Preferably, said coating is applied to said inner and outer sheets on either or both sides of each of said sheets.

**[0079]** According to a third aspect of the invention there is provided a low sidestream smoke cigarette comprising a conventional tobacco rod and a combustible treatment paper having a sidestream smoke treatment composition, said treatment composition comprising an oxygen storage and donor metal oxide oxidation catalyst, an essentially non-combustible high surface area adjunct for said catalyst incorporated in said treatment paper and a coating of calcium carbonate on an exterior surface of said treatment paper to modify ash characteristics.

**[0080]** Preferably, said adjunct includes a zeolite based material.

**[0081]** Preferably, said zeolite based material is in an amount ranging from about 0.1% by weight of total dry weight composition to about 60% by weight of total dry weight composition and preferably less than 25% and most preferably less than 15%.

**[0082]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst is selected from a group consisting of transition metal oxides, rare earth metal oxides and mixtures thereof.

**[0083]** Preferably, said transition metal oxides are selected from the group consisting of oxides of group IVB, VB, VIB, VIIB, VIIIB, IB metals and mixtures thereof.

**[0084]** Preferably, said rare earth metal oxide is selected from the group consisting of oxides consisting of scandium, yttrium, lanthanide metals and mixtures thereof.

**[0085]** Preferably, said lanthanide metal oxide is selected from the group consisting of lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide and mixtures thereof.

**[0086]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst and adjunct therefor is a solid solution of mixed metal oxides where the adjuncts are selected from the group consisting of zirconium oxide, aluminium oxide, magnesium oxide, titanium oxide and mixtures thereof.

**[0087]** Preferably, said solid solution comprises a metal catalyst selected from the group consisting of palladium,

um, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof.

**[0088]** Preferably, said solid solution of mixed metal oxides includes cerium/lanthanum mixed oxides, cerium/zirconium mixed oxides, cerium/aluminum mixed oxides, cerium/magnesium mixed oxides, cerium/titanium mixed oxides, cerium/zirconium/lanthanum mixed oxides, cerium/lanthanum mixed oxide, cerium/zirconium mixed oxide, cerium/zirconium/lanthanum mixed oxide, cerium/zirconium/praseodymium mixed oxide, cerium/zirconium/lanthanum/praseodymium mixed oxide, cerium/zirconium/neodymium mixed oxide.

**[0089]** Preferably, said solid solution being a high surface area porous particulate.

**[0090]** Preferably, an oxidation catalyst is used with said oxygen storage and donor metal oxide oxidation catalyst, said oxidation catalyst being selected from the group consisting of palladium, platinum, rhodium, tin oxides, copper oxides, iron oxides, manganese oxides, and mixtures thereof.

**[0091]** Preferably, said zeolite is a Y-type zeolite, ZSM-5 type zeolite or Beta type zeolite.

**[0092]** Preferably, said oxygen storage and donor metal oxide oxidation catalyst is a porous particulate cerium/zirconium mixed oxide high surface area material.

**[0093]** Preferably, an oxidation catalyst is used with said cerium/zirconium mixed oxide, zirconium oxide and/or zeolite.

**[0094]** Preferably, said oxidation catalyst is selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide, and mixtures thereof, said selected oxidation catalyst being either incorporated in said solid solution of cerium/zirconium mixed oxide or applied to surfaces of particulate cerium/zirconium mixed oxide, zirconium oxide and/or zeolite.

**[0095]** Preferably, said zeolite is a Y-type zeolite.

**[0096]** Preferably, a binder for said calcium carbonate coating is selected from the group consisting of polyvinylalcohol, starches, CMC, casein, soya, binding clays, inorganic binders and mixtures thereof.

## SUMMARY OF THE INVENTION

**[0097]** In accordance with various aspects of this invention, cigarette paper, cigarette wrapper, wrapper for a cigar or other like tobacco products is provided for reducing visible sidestream smoke with an improved of modified ash.

**[0098]** In accordance with an aspect of the invention, in a low sidestream smoke cigarette having a conventional tobacco rod and a combustible treatment paper, said treatment paper having a sidestream smoke treatment composition comprising an oxygen storage and donor metal oxide oxidation catalyst and an essentially non-combustible finely divided particulate adjunct for said catalyst, the improvement comprising the use of a solid solution of particulate mixed metal oxides as said catalyst

and said adjunct.

**[0099]** The oxygen storage and donor metal oxide oxidation catalyst as part of the solid solution is preferably selected from the group consisting of lanthium oxide, cerium oxide, praseodymium oxide, neodymium oxide and mixtures thereof. The adjunct which is also part of the solid solution is preferably selected from the group of metal oxides consisting of zirconium oxide, aluminum oxide, magnesium oxide, titanium oxide and mixtures thereof.

**[0100]** The solid solution of mixed metal oxides may further include in the solid solution metal catalyst selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof. Preferred mixed oxides of the solid solution are cerium/lanthium mixed oxide, cerium/zirconium mixed oxide, cerium/zirconium/lanthium mixed oxide, cerium/zirconium/praseodymium mixed oxide, cerium/zirconium/lanthium/praseodymium mixed oxide, cerium/zirconium/neodymium mixed oxide and mixtures thereof.

**[0101]** In accordance with another aspect of the invention, a low sidestream smoke cigarette comprises a conventional tobacco rod and a combustible treatment paper having a sidestream smoke treatment composition, the treatment composition comprises an oxygen storage and donor metal oxide oxidation catalyst, an essentially non-combustible adjunct for said catalyst and a metal oxide for modifying ash characteristics.

**[0102]** In accordance with another aspect of the invention, the adjunct may comprise a mixed metal oxide or carbonate filler used in conjunction with a zeolite based material. The zeolite based material is preferably in an amount ranging from about 0.1% to 35% by weight of the total dry weight of the composition, although the amount could be higher. The mixture of metal oxides may include mixtures of zirconium oxide, tin oxide, titanium oxide, magnesium oxide, alumina, cerium oxide tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof. The metal oxides may be of various surface areas and most preferably either low surface area in the range of about 5 to 15 m<sup>2</sup>/g and high surface area of over 20 m<sup>2</sup>/g. A cerium oxide hydrate sol may be applied to the adjunct, for example, the metal oxides to provide increase catalytic activity.

**[0103]** In accordance with another aspect of the invention, the oxygen storage and donor metal oxide oxidation catalyst material preferably include lanthium oxide, cerium oxide, praseodymium oxide, neodymium oxide and mixtures thereof. Oxidation catalyst of the precious metal and transition metal type may also be included such a palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof. These catalyst may also be fixed on the adjunct or the ash modification material or as part of the solid solution of the mixed oxides.

**[0104]** The sidestream smoke treatment composition

may be incorporated in the combustible treatment paper, coated on the combustible treatment paper, impregnated into treatment paper or a combination of the above steps. The treatment paper may be double wrapped and be of the same or different compositions. One of the double wraps may be conventional paper. Alternatively, one of the double wraps may have a composition directed primarily to sidestream smoke reduction and the other double wrap paper include a composition directed towards ash modification.

**[0105]** In accordance with another aspect of the invention, a low sidestream smoke cigarette comprises a conventional tobacco rod and a combustible treatment paper having a sidestream smoke treatment composition. The treatment composition comprises an oxygen storage and donor metal oxide oxidation catalyst and an essentially non-combustible high surface area adsorptive adjunct for the catalyst incorporated in said treatment paper. A coating of calcium carbonate is provided on an exterior surface of the treatment paper to modify ash characteristics.

**[0106]** For ease of description, whenever the term cigarette is used, it is understood to not only include smokable cigarettes but as well any form of wrapped smokable tobacco product, such as cigars, or the like. Whenever the term treatment paper is used, it is understood to encompass combustible wrappers and the like which may be used on cigarettes, cigars, and the like. The wrapper may be used as a single layer of cigarette paper or multiple layer of cigarette paper. The wrapper may be applied as the sole layer of cigarette paper or as a wrap over conventional cigarette paper of a cigarette. The treatment paper may include as its substrate conventional cigarette paper or similar combustible product with a wide range of porosities. The conventional tobacco rod encompasses tobacco compositions normally used in smokable cigarettes. These rods are to be distinguished from tobacco components used in aerosol cigarette.

#### BRIEF DESCRIPTION OF THE DRAWINGS

**[0107]** Preferred embodiments of the invention are shown in the drawings wherein:

Figure 1 is a schematic view of a spray technique for applying the treatment composition to a cigarette paper;

Figure 2 is a schematic view of extruding a film of the treatment composition onto the cigarette paper;

Figure 3 is a schematic view of roll coating the treatment composition on cigarette paper;

Figure 4 is a schematic view of the impregnation of a coating of the treatment composition into the cigarette paper;

Figure 5 is a schematic view of mixing the treatment composition with the paper pulp in the manufacture of cigarette paper;

Figure 6 is a perspective view of a tobacco rod having the treatment paper of this invention applied thereto;

Figure 7 shows an alternative embodiment of Figure 6;

Figure 8 is a perspective view of a tobacco rod having the treatment composition sandwiched between two layers of cigarette paper as applied to the tobacco rod; and

Figure 9 is a perspective view of a double wrap for the tobacco rod where treatment paper is applied over conventional cigarette paper.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0108]** In accordance with an aspect of this invention, the sidestream smoke treatment composition provides the desired degree of visible sidestream smoke control while at the same time providing a suitable ash of desired characteristics. The sidestream smoke treatment composition of this invention comprises, an oxygen storage and donor metal oxide oxidation catalyst used in combination with a non-combustible finely divided porous particulate adjunct for the catalyst. As taught in applicant's co-pending U.S. patent application serial number 09/954,432 filed September 18, 2001, it was unexpectedly found that when these two components are used in combination either alone or with other constituents, a very surprising degree of visible sidestream smoke control is provided. It has been found that with certain types of catalytic material and/or adjuncts, ash characteristics, such as, appearance can sometimes be less than acceptable due to, for example, discolouration, delamination and defoliation. In accordance with this invention, enhancements have been made to the composition and in particular to the catalyst and/or adjunct to modify ash characteristics to provide for example an acceptable appearance, acceptable strength, colour, integrity and reduction or elimination of ash defoliation, delamination and the like.

**[0109]** The adjunct may be any suitable essentially non-combustible, finely divided particulate material which does not affect the flavour and taste of the mainstream smoke and does not give off any undesirable odours in the sidestream vapours. The particulate material is physically stable at the elevated temperatures of the burning cigarette coal. The adjunct may have a low surface area usually less than 20 m<sup>2</sup>/g and preferably 1 m<sup>2</sup>/g to 15 m<sup>2</sup>/g and most preferably 3 m<sup>2</sup>/g to 10 m<sup>2</sup>/g. It is understood for the low surface area materials the particulates are finely ground and are usually not porous. However, as the surface area increases towards 20 m<sup>2</sup>/g it is understood that the particles may be porous. Conversely the adjunct may also have a high surface area usually greater than 20 m<sup>2</sup>/g and at this level of surface area usually the particulate material is porous. The porous adjunct may have pores with an average diameter of less than 100 nm (1000 Å). More preferably, the pores have an average diameter of less than 20 nm (200 Å) and even more preferred are pores with an average di-

ameter of 0.5 to 10nm (5-100 Å). With zeolite based materials, the pores have an average diameter in the range of about 0.5 to 1.3 nm (5-13 Å).

**[0110]** The particulate adjunct may have an average particle size of less than about 30 μm, more preferably less than about 20 μm and most preferably ranging from about 1 μm up to about 10 μm. Non-combustible materials may be porous clays of various categories commonly used in cigarette paper manufacture, such as the bentonite clays or treated clays having high surface areas. Non-combustible carbon materials may also be used including milled porous carbon fibres and particulates. Various metal oxides and/or carbonates may be used such as porous monolithic mineral based materials such as zirconium oxide, titanium oxides, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof, metal oxide fibres such as zirconium fibres and other ceramics such as milled porous ceramic fibres and mixtures thereof. In respect of cerium oxide, it has been found that it is capable of functioning as a finely divided adjunct and as an oxygen storage and donor cerium oxide oxidation catalyst. Other adjunct materials include high surface area materials such as activated carbon and zeolites.

**[0111]** The adjunct may also comprise high surface area highly sorptive materials which are non-combustible, inorganic finely divided particulate, such as molecular sieves which include zeolites and may also comprise amorphous materials such as silica/alumina, zirconium oxide, zirconium hydroxide and the like. Zeolites such as silicalite zeolites, faujasites X, Y and L zeolites, beta zeolites, Mordenite zeolites and ZSM zeolites are acceptable. Preferred zeolites include hydrophobic zeolites and mildly hydrophobic zeolites which have affinity for hydrophobic and mildly hydrophobic organic compounds of such sidestream smoke whereby water vapour is avoided. The zeolite materials provide a highly porous structure which selectively absorbs and adsorbs components of sidestream smoke. The highly porous structure generally comprise macropores amongst the particles and micropores within the particles which branch off of the macropores. It is believed that the captured components in the macropores and micropores in presence of the cerium oxide or other suitable oxidation catalysts at the high temperature of the burning cigarette, converts such captured components into oxidized compounds which continue to be trapped in the adsorbent material or are released as invisible gases which have sufficiently low tar and nicotine levels so that the sidestream is invisible or at a low desired level.

**[0112]** The zeolite materials may be characterized by the following formula:  $M_m M'_n M''_p [aAlO_2 \cdot bSiO_2 \cdot cTO_2]$  wherein

M is a monovalent cation,

M' is a divalent cation,

M'' is a trivalent cation,

a, b, c, n, m, and p are numbers which reflect the stoi-



chiometric proportions, c, m, n or p can also be zero, A1 and Si are tetrahedrally coordinated A1 and Si atoms, and

T is a tetrahedrally coordinated metal atom being able to replace A1 or Si,

wherein the ratio of b/a of the zeolite or the zeolite-like material, has a value of about 5 to 300 and the micropore size is within the range of about 0.5 to 1.3 nm (5 to 13 Å).

**[0113]** Preferred zeolites of the above formula, have the specific formulas of faujasites ((Na<sub>2</sub>, Ca, Mg)<sub>29</sub>[Al<sub>58</sub>Si<sub>134</sub>O<sub>384</sub>] · 240 H<sub>2</sub>O; cubic), β-zeolites (Na<sub>n</sub>[Al<sub>n</sub>Si<sub>64-n</sub>O<sub>128</sub>] with n<7; tetragonal), Mordenite zeolites (Na<sub>8</sub>[Al<sub>8</sub>Si<sub>40</sub>O<sub>96</sub>] · 24 H<sub>2</sub>O; orthorhombic), ZSM zeolites (Na<sub>n</sub>[Al<sub>n</sub>Si<sub>96-n</sub>O<sub>192</sub>] ~ 16 H<sub>2</sub>O with n<27; orthorhombic), and mixtures thereof.

**[0114]** It is appreciated that various grades of the sorptive material may be used. This is particularly true with gradients of zeolites which can be custom designed to selectively adsorb, for example, high boiling point materials, mid boiling point materials and low boiling point materials. This can lead to layers of the zeolite composition where the cerium oxide or other suitable catalyst contemplated by this invention is preferably dispersed throughout these layers. The layers may then be bound on cigarette paper for the tobacco rod by using a binder or an adhesive which may be, for example, polyvinylacetate, polyvinyl alcohol, carboxy methyl cellulose (CMC), starches and casein or soya proteins, and mixtures thereof

**[0115]** The oxygen donor and oxygen storage metal oxide oxidation catalyst may be selected from the transition metal oxides, rare earth metal oxides, (such as scandium, yttrium, and lanthanide metal series, i.e. lanthanum) and mixtures thereof. It is appreciated that the catalyst may be in its metal oxide form or a precursor of the metal oxide which, at the temperature of the burning cigarette, is converted to a metal oxide to perform its catalytic activities. The transition metal oxides may be selected from oxides of the group of metals from the Periodic Table consisting of groups IVB, VB, VIB, VIIB, VIII and IB metals and mixtures thereof. Preferred metals from the transition metal group are oxides of iron, copper, silver, manganese, titanium, zirconium, vanadium and tungsten and from the rare earth group are oxides of lanthanide metals such as oxides of lanthanum, cerium, praseodymium, neodymium and mixtures thereof. For example, cerium may be used in admixture with any one of the transition metals such as Ce/Zr mixed oxide. It is appreciated that other metal oxide oxidation catalysts may be used with the oxygen storage and oxygen donor type of catalyst. Such other metal catalysts include precious metals and metals from groups IIA, IVA and mixtures thereof. Examples include palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof.

**[0116]** The cerium catalyst precursor may be in the form of a cerium salt such as a cerium nitrate or other dispersible forms of cerium such as a cerium sol made

up of a cerium oxide hydrate or as it is also referred to as a cerium hydroxide which is applied in solution or sol to the sorptive material or to a paper as a coating and which is converted to cerium oxide at the high temperature of the burning cigarette to then function as a catalyst. It is understood that the sol may be a low nitrate cerium oxide hydrate sol. For purposes of describing the invention, the term catalyst is intended to include any catalyst precursor.

**[0117]** The catalyst such as, cerium oxide, is used in combination with the adjunct material. It has been found that when the two are used separate from one another or in spaced apart, non-adjacent layers, the ability to control sidestream smoke is greatly reduced. Although in certain arrangements, some sidestream smoke control can be achieved. Preferably the catalyst is substantially adjacent the adjunct material. This can be achieved by co-mingling the particulate catalyst, in admixture with the adjunct, contacting a layer of the adjunct with a catalyst layer, coating the catalyst on the adjunct or impregnating the catalyst within or on the porous surfaces of the adjunct, to bring about the desired surprising sidestream smoke control properties. It should be appreciated that many other constituents may be used in addition to the combination of the oxygen storage and oxygen donor metal oxide oxidation catalyst and the adjunct. Additional additives may be used to further enhance the treatment of the sidestream smoke or alter other characteristics of the cigarette. Such additional additives may be mixed in with the treatment composition or used elsewhere in the cigarette construction, providing of course that such additives do not appreciably impact negatively on the ability of the treatment composition to treat the sidestream smoke.

**[0118]** The composition may be formulated in a variety of ways which achieve co-mingling of the cerium with the adsorptive material. For example, the adsorptive material may be sprayed with or dipped in a cerium salt solution such as cerium nitrate or cerium oxide hydrate sol to impregnate the surface of the adsorptive material with cerium material. Cerium oxide may be prepared as a separate fine powder which is mixed with the fine powder of the adsorptive material. It is particularly preferred that the catalyst powders have an average particle size of less than about 30 μm and preferably less than 20 μm and most preferably about 1.0 to 10 μm and more preferably 6 to 10 μm to ensure intimate mixing and co-mingling of the materials.

**[0119]** As a general guide to selecting catalyst particle size and surface area, it is appreciated by one skilled in the art that the selected catalyst has a surface area which is such to ensure that the catalyst active sites are available to the migrating sidestream smoke components. This may result in catalyst particle size being greater than 30 μm in certain embodiments, if the catalyst particles are properly distributed to achieve the necessary degree of sidestream smoke component oxidation.

**[0120]** It has been surprisingly found that the cerium

oxide, particularly high surface area cerium oxide, is one of the few metal oxides which can perform both functions of the invention, namely as the oxygen storage and oxygen donor catalyst and as well as the adjunct. The porous cerium oxide particles can be made with the high surface areas and an average particle size required for the adjunct. The cerium oxide is used with the cigarette paper in a first amount as the catalyst and a second amount as the adjunct in the treatment composition. Such amounts of the cerium oxide correspond generally with the amounts used for the catalyst and adjunct in accordance with other aspects of the invention to make up the total loading. Alternatively the high surface area cerium oxides can be used with adjuncts such as zeolites or other high surface metal oxides such as zirconium oxide or zirconium hydroxide.

**[0121]** The cerium may be formulated as a solution dispersion, such as cerium oxide sol, or the like and applied to the sorptive material such as zeolite. It is then dried and fired to provide cerium oxide particles fixed on the surfaces of the adsorptive material. When the cerium oxide particles are fixed to adjunct surfaces such as surfaces of zeolite, the average particle size may be less than about 1.0 $\mu$ m. The relative amounts of cerium oxide fixed to the zeolite may range from about 1% to 75% by weight based on the total equivalent cerium oxide and zeolite content. The preferred relative amounts of cerium oxide fixed to the zeolite may range from about 5% to 70% by weight based on the total equivalent cerium oxide and zeolite content.

**[0122]** One possible method for making the combination product of cerium oxide fixed on the surfaces of the zeolite is described in published a co-pending application Serial No. 60/318,878, entitled A Process For Making Metal Oxide-Coated Microporous Materials, filed in the U.S. Patent Office on September 14, 2001, the subject matter of which is incorporated herein by reference.

**[0123]** The method generally involves making a catalytic cerium oxide-coated zeolite particulate material having at least 1% by weight of cerium oxide coated on outer surfaces of the zeolite particulate material, based on the total equivalent cerium oxide and zeolite content. In one aspect, the method generally comprises the steps of:

- i) combining an amount of a colloidal dispersion of cerium oxide hydrate (cerium hydroxide) with a compatible zeolite particulate material to form a slurry, the amount of the colloidal dispersion being sufficient to provide, when heat treated as per step (ii), greater than 20% by weight of the cerium oxide, the zeolite particulate material having an average pore size of less than 20 $\text{\AA}$  and the colloidal dispersion having an average particle size of at least 20 $\text{\AA}$ , to position thereby, the colloidal dispersion on the outer surfaces of the zeolite; and
- ii) heat treating the slurry firstly, at temperatures below about 200°C and secondly, above about 400°C, to fix the resultant cerium oxide on the outer surfaces

of the zeolite particulate material, to provide a free flowing bulk particulate.

**[0124]** Some of the combinations for the treatment composition can result in what could be considered as unacceptable ash appearance. Unacceptable ash appearance characteristics include delamination, defoliation, ash smear, oily appearance and color. It was thought that various ash modifiers could be added to the paper to improve ash appearance. Such ash modifiers include metal oxides and/or carbonates such as zirconium oxide, titanium oxides, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof.

**[0125]** It is been found that the treatment composition may require modifications to improve ash characteristics. Such modifications may include selection of a particular chemical or physical type of oxygen donor/oxygen storage catalyst and/or of the type of adjunct. In particular to enhance the color of the ash so that it is more a white or gray rather than a dark coal color, it has been found that reduced amounts of zeolite base material for the adjunct is appropriate. The reduce amount of zeolite material based on the dry weight of the paper is preferably less than 35% by weight and more preferably less than 25% by weight and most preferably less than 15% by weight. It is appreciated that other types of fillers have to be added to compensate for the reduced amount of zeolite based adjunct. Suitable substitute metal oxides and/or carbonates include zirconium oxide, titanium oxides, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof. Low or high surface area cerium/zirconium mixed oxides as a solid solution are preferred. Such adjuncts may be made for example by co-precipitating zirconium and cerium species, drying the precipitate and then firing to form a crystalline solid solution product of high surface area cerium oxide and zirconium oxide. The ratio of cerium oxide to zirconium oxide in this crystalline structure may range from about 5:95 through to 95:5. Alternatively, the ratio may range from about 20:80 to 80:20 and most preferred ranging from about 50:50 to 80:20. This material in its high surface area form also has catalytic properties and also provides for oxygen storage and donor properties where the zirconium oxide functions as the adjunct for the cerium oxide.

**[0126]** In respect of the catalyst selection, there has also found that combinations with cerium oxide contribute to a better ash appearance. For example cerium oxide may be deposited on high surface area cerium oxide, cerium oxide hydrate deposited on high surface area cerium/zirconium oxides, cerium oxide hydrate deposit and dried on a high surface area cerium oxide particle. Furthermore, oxidation catalyst of the aforementioned precious metal or transition metal types may be combined with the cerium based materials such as palladium, plat-

inum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide, and mixtures thereof.

**[0127]** Solid solutions of mixed metal oxides are particularly preferred as the oxygen donor catalyst because of an improved lighter colour ash. The solid solution of the mixed metal oxides includes the oxygen donor oxygen storage oxidation catalyst and the adjunct. Preferred metal oxides in a solid solution as the oxygen donor oxygen storage material include lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide and mixtures thereof. The preferred metal oxides as adjuncts include zirconium oxide, aluminum oxide, magnesium oxide, titanium oxide and mixtures thereof. Examples of these solid solutions include cerium/lanthanum mixed oxide, cerium/zirconium mixed oxide, cerium/zirconium/lanthanum mixed oxide, cerium/zirconium/praseodymium mixed oxide, cerium/zirconium/lanthanum/praseodymium mixed oxide, cerium/zirconium/neodymium mixed oxide. These solid solutions of mixed oxides and other mixed oxides are readily available as commercial grade catalyst and are available from any of a number of catalyst suppliers. Other alternatives to the solid solutions include physical mixtures of zirconium oxide, aluminum oxide, magnesium oxide, titanium oxide with a solid solution for example cerium/zirconium mixed oxide solid solution. Other solid solutions and mixed oxides contemplated by this invention include cerium/aluminum mixed oxide, cerium/magnesium mixed oxide, cerium/titanium mixed oxide.

**[0128]** The oxidation catalysts which maybe included in the solid solutions are usually present in trace amounts. Such catalyst include palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof. They are usually included in the solid solutions at levels less than 1% by weight of the total solid solution. A preferred combination and in respect of the solid solution with trace amounts of other oxidation catalyst is a combination of the above catalyst with a solid solution of cerium/zirconium mixed oxide. It is preferred that the above oxidation catalyst either individually or mixtures thereof be included in the solid solution. Although alternatively it is understood that the above catalyst or mixtures thereof maybe applied to the surfaces of the cerium/zirconium mixed oxide solid solution particulate material.

**[0129]** Multiple purpose solid solution of mixed oxides include ceria/zirconia/magnesia/titania/ where ceria makes up about 5% to about 75% of the solid solution.

**[0130]** It has also been found that a coating on the wrapper of particulate calcium carbonate is useful in improving ash characteristics. As previously described the treatment composition maybe incorporated or coated on a wrapper which is the sole wrapper for the tobacco rod. As noted above, one approach to improving ash is to reduce the amount of the absorptive adjunct such a zeolites and substitute therefor a selected metal oxide. Alternatively it has been found that particularly with single wrappers having incorporation of the treatment compo-

sition, a coating of calcium carbonate on the exterior of the wrapper greatly improves the ash particularly from the stand point of appearance. It is quite surprising that a coating of particulate calcium carbonate could have this effect on improving the ash characteristics. Perhaps the calcium carbonate chemically or physically binds constituents in the wrapper to produce a more uniform light to gray coloured ash. The particulate calcium carbonate maybe slurried with a suitable binder for coating on the wrapper. Suitable binders include those commonly used in coating calcium carbonate on wrapper materials such a polyvinylalcohols, starches, CMC, casein, soya, binding clays and other acceptable binders or glues. The particulate calcium carbonate has a particle size of that normally associated with its use as a filler in manufacture of cigarette paper. The particle size is therefore usually below 10  $\mu\text{m}$  and preferably above 3  $\mu\text{m}$ . Although some grades of calcium carbonate less than 1  $\mu\text{m}$  may also be useful.

**[0131]** The surprising activity of the sidestream smoke treatment composition permits its use in cigarette papers having a wide range of porosities. It has also been found that the composition does not have to be used in cigarette papers that just have high porosities. The treatment composition works equally well in papers with very low porosities of about 0.5 through to very high porosities of about 1,000 Coresta units. Preferred porosities are usually less than 200 Coresta units and most preferred porosities are usually in the range of about 15 to 60 Coresta units. It is appreciated that the paper may be used as a double or multiple wrap. The paper may be applied as an outer wrap over a cigarette having conventional cigarette paper. It is appreciated that depending upon the porosity, certain combinations of the catalyst and adjunct may work better than others.

**[0132]** The composition may be simply sprayed onto either side or both sides of the cigarette paper and absorbed into the paper. As shown in Figure 1, the paper 10 is conveyed in the direction of arrow 12. The treatment composition 14 as a slurry is sprayed by spray nozzle 16 onto the paper 10 to provide a coating 18 which is dried on the paper. Alternatively, the composition may be extruded as a film to the surface of the paper and may be used as a single or multiple wrap. As shown in Figure 2, a film coating device 20 contains the slurried treatment composition 14. The film coater 20 lays a thin film 22 on the paper 10 which is conveyed in the direction of arrow 12. The film is dried to provide a coating 24 on the paper 10. With these arrangements, it is quite surprising that the visual sidestream smoke from a burning cigarette virtually disappears. The treatment composition may be applied to a conventional cigarette on the exterior of the cigarette paper.

**[0133]** Coating may be achieved by a roller applicator 26, as shown in Figure 3. The treatment composition 14 is applied as a layer 28 on the roller 30. A doctor knife 32 determines the thickness of a layer 34 which is then laid onto the paper 10 which is conveyed in the direction

of arrow 12. The layer is then dried to form a coating 36 on the paper 10.

**[0134]** Impregnation is achieved by using the coating roller 24 of Figure 4 and the resultant layer 36 with paper 10 is passed in the direction of arrow 12 through pressure rollers 38 and 40 which force the layer of material into the paper 10 to thereby impregnate constituents of the treatment composition into the paper.

**[0135]** It is also understood by one of skill in the art that various other coating processes including transfer coating processes, may be used for making the treatment paper of the invention. In the transfer coating process, Mylar™ sheet or other suitable continuous sheet may be used to transfer a coating composition from the Mylar™ sheet to the surface of the cigarette paper. This type of transfer coating is useful when the substrate sheet may not readily accept the roll coating of a composition due to physical strength characteristics of the paper or the like.

**[0136]** A further alternative is to incorporate the treatment composition into the manufacture of paper. The composition may be introduced to the paper furnish as a slurry. With reference to Figure 5, the treatment composition in the furnish 42 is stirred by stirrer 44 to form a slurry in the tank 46. The slurry is transferred in the conventional paper making manner and is laid as a layer 48 on a moving conveyor 50 to form the resultant cigarette paper 52. As a result the treatment composition is incorporated in the final paper product.

**[0137]** Another alternative is to sandwich the treatment composition between paper layers to form a double cigarette paper wrap on tobacco rods. For example, the composition may be applied such as by the spraying technique of Figure 1 on the interior of the outer paper and/or the exterior of the inner paper. Once the two papers are applied to the tobacco rod the composition as a layer is sandwiched between the two papers. Each paper may be of half of the thickness of conventional cigarette paper so that the double wrap does not add appreciably to the overall diameter of the cigarette as is readily handled by cigarette making machines.

**[0138]** With reference to Figure 6, the tobacco rod 54 has, for example, the cigarette paper 10 wrapped there-around with the coating 18 on the outside of the paper. Conversely, as shown in Figure 7, the cigarette paper 10 can be applied with the coating 18 on the inner surface of the paper adjacent the tobacco rod 54.

**[0139]** Another alternative, as shown in Figure 8, is to sandwich the coating 18 between cigarette papers 56 and 58. The papers 56 and 58 with the intermediate coating 18 may be formed as a single cigarette wrapper which is applied to the tobacco rod 54. A further alternative is shown in Figure 9 where the tobacco rod 54 is covered with conventional cigarette paper 60. Over the conventional paper 60 is the cigarette paper 52 of Figure 5 with the treatment composition incorporated therein. It is also appreciated that paper 52 with the treatment composition incorporated therein may be applied directly to the tobacco rod 54.

co rod 54.

**[0140]** In yet another alternative embodiment of the invention, various combinations for the sidestream smoke treatment paper may be provided in a double wrap configuration for example, a coated paper of Figure 7 could be used as the inner layer of paper and a different paper could be used as the outer layer of the double wrap which could be conventional paper. The inner layer paper could also be a paper having the treatment composition incorporated therein such as that of Figure 9. The inner layer paper could be designed to provide for sidestream smoke reduction by including all the necessary components of the composition such as an oxygen storage and donor metal oxide oxidation catalyst and the non-combustible adjunct for the catalyst. Preferred examples of this type of composition includes a high surface area, cerium/zirconium mixed oxide with zeolite and optionally enhanced with an oxidation catalyst such as platinum or palladium. In a double wrap system, the amount of zeolite may exceed 30% and may be in the range for example of 50% to 60% by weight.

**[0141]** The outer layer of the double wrap may have a different composition and be designed to provide for ash modifications to achieve desired characteristics. For example, the outer paper may be designed to enhance not only ash appearance but as well modify the burn rate of the cigarette and also minimized if not eliminate flare ups on lightning and puffing of the cigarette. The outer layer may include, for example, metal oxides such as low surface area cerium oxide, solid solution of cerium oxide/zirconium oxide, alumina, zirconium oxide, titanium oxide, tin oxide and the like. In addition cerium oxide hydrate may be coated on the metal oxide materials of the outer layer to ensure sufficient oxygen is present to support combustion of the outer layer of the cigarette. The two layers when combined as a double wrap provide effective control of visible sidestream smoke. The adjacent papers burn evenly to produce desired ash and the outer paper may function to minimize or eliminate the highly active oxygen donor material from causing flare ups.

**[0142]** The double wrap feature of the invention provides significant flexibility in the design of a low sidestream smoke cigarette. The individual sheets of the double wrap design has the selected treatment composition impregnated, coated or incorporated in the respective sheet. Alternatively sheets that have a treatment composition incorporated therein may also be coated with the same or different treatment composition to further enhance the sidestream smoke control and/or ash modification. To demonstrate such flexibility in the design of the low sidestream smoke cigarette, exemplary treatment composition for the inner and outer papers are as follows:-

Outer paper

i) High surface area of cerium/zirconium mixed oxide (75:25) + low surface area zirconium ox-

- ide;
- ii) High surface area alumina coated with cerium hydrate;
- iii) Low surface area cerium oxide coated with cerium hydrate;
- iv) High surface area zirconium oxide coated with cerium hydrate; or
- v) High surface area cerium/zirconium mixed oxide (25:75).

#### Inner paper

- i) High surface area of cerium/zirconium mixed oxide (75:25) enhanced with palladium catalyst + zeolite enhance with palladium catalyst;
- ii) High surface area of cerium/zirconium mixed oxide (75:25) + zeolite enhanced with palladium;
- iii) High surface area of cerium/zirconium mixed oxide (75:25) + zeolite where the cerium/zirconium mixed oxide is enhanced with palladium catalyst; or
- iv) High surface area of cerium/zirconium mixed oxide (75:25) + zeolite where the cerium/zirconium mixed oxide is enhanced with platinum and tin catalyst

**[0143]** These various compositions for the inner and outer papers may be combined in various combinations to provide for sidestream smoke control and ash improvement.

**[0144]** The preferred combination is a solid solution of high surface area cerium/zirconium mixed oxide (75:25) and zirconium oxide for the outer paper. For the inner paper the preferred treatment composition is a solid solution of high surface area cerium/zirconium mixed oxide (75:25) enhanced with palladium catalyst plus zeolite enhanced with palladium catalyst. On a dry weight basis in the outer paper coating formulation has 25% of high surface area cerium/zirconium mixed oxide and 75% of low surface area zirconium oxide. The inner paper on a dry weight basis has about 44% of high surface area cerium/zirconium mixed oxide and 56% of zeolite both enhanced with palladium.

**[0145]** As is appreciated by one of skill in the art, the aforementioned procedures for providing the sidestream smoke treatment composition within or onto a desired cigarette paper may be varied with respect to the loadings provided and the number of wraps used on a tobacco rod. For example, two or more papers with various loadings of the composition, on both sides of the papers, may be used such that the loading to one side is reduced, making the coating application easier.

**[0146]** With any of these combinations, it has been surprisingly found that visible sidestream smoke is virtually eliminated. At the same time, the cigarette paper demonstrates conventional ashing characteristics. It is particularly surprising that the simple application of the composition to the exterior of the cigarette paper can minimize

to an almost undetectable level, visible sidestream smoke.

**[0147]** It is appreciated that depending upon the manner in which the composition is used and applied to a cigarette, various processing aids and mixtures thereof may be required to facilitate the particular application of the treatment composition. Such processing aids include laminating materials such as polyvinyl alcohol, starches, CMC, casein, soya and other types of acceptable glues, various types of binding clays, inert fillers, whiteners, viscosity modifying agents, inert fibrous material such as zirconium fibres and zirconium/cerium fibres, such as described in U.S. application Serial No. 60/318,614 entitled Zirconium/Metal Oxide Fibres, filed September 13, 2001, the subject matter of which is incorporated hereby by reference.

**[0148]** Penetrating agents may also be employed to carry the composition into the paper. Suitable diluents such as water are also used to dilute the composition so that it may be spray coated, curtain coated, air knife coated, rod coated, blade coated, print coated, size press coated, roller coated, slot die coated, technique of transfer coating and the like onto a conventional cigarette paper.

**[0149]** Desirable loadings of the treatment composition onto or into the cigarette paper, wrapper or the like is preferably in the range of from about 2.5 g/m<sup>2</sup> to about 125 g/m<sup>2</sup>. Most preferably the loading is in the range of about 2.5g/m<sup>2</sup> to about 100 g/m<sup>2</sup>. Expressed as a percent by weight, the paper may have from about 10% to 500% by weight and most preferably about 10% to 400% by weight of the treatment composition. While these loadings are representative for single paper, it is understood by one skilled in the art that these total loadings may be provided with the use of two or more papers.

**[0150]** The sidestream smoke reduction composition is used normally as a water slurry of the composition. The make up of the dry composition which can be made into a slurry, may vary depending on its use as a paper coating, incorporation or impregnation. For example the incorporation formulation may contain by weight from about 10% to 33% of a cerium based catalyst, 20% to 62% of an adjunct and 10% to 75% of an ash modifier. Another alternative may contain by weight about 10% to 25% of a cerium based catalyst, 40% to 55% of an adjunct and 20% to 50% of a zeolite which is other than the adjunct.

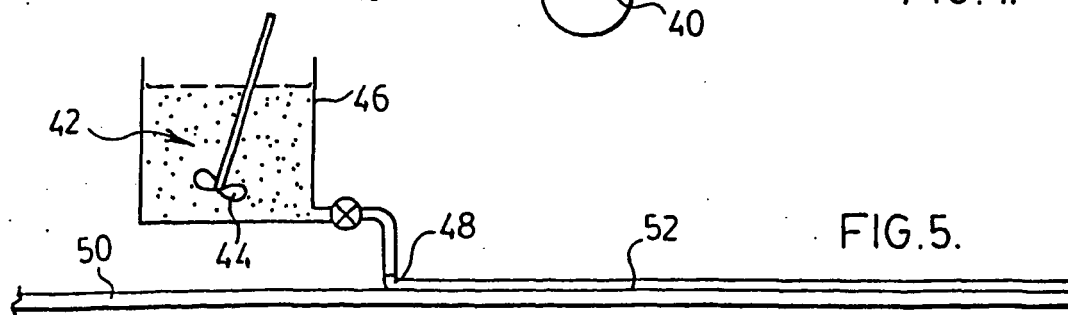
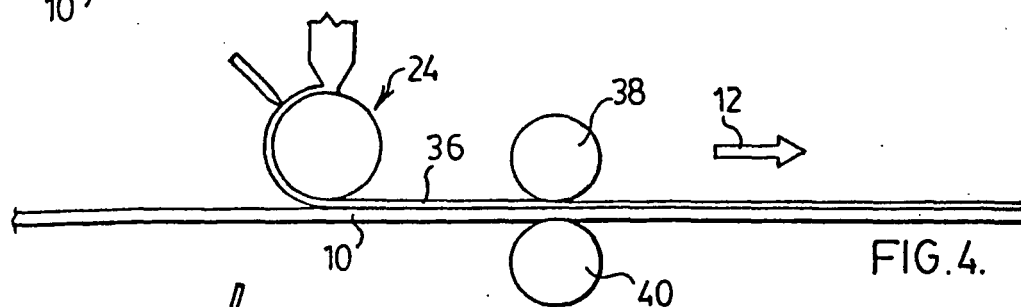
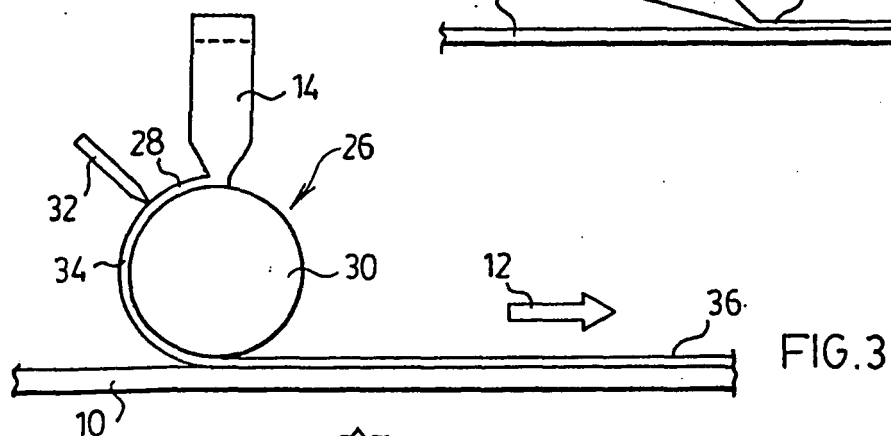
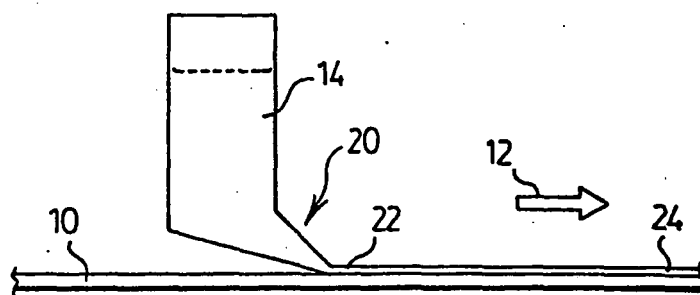
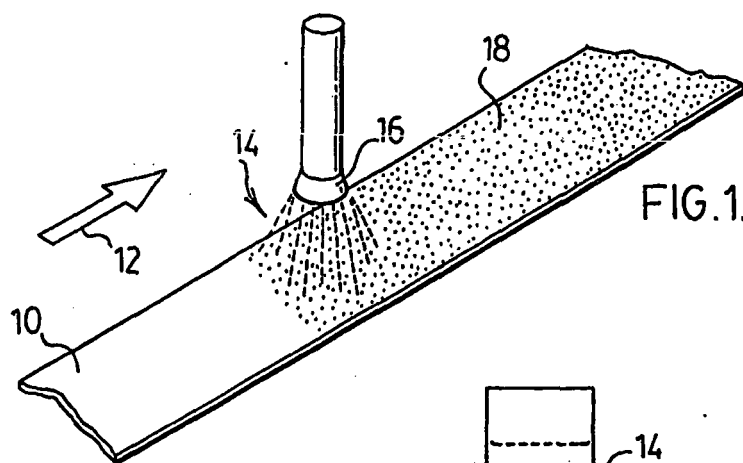
**[0151]** The slurry may be incorporated in the furnish of the paper in the paper making process, or is coated onto the paper by various coating processes or impregnated into the paper by various impregnating methods. The preferred average particle size of the catalyst and adjunct for the slurry is in the range of about 1 µm to about 30 µm and most preferably about 1 µm to about 10 µm. The preferred relative amounts of catalyst fixed to the adjunct may range from about 1% to 75% for cerium, more preferably from about 10% to 70%, and even more preferably from about 20% to 70% by weight based on

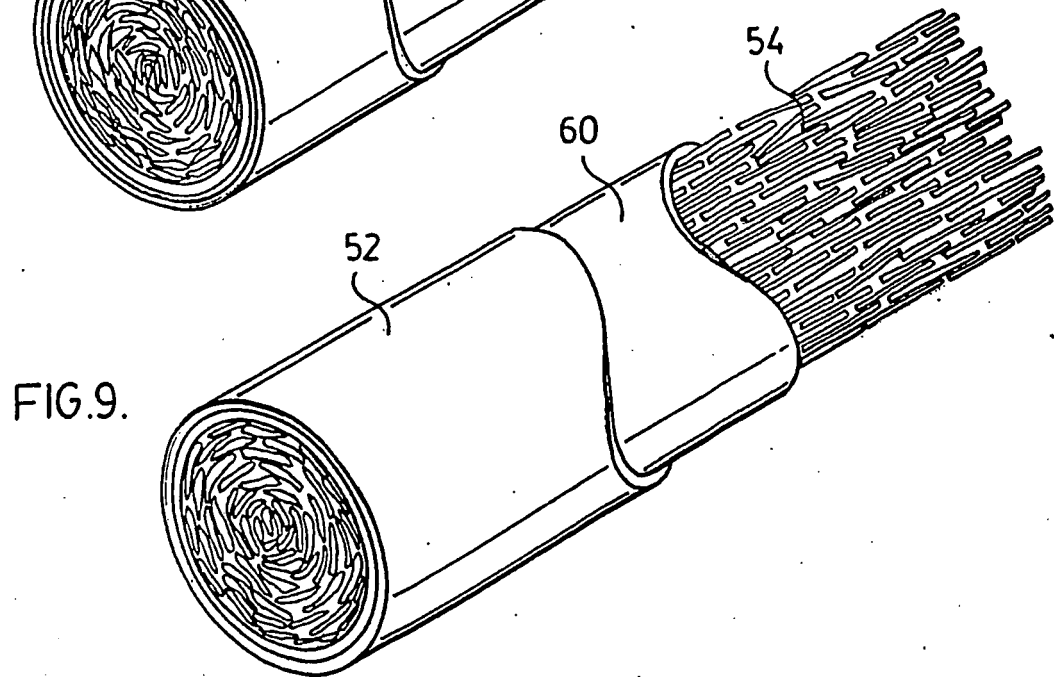
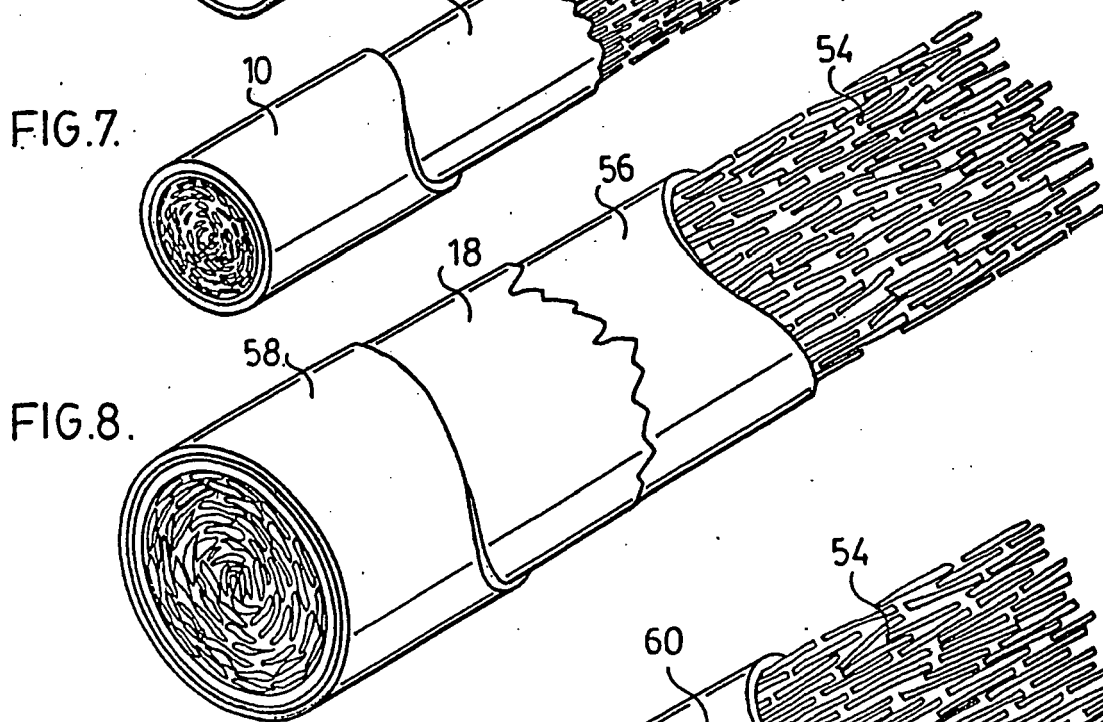
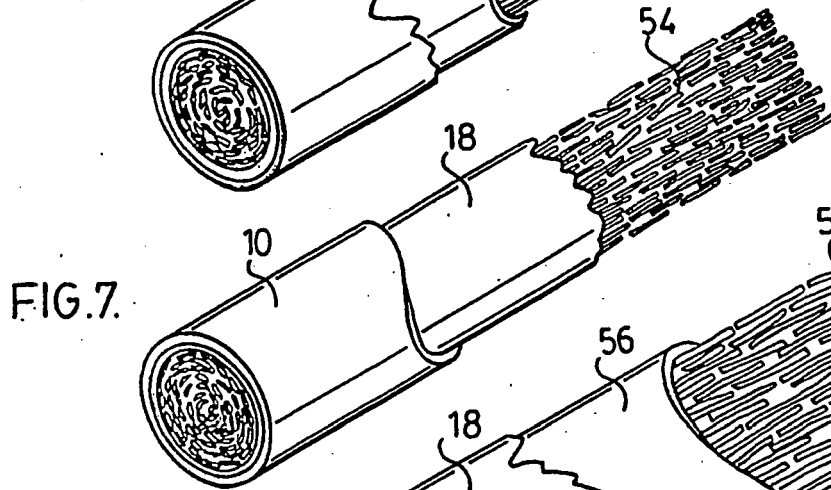
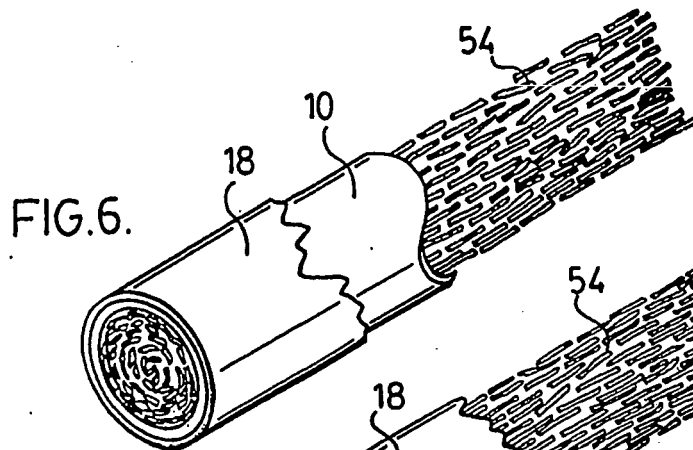
the total equivalent catalyst and adjunct content. Less than 1% of other catalyst such as precious metal catalyst may be fixed to the adjunct.

**[0152]** Although preferred embodiments of the invention have been described herein in detail, it will be understood by those skilled in the art that variations may be made thereto without departing from the spirit of the invention or the scope of the appended claims.

## Claims

1. In a low sidestream smoke cigarette having a conventional tobacco rod and a combustible treatment paper, said treatment paper having a sidestream smoke treatment composition comprising an oxygen storage and donor metal oxide oxidation catalyst and an essentially non-combustible finely divided particulate adjunct for said catalyst, the improvement comprising the use of a solid solution of particulate mixed metal oxides as said catalyst and said adjunct.
2. In a slow sidestream smoke cigarette of claim 1, said oxygen storage and donor metal oxide oxidation catalyst for the solid solution being selected from the group consisting of lanthanum oxide, cerium oxide, praseodymium oxide, neodymium oxide and mixtures thereof.
3. In a slow sidestream smoke cigarette of claim 1, said adjunct is selected from the group of metal oxides consisting of zirconium oxide, aluminum oxide, magnesium oxides, titanium oxide and mixtures thereof.
4. In a slow sidestream smoke cigarette of claim 1, 2 or 3, said solid solution of mixed metal oxides further comprising an oxidation catalyst selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof.
5. In a slow sidestream smoke cigarette of claim 1, 2, 3 or 4, said solid solution of mixed metal oxides being selected from the group consisting of cerium/lanthanum mixed oxide, cerium/zirconium mixed oxide, cerium/zirconium/lanthanum mixed oxide, cerium/zirconium/praseodymium mixed oxide, cerium/zirconium/lanthanum/praseodymium mixed oxide, cerium/zirconium/neodymium mixed oxide and mixtures thereof.
6. In a slow sidestream smoke cigarette of claim 1 to 5, said solid solution being a high surface area porous particulate.
7. In a slow sidestream smoke cigarette of claim 6, wherein said catalyst and said adjunct is said high surface area cerium/zirconium mixed oxide.
8. In a slow sidestream smoke cigarette of claim 7, wherein a catalyst selected from the group consisting of palladium, platinum, rhodium, tin oxide, copper oxide, iron oxide, manganese oxide and mixtures thereof is either included in said solid solution of cerium/zirconium mixed oxide or is applied to the surface of said high surface area cerium/zirconium mixed oxide.
9. In a slow sidestream smoke cigarette of claim 8, wherein said cerium/zirconium mixed oxide has a particle size greater than about 1  $\mu\text{m}$ .
10. In a slow sidestream smoke cigarette of claim 9, wherein said cerium/zirconium mixed oxide has a particle size less than about 30  $\mu\text{m}$ .
11. In a slow sidestream smoke cigarette of claim 7, wherein said cerium/zirconium mixed oxide have a ratio ranging from about 5:95 to about 95:5.
12. In a slow sidestream smoke cigarette of claim 11, wherein said ratio is about 75:25 and said particle size is about 6  $\mu\text{m}$  to 10  $\mu\text{m}$ .
13. In a slow sidestream smoke cigarette of claim 1, wherein said treatment composition is incorporated within said treatment paper at a loading rate of about 2.5 g/m<sup>2</sup> to about 125 g/m<sup>2</sup>.
14. In a slow sidestream smoke cigarette of claim 1, wherein said treatment composition is coated on said treatment paper.
15. In a slow sidestream smoke cigarette of claim 8, wherein said treatment composition includes particulate zirconium oxide, titanium oxide, magnesium oxide, aluminum oxide, cerium oxide, tin oxide, iron oxide, manganese oxide, calcium carbonate, zirconium carbonate, magnesium carbonate and mixtures thereof.
16. In a slow sidestream smoke cigarette of claim 7, wherein said treatment composition includes particulate zeolite.







## REFERENCES CITED IN THE DESCRIPTION

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