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(54) **TOBACCO/CATALYST MIXTURES FOR REDUCING TOXIC COMPOUNDS IN TOBACCO SMOKE**

(57) Tobacco-catalyst mixtures for reducing the toxic compounds present in tobacco smoke.

The use of certain additives to be mixed in with tobacco to reduce the quantity of toxic and cancerous sub-

stances present in tobacco smoke. The composition of tobacco-additive as well as preparation procedures is also an objective of this invention.

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Description

[0001] This invention fits within the smoking products preparation industry. Specifically, this invention refers to the use of tobacco-catalyst mixtures for reducing the toxic compounds present in tobacco smoke.

STATE OF PRIOR ART

[0002] In current society, the smoking habit represents a global problem with very serious human health consequences and a very significant impact on the public health ministries or departments. The smoke that is generated from burning tobacco contains a series of toxic and carcinogenic compounds, which are inhaled by active and passive smokers and on a global scale has made tobacco one of the main causes of death.

[0003] In tobacco and in the smoke that is generated from its combustion, more than 4000 different compounds have been identified [R.R. Baker and L.J. Bishop, J. Anal. Appl. Pyrol., 74 (2005), 145], among which at least 60 are known to be toxic and carcinogenic. Among these compounds are tar, carbon monoxide, carbon dioxide, acetaldehyde, phenols, acetone, formaldehyde, benzene, toluene and nicotine. Nicotine is the main addictive component present in tobacco. In the human body, nicotine is transformed into a metabolite called cotinine and since this compound has only been found in active and passive smokers, it is used as a reference index to measure the degree of exposure to tobacco smoke.

[0004] The process of smoking a cigarette generates two types of smoke, the one called "main stream", which consists of the smoke that is inhaled and exhaled by the smoker directly from the cigarette; and the secondary stream, which consists of the smoke that is eliminated through the lit cigarette, which is diluted through the surrounding air and is inhaled by passive smokers. The main stream corresponds to the smoke that is generated from the combustion of tobacco and travels through the cigarette from the lit tip and exits at the filter end. Since this is the stream that is inhaled by smokers, it is of great interest to eliminate or reduce the toxic substances it contains.

[0005] Different methods and additives have been proposed with the purpose of reducing the toxicity of tobacco smoke. Most of these use different types of zeolite or aluminosilicate materials. One of the first proposals was made by Seeofer et al. [Seeofer, F., Kausch, E., "Removal of nitric oxide and carbon monoxide from tobacco smoke", US 4,182,348, Jan 8, 1980], which uses a compound with the formula $M_2M'RuO_6$, where M is a divalent metal, M' is a trivalent lanthanoid or actinoid, Ru acts with valence 5, and M and M' can form a perovskite coating with the Ru ions. Once this compound is mixed with tobacco or is incorporated in the paper or filter, it contributes to the elimination of NO and CO from tobacco smoke. Along the same lines, Rongved [Rongved, P., "Catalytic cigarette smoke cleaning device and process", US 5,671,758A, Sept 30, 1997] also describes a type of filler that allows to reduce toxic substances such as CO from the tobacco combustion gases by adding solid, inert, stable and non contaminating catalysts attached to or near the tobacco. Among these catalysts, the use of vanadium pentoxide, molybdenum trioxide and rhodium oxides are proposed.

[0006] Among the first patents, the one created by Rosen can also be found [Rosen, W.E., "Method of treating tobacco", US 3,840,026, Oct 8, 1974], which proposes the use of an absorption material with a high degree of humidity and a proportion found between 1 and 50% in order to reduce non desirable products generated from the combustion of tobacco. The material type belongs to the ground infusorian type, diatoms and calcium or magnesium silicates.

[0007] More recently, Li et al. [Li, P., Hajaligol, M., "Oxidant/catalyst nanoparticles to reduce carbon monoxide in the mainstream smoke of a cigarette", US 20030075193, 24 April 2003] have described the use of nanoparticles of Fe_2O_3 , CuO, TiO_2 , CeO_2 , Ce_2O_3 , Al_2O_3 , Y_2O_3 doped with Zr, Mn_2O_3 doped with Pb, as well as mixtures of these materials to increase the degree of conversion from CO to CO_2 . This patent also describes the procedure for preparing the cigarettes, which includes a) addition of the additive composed of Nan particles to the tobacco mixture, b) addition of more additives to the tobacco mixture at the cigarette manufacturing machine that make a cigarette and c) placing of a paper wrap around the tobacco to give the cigarette its final shape. In a continuation of this patent [Li, P., Hajaligol, M., "Oxidant/catalyst nanoparticles to reduce tobacco smoke constituents such as carbon monoxide", US 200313118759, 17 July 2003], these same authors make evident the capacity of the described additives for reducing the generated amount of tobacco constituents like for example, aldehydes, 1,3-butadiene, isoprene, acrolein, acrylonitrile, HCN, o-toluidine, 2-naftilamine, nitrogen oxides, benzene, N-nitrosornicotine, phenol, catechole or benzantracene. In a different patent, Li et al. [Li, P., Rasouli, F., Hajaligol, M., "Manganese oxide mixtures in nanoparticle form to lower the amount of carbon monoxide and/or nitric oxide in the mainstream smoke of a cigarette", US 6,782,892, 31 August 2004] have demonstrated that the coprecipitation of manganese oxide with any of the previously studied nanoparticles also contributes to increasing the degree of conversion of nitric oxide to nitrogen. Along the same lines as previous patents, Li et al. [Li, P., Rasouli, F., Hajaligol, M., "Catalysts to reduce carbon monoxide and nitric oxide from the mainstream smoke of cigarette", WO 2004/110184, 23 December 2004] also describes an additive that consists of a catalyst that contains nanoparticles of a metal and/or a metal oxide supported over a fibrous material that increases the conversion of carbon monoxide into carbon dioxide and of nitric oxide into nitrogen, while a different patent [Rasouli, F., Li, P., Zhang, W.-J., Gedevanishvili, S., "Use of oxyhydroxide compounds in cigarette paper for reducing carbon monoxide in the mainstream smoke of a cigarette", WO 2005/039326, 6 May 2005], proposes using additives based on oxyhydroxide transition metals or strange

soil or a mixture of both these materials. All of these patents also describe the paper and the methods used for preparing cigarettes as well as the conditions in which these were smoked.

[0008] In 2004, Li et al. [Li, P., Rasouli, F., Hajaligol, M., "Application of nanoparticle iron oxide in cigarette for simultaneous CO and NO removal in the mainstream smoke", *Beitraege zur Tabkforschubg International* 21 (1) (2004), 1] described the use of an additive formed by nanoparticles of iron oxide that is generated in place while the cigarette is burning and is capable of increasing the degree of conversion of CO and NO to CO₂ and N₂ respectively. On the other hand, potassium organic salts can also be used as additives that allow reducing the CO, nicotine and nicotine free dry material particles (NFDMP) [Li, C., Parry, A., "Potassium organic salts as burn additives in cigarettes", *Beitraege zur Tabkforschubg International* 20 (5) (2003), 341].

[0009] Other patents or scientific publications have also been found that describe the use of zeolites as tobacco additives. Cvetkovic et al. [Cvetkovic, N, Adnadjevich, B., Nikolic, M, "Catalytic reduction of NO and NO_x content in tobacco smoke", *Beitraege zur Tabkforschubg International* 20 (1) (2002), 43] use a catalyst based on zeolyte Cu-ZSM-5 in order to reduce the quantity of NO and NO_x in the tobacco's main smoke stream. This additive can be incorporated into the filter or can be mixed directly with the tobacco and according to the mechanism proposed by the authors; it is the additive's absorption properties and its diffusivity what determines its activity. There are other authors that propose using certain additives based on their absorption capacity. For Example Jianhua et al. [Jianhua, Z., Ying, W., Yilun, W, "Mesopore solid alkali, mesopore functional material, its preparation method and application", CN 1460641, 2003-12-10] describe the use of a solid alkali catalyst and a functional material based on a silicon based mesoporous molecular screen (for example, MCM-41 or zeolytes NaA, NaY and ZSM-5), which contains a lanthannoid or actinoid transition metal for reducing nitrosamines by selective absorption. The use of zeolites for reducing NFDMP and Polynuclear aromatic hydrocarbons (PAH) has also been made clear by Radojicic et al. [Radojicic, V., Nikolic, M., Adnadevic, B., Jovanovic, A., "Selective reduction of PAH content in cigarette tobacco smoke by catalytic cracking process", *Physical Chemistry*, 2004].

[0010] Other inventions that are related to the ones mentioned above are for example, Shahtar et al. [Shahryar R. R., Firooz Rasouli M., Hajaligol R.M., "Tobacco cut filler including metal oxide supported particles", US 2005/0126583 15 June 2005], which describes the procedure for preparing additives made of metal oxide supported particles. In this study, the additive is formed by combining the particles and a metal oxide precursor solution composed of the smoking material. Other patents like the one from Stanbridge [Stanbridge K.A., "Incorporating additives into cigarette rods", GB 2229079, 19 September 1990], center their objective on the procedure used to mix the additives into the tobacco. In this case, the additive is deposited into the tobacco stream during the cigarette manufacturing process by using a device that allows placing the material in dust or liquid form, in suspension or foam. On the other hand, any of the mentioned additives can also be added directly to tobacco by using the cigarette rolling machines described by Pascual [Pascual U.A., "Máquinas de liar cigarillos y liar tabaco" (cigarette and tobacco rolling machines), U200202253, 18 September 2002].

[0011] EP 740907 describes the use of natural and synthetic zeolitic materials used as additives to reduce the toxic compounds found in tobacco smoke. This invention claims an article for smoking that is made of a filter, tobacco and the paper wrapper. The additives, which have different characteristics depending on the purpose of the additive, are added to the filter as well as the tobacco. Therefore, while the additive that is inserted in the filter is hydrophobic, for mixing in with tobacco hydrophilic materials are preferred. These hydrophilic additives are used saturated in water and consist of X, Y, L, mordenites and BETA zeolites, and are added to tobacco by using or not using adhesive agents such as silica gel. At elevated temperatures, these materials act as catalysts and have positive effects regarding the reduction of toxic compounds generated during the combustion of tobacco without affecting its taste.

[0012] Another similar patent [Meier, M.W., "Process for treating tobacco with catalytically active material for reducing toxic components in tobacco smoke", EP 1,234,511 26.02.2001] centers itself on the cigarette manufacturing process using the before mentioned additives without needing to use adhesive agents. The procedure consists of 1) distribute the catalytically active material inside the tobacco and 2) press this material onto the tobacco.

[0013] Therefore, it is desirable to have additives available to mix in with tobacco to reduce the quantity of toxic and cancerous substances present in tobacco smoke. Additives that otherwise avoid or at least minimize some of the known inconveniences of the technique.

EXPLANATION OF THE INVENTION

[0014] In accordance with a prime aspect of this invention, this invention provides the use of an additive that is mixed in with the tobacco to reduce the quantity of toxic and cancerous substances present in tobacco smoke, where such additive is selected among a group formed by:

- a) zeolytes in their acid, sodium or interchanged with iron forms;
- b) mesoporous aluminosilicates in their acid, sodium or interchanged with iron forms;
- c) mixtures of the above mentioned materials with iron oxides, cerium or zirconium; and

d) a mixture of the materials mentioned above.

[0015] According to another aspect, this invention provides a composition that consists of any form of tobacco i.e. soft, black, leaf, fine cut, hand rolling (RYO), pipe tobacco (MYO) or any other item capable of being smoked with at least one additive from the following list:

- a) zeolites in their acid, sodium and interchanged with iron forms;
- b) mesoporous aluminosilicates in their acid, sodium or interchanged with iron forms;
- c) mixtures of the above mentioned materials with iron oxides, cerium or zirconium;
- d) a mixture of the materials mentioned above.

[0016] Based on a different aspect, this invention provides a method for reducing the quantity of toxic and cancerous substances present in tobacco smoke, which includes the use of these additives dry mixed with the tobacco.

[0017] Based on a different aspect, this invention provides a method for preparing the composition according to the invention, which is comprised by placing the right amount of additive in contact with the tobacco and mixing both ingredients.

[0018] Based on a different aspect, this invention provides a KIT that administers the right amount of catalyst for preparing the above mentioned tobacco-additive mixture "on the spot". This kit includes separate compartments for tobacco and additive in the right proportions as well as instructions for preparing the mixture.

DESCRIPTION OF THE INVENTION:

[0019] According to the embodiment of this invention, the use of an additive that belongs to the group formed by the following materials used to reduce the presence of toxic and cancerous compounds in tobacco smoke are described.

Acid, sodium or interchanged with iron forms of BETA zeolites (H-BETA, Na-BETA, Na-Fe-BETA, Na-Ce-BETA, Na-Zr-BETA); acid, sodium or exchanged with iron forms of zeolite ZSM-5 (H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5, Na-Ce-ZSM-5, Na-Zr-ZSM-5); acid, sodium or interchanged with iron zeolite forms USY (H-USY, Na-USY, Na-Fe-USY, Na-Ce-USY, Na-Zr-USY); acid, sodium or interchanged with mesoporous aluminosilicate iron forms MCM-41 (Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41); acid, sodium or exchanged with aluminosilicate iron MCM-22 (Na-MCM-22, Na-Fe-MCM-22, Na-Ce-MCM-22, Na-Zr-MCM-22); mixtures of the above mentioned compounds with Fe, Ce or Zr oxides; and mixtures of these materials.

[0020] Preferably, the additive used is selected among the group formed by H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5, Na-Ce-ZSM-5, Na-Zr-ZSM-5, H-USY, Na-USY, Na-Fe-USY, Na-Ce-USY, Na-Zr-USY, Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, Na-MCM-22, Na-Fe-MCM-22, Na-Ce-MCM-22, Na-Zr-MCM-22, mixture of these with Fe, Ce or Zr oxides and mixtures of these materials.

[0021] According to the embodiment of this invention, the additive is selected from the group formed by the sodium and exchanged with iron zeolites or aluminosilicate forms, Fe, Ce or Zr oxides mixed with any of the above mentioned materials, and their mixtures.

[0022] In a preferred embodiment, the additive is selected between Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, its mixtures with Fe, Ce or Zr oxides and mixtures of these materials. The invention compositions are characterized by containing the above mentioned materials as additives. Therefore, according to the embodiment of this invention, the additive is selected from a group formed by:

- a) zeolites in their acid, sodium and exchanged with iron forms of BETA zeolite: H-BETA, Na-BETA, Na-Fe-BETA;
- b) acid, sodium and exchanged with iron forms of zeolite: H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5;
- c) acid, sodium and exchanged with iron forms of USY zeolite: H-USY, Na-USY, Na-Fe-USY;
- d) acid, sodium and exchanged with iron forms of mesoporous aluminosilicate MCM-41: Na-MCM-41, Na-Fe-MCM-41;
- e) acid, sodium and exchanged with iron forms of aluminosilicate MCM-22: Na-MCM-22, Na-Fe-MCM-22;
- f) mixture of Fe, Ce or Zr oxides with any of the above mentioned materials;
- g) mixtures of the above mentioned materials.

[0023] Preferably, the additive is selected between H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5, Na-Ce-ZSM-5, Na-Zr-ZSM-5, H-USY, Na-USY, Na-Fe-USY, Na-Ce-USY, Na-Zr-USY, Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, Na-MCM-22, Na-Fe-MCM-22, Na-Ce-MCM-22, Na-Zr-MCM-22, mixture of these with Fe, Ce or Zr oxides and mixtures of these materials. In an alternative embodiment, the additive is selected from the group formed by the sodium and exchanged with iron zeolites or aluminosilicate forms, Fe, Ce or Zr oxides mixed with any of the above mentioned materials, and their mixtures. In a preferred way, the additive is selected between the group formed by Na-MCM-41,

Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, its mixtures with Fe, Ce or Zr oxides and mixtures of these materials.

[0024] In an embodiment of this invention, the composition is characterized by the additive being found in concentrations between 0.5 and 15% of the tobacco weight. Preferably found in concentrations amounts between 2 and 7% of tobacco weight.

[0025] As has already been stated and unlike other applications that also use zeolites or related materials; in this patent, the considered additives in dust form are added and mixed directly with the tobacco fine cut without needing to use any type of adhesive agent or any other specific type of technology for preparing the mixtures. Among the additives of this invention, no toxic or fibrous materials are included. On the other hand, the use of additives belonging to the above mentioned group of materials allows obtaining important reductions in the generation of a considerably high amount of toxic and cancerous compounds generated when smoking tobacco (CO, nicotine, tars, aldehydes, etc.) apart from what is claimed in the state of the art documents, which refer only to the reduction of a few compounds (NO and NO_x, in the case of Cvetkovic et al., nitrosamines in the case of Jianhua et al. or NFDMP and polynuclear aromatic hydrocarbons (PAH) in the case of Radojicic et al.). On the other hand, as has already been stated, the materials proposed in this patent cause a very significant reduction in the amount of toxic and cancerous compounds present in tobacco smoke due to its role as cracking catalysts in the tobacco pyrolysis and combustion processes more than to its absorption properties, which is the basis of the mechanism proposed by some of the prior authors [Cvetkovic et al. And Jianhua and co.].

[0026] We must highlight that the use of additives and the methodology proposed in this patent produces results that are significantly better than the ones achieved in some of the mentioned patents, which also propose the use of some material listed in the above mentioned group. For example, the results described by Meier et al. [Meier M. W., Jost, W., Scanlan, F., EP 0 740 907] for the generation of tar or nicotine when the acid and sodium forms of BETA zeolite are used, make minimum differences evident regarding the reference cigarette, smoked without additive, while the results observed when using the procedure described in this patent produce an important reduction of these substances. This fact has become one of the main objectives of this invention. This improvement is even more noteworthy when the results of Meier et al. are compared with the ones obtained using other materials proposed herein for example, with MCM-41. On the other hand, this patent describes and makes special emphasis of the fact that a drastic reduction in very important certain toxic substances is produced, for example in CO, which is not mentioned in any of the reviewed patents that use materials related with the ones proposed in this work.

[0027] The proposed procedure can be used in a highly satisfactory way with any type of tobacco preparation (soft, black, leaf, fine cut, hand rolling, pipe tobacco and any other item capable of being smoked). Nevertheless, applying a few drops of water, ethanol or any other moistening agent can facilitate the manufacturing process. Additionally, as has already been mentioned, reductions in toxic compounds that are significantly greater than the ones described in other related patents are obtained using the described procedure. It is worth highlighting that even in those patents, which propose the possibility of using the additives with or without the adhesive agents [Meier M. W., Jost, W., Scanlan, F., EP 0 740 907], when the different examples are described, these are mixed in with the tobacco by vaporizing them into a zeolite suspension with C-Gel and LC-674, while this invention mixes the zeolites directly into the fine cut tobacco and, at most, a few drops of ethanol are used to moisturize the catalyst.

[0028] On the other hand, the Meier et al. Patent explicitly recognizes that in the smoking product, the catalyst is added to the tobacco using an adhesive. This is a very important fact since the presence of adhesive or the mixing of active element with other components can cause the undesired effects of interparticle diffusion or even partially or totally block the catalyst pores with the resulting loss of effectiveness.

[0029] Apart from the above mentioned, different types of equipment can be used for making cigarettes that facilitate, and can even improve, the incorporation of the additive to the fine cut tobacco like for example orbital or quick mixers, fluidized and entrained beds, among others, as well as sieves to separate and re-circulate the additive that has not stuck to the tobacco fibers. On the other hand, for other preparations different than conventional cigarettes, where the preparation of tobacco-additive mixtures must be performed manually by the smoker, a kit can be used with separate containers for tobacco and additive. This kit or dispenser provides the proper amount of catalyst for the preparation of soft, black, leaf, fine cut, hand rolling, pipe tobacco and any other item capable of being smoked. This kit can consist of a blister, where each cavity contains the selected amount (between 5 and 70 mg, in order to obtain a dose between 0.5 and 15 % of additive with respect to tobacco, preferably between 2 and 7% weight, which will usually be consumed in portions of around 1 g of tobacco), individual capsules that contain these quantities, a container that includes a calibrated or graduated spoon or any other type of calibrated dispenser.

[0030] This invention describes the use of catalysts with the required characteristics from this point of view since they possess a non fibrous morphology, are approximately spherical and of such a particle or aggregate size that in the proportions described in the examples, none are observed in the secondary filters used and therefore guarantees they are not going to travel through the conventional filter. For other types of applications, it may be necessary to adjust the particle size in order to guarantee this behavior.

[0031] As has been made evident in the prior section, different methods have been described for reducing the amount

of toxic and cancerous substances created from the combustion of tobacco, which are present in the primary and secondary smoke streams that are generated when smoking tobacco.

[0032] This patent describes the use of certain zeolites and other aluminosilicates and mesoporous solids in their neutral, acid or exchanged with metallic ion forms as well as modifications and/or mixtures of these materials with non-toxic metallic ions or with oxides from these metals as additives of tobacco to drastically reduce the amount of toxic and/or cancerous compounds that are generated when smoking and which appear in the primary and secondary tobacco smoke. These additives also reduce the fraction of condensable and non-condensable products which are generated during the combustion of tobacco without substantially altering their organoleptic characteristics while the amount of solid residue (coke) in the ashes increases.

[0033] These additives in dust form can be added and mixed directly with the tobacco without needing to use any type of adhesive or special technology. These are useful and can be used for this purpose with any direct smoking tobacco type (conventional cigarette packs, leaf and fine cut cigars, etc.) as well as with those forms that require prior handling in order to obtain the product that can be smoked (MYO, RYO, pipe tobacco, etc.).

[0034] Therefore, an objective of this invention refers to the use of additives for the direct elimination of a large part of these undesirable gas and condensable product compounds that are found in the tobacco smoke of direct consumable products (cigarette packs, leaf and fine cut cigars, etc.) as well as a kit that incorporates separate containers for tobacco and additive. This kit or dispenser can be used preferably for those forms that require prior handling in order to obtain the product that can be smoked (rolling tobacco-RYO-, pipe filling tobacco-MYO-, pipe tobacco, etc.)

[0035] The additives used in this invention have morphological and structural characteristics that are typical of molecular sieves. Therefore, the USY zeolite has a smaller Si/Al relation and a larger pore size than the ZSM-5 zeolite and a structure that is characterized for having large internal cavities that are essentially spherical ("supercages"), joined tetrahedrally by the pore apertures, defined by 12 oxygen atom rings (12 member or 12MR rings) [Boxiong S., Chunfei W., Rui W., Binbin G. and Cai L., "Pyrolysis of scrap tyres with zeolite USY", Journal of hazardous materials, in Press (2006)]. The ZSM-5 zeolite has a 10 member (10MR) ring system with a three dimensional network of interconnected sinusoidal and circular canals with a pore size of 5.3x5.6 Å and 5.1x5.5 Å and intersections between canals measuring 0.9nm [N. Kumar, "Synthesis, modification and application of high silica catalysts in the transformation of light hydrocarbons to aromatic hydrocarbons", N. Kumar, Ph.D. thesis, Abo Akademi University, Abo/Tuku, Finland, 1996]. The BETA zeolite has a structure with 12MR type orifices [J.M. Newsam, M.M.J. Tracy, W.T. Koetsier, Proc. R. Soc. Lond. A, 420 (1988), 375]. This zeolite presents a structure that is highly unorganized consisting in the aleatory growing of A and B polymorphs with tetragonal and monoclinic symmetries respectively, usually in an approximate ratio of 60:40 [Q, Li, A. Navrotsky, F. Rey, A. Corma, Micropor. Mater., 59 (2003), 177]. It presents two types of straight canals in the /a/ and /b/ directions with diameters of 7.3 x 6.8 Å for the tetragonal system and 7.3 x 6.0 Å for the monoclinic system and a sinusoidal canal in the /c/ direction measuring 5.5 x 5.5 Å. The intersection of these canals forms a system of pores that are readily accessible [J.C. Jansen, E.J. Creghton, S.L. Njo, H. Koningsveld and H. Bekkum, Catal. Today, 38 (1997), 205].

[0036] The material MCM-22 [M.K. Rubin, P. Chu, US patent 4954325, 1990] is a relatively recent aluminosilicate preparation that was obtained for the first time by Rubin et al. in 1990. The MCM-22 structure consists of two independent pore systems, one of them made up of two-dimensional canals with 10 member apertures (10MR) and the other one consisting of a supercage system with 12 member apertures (12MR). Due to this porous structure, the MCM-22 combines the behavior of both systems, the 10MR and 12 MR, which grant it some unique catalytic properties. The MCM-41 material is also a mesoporous aluminosilicate that was synthesized for the first time by Beck et al. in 1992 [J. S. Beck, J. C. Vartuli, G. J. Kennedy and C. T. Kresge, S. E. Schramm, Chem. Mater., 6 (1994), 1816]. The MCM-41 presents a hexagonal mesoporous composition with a highly regular pore system of a variable size between 1.5 and 10 nm, which grants it a considerably large surface area. This property is of great importance regarding the reduction of the harmful effects of tobacco.

[0037] All of these materials are described in detail in the bibliography regarding procedures for obtaining the material as well as their physical/chemical and structural characteristics.

[0038] Within the group of materials mentioned in this patent, the non acid forms, when used as additives for tobacco in the way described in this procedure, provide excellent results from the point of view of reducing the toxic and dangerous products present in tobacco smoke since they avoid the negative effects associated to the possible hydrolysis of lignocellulosic materials present in tobacco that can be produced when acid forms are used in environments with a high degree of humidity.

[0039] Table 1 shows the chemical and structural characteristics of the additives that are studied in this application, as representative examples of these type of materials. For all of them, the Si/Al ratio, the external surface and other characteristics can be modified within relatively wide intervals with different aims without substantially modifying the behavior and the general properties of the material.

[0040] Another important aspect is the size and shape of the catalyst particles. Particles of small size improve contact with the solid and the released gases but can travel easier through filters or the tobacco bed and enter the lungs.

Therefore, it is important to consider this aspect and reduce or eliminate the possibility of this occurring. In any case, it is very important that these types of additives not contain toxic compounds or elements or have a fibrous morphology that could be hazardous to health. The materials used have particle sizes of around 0.1-2 μm , which in many cases are found forming aggregates measuring 20-30 μm . Under the experimental conditions used in the examples described in this invention, the described materials with these particle sizes allow to achieve highly satisfactory results from a toxic compound reduction in tobacco smoke point of view without observing a significant presence of particles capable of traveling through the cigarette filters. However, for other types of smoking tobacco it will be necessary to optimize the particle size of additives so that these are present in a small enough size to produce good results but not so small that they travel through the cigarette filters or the tobacco bed.

[0041] In both the description and claims, the word "encompasses" and its synonyms do not intend to exclude other technical characteristics, additions, components or steps.

[0042] For the experts in the field, other objectives, advantages and characteristics of this invention will in part be derived from the description and in part from placing the invention into practice. The following examples provide an illustration and are not intended to limit this invention.

DETAILED DESCRIPTION OF AN EMBODIMENT OF THE INVENTION

Example 1. Comparative study of smoking cigarettes with and without additive.

[0043] With the objective of proving that the role of the additives proposed in this patent, the following were smoked: a) referenced commercial cigarettes and b) cigarettes that had additives added using a smoking machine that operated in accordance with the following operation variables:

Conditions for smoking cigarettes and generated products analysis

[0044]

- 5 cigarettes are smoked simultaneously following the specifications listed in standard ISO 3308 (drag 2 s long, 35 ml of inhaled volume, drag frequency 60 s and loss of drag pressure less than 300 Pa).
- The cigarettes are kept at room temperature and 60% relative humidity, keeping them in desiccators provided with a saturated solution of nitric sodium at least 48 hours prior to them being smoked.
- During the smoking process, the smoke including the CO, CO₂ and other non condensable products pass through the cigarette filter and enter a trap located immediately behind it. The non-condensable products are collected in a Tedlar bag for gases that is kept for post analysis by gas chromatography (GC) and the condensable products are collected in the cigarette filter and in the rear trap. This bag holds the condensable products that would have been directly inhaled by the smokers.
- The inhaling pressure of the smoking machine is around 150 cm of H₂O.
- The condensable products retained in the trap at the rear end of the filter are extracted with 2-propanol, ensuring that all the compounds collected in the trap are extracted. Then, the extracted material is dried with sodium sulfate and is kept for post analysis by GC.
- Determining the non-condensable fraction of CO and CO₂ content is obtained by GC using a thermal conductivity detector (GC-TCD) and a Porapack Q column in a SHIMADZU GC-14A unit that uses a calibration based on external patterns. The conditions for analysis are:

Gas carrier: He
 Injector temperature: 100°C
 Detector temperature: 110°C
 Injected volume: 250 μL

- The rest of non-condensable components will be analyzed by GC with a flame ionization detector (GC-FID) using a GAS-PRO column under the following conditions:

Gas carrier: He
 Injector temperature: 150°C
 Detector temperature: 230°C
 Injected volume: 150 μL

- The condensable compounds (extracted with 2-propanol) will be analyzed by GC mass spectrometry detector (GC-

MS) using a HP-5MS column under the following conditions:

Gas carrier: He
 Injector temperature: 50°C
 Detector temperature: 230°C
 Injected volume: 1 µL

- For determining the quantities obtained for each compound, a chromatographic peak integration of the area is performed and the corresponding response factors are used.

Conditions for making the cigarettes

[0045] In order to carry out all the tests, cigarettes are made by manually mixing the tobacco fiber with the catalyst by using a few drops of ethanol. This task was performed over a sieve to separate the catalyst that would not adhere to the tobacco and in this way achieving a nominal catalyst percentage in the mixtures that corresponded to the amount of catalyst that was initially weighed and an actual percentage, which was the one finally retained by the sample. Other agents alternative to ethanol that can help the tobacco-catalyst mixing process are water, glycerin and other similar solvents that do not affect the properties of tobacco and evaporate with relative ease. Nevertheless, the mixtures can also be performed in a satisfactory manner without needing to use any of these substances.

Characteristics of the samples used

[0046] The following lists the characteristics corresponding to some of the examples, which allow illustrating the results that can be achieved using the proposed additives. The nominal percentage for each type of additive is listed. The tobacco used for the reference cigarettes as well as for the different mixtures with additives has always been of the same brand of commercial soft tobacco.

a) Examples corresponding to the different mixtures of tobacco-additive

[0047] In all cases, a nominal percentage of 10% of additive weight is used. The cigarettes are made using the procedure described in "conditions for making the cigarettes" using the following listed additives:

Mixtures
Tobacco
Tobacco + H-MCM-22 10%
Tobacco + Na-MCM-22 10%
Tobacco + Na-Fe-MCM-22 10%
Tobacco + H-MCM-41 10%
Tobacco + Na-MCM41 10%
Tobacco + Na-Fe-MCM41 10%
Tobacco + Na-Fe-MCM-41 + CeO ₂ 10%
Tobacco + H-USY 10%
Tobacco + H-ZSM-5 10%
Tobacco + Beta 10%
Tobacco + Na-Beta 10%

b) Examples corresponding to tobacco-additive mixtures with different additive concentration.

[0048] The additive used in all cases is Na-Fe-MCM-41. The catalyst weight percentages are listed. The cigarettes are made using the procedure described in "conditions for making the cigarettes" using the following nominal concentrations (weight percentage):

<i>Mixtures</i>	<i>% additive</i>
Na-Fe-MCM-41 1%	1
Na-Fe-MCM-41 4%	4
Na-Fe-MCM-41 7%	7
Na-Fe-MCM-41 10%	10

Obtained results: a) Examples corresponding to the different mixtures of tobacco-additive

[0049] Tables 2, 3 and 4 list the results obtained when smoking the cigarettes using the cigarette preparation conditions, the smoking conditions, the conditions of generated product analysis and the examples from group a), which correspond to the different tobacco-additive mixtures. The values obtained for the following are listed:

- CO and CO₂, in mg of compound/cigarette
- quantity of some toxic products in mg of compound/cigarette
- percentage of the generated liquids, gases and ashes
- total particulate matter (TMP) in mg/cigarette calculated as:

$$m_{TPM} = \frac{m_1 - m_0}{q}$$

where

m_0 is the mass of the rear filter trap in mg before smoking

m_1 is the mass of the rear filter trap in mg after smoking q cigarettes

q is the number of cigarettes smoked

[0050] Tables 2 and 4 make evident that the proposed additives in their acid, sodium and exchanged with iron forms as well as their mixtures with Ce and Zr oxides when they are mixed in with tobacco in the proportions described provide a significant reduction in the amount of toxic compounds that appear in tobacco smoke. This reduction at the same time supposes a decrease of the potentially negative effects caused by tobacco smoke in active and passive smokers without causing any appreciable change in the organoleptic properties or in the taste and consistency of the tobacco and without any apparent generation of undesirable compounds. On the other hand, not only are the toxic compounds reduced but in general, the total amount of gases and liquids that are formed when smoking a cigarette (total particulate matter TMP, plus the liquid retained in the filter) also decrease in an appreciable way while the solid waste and ashes increase. When the smoking process is finished, the additives are retained in the ashes or in the tobacco that has not been smoked.

[0051] As has been stated before, the use of these additives cause an important reduction in the toxic substances present in tobacco smoke like for example, CO, CO₂, nicotine, etc., as well as in the total amount of liquid and gaseous products. For example Table 2 shows the results obtained for the production of CO and CO₂, expressed in mg of compound/cigarette for a reference cigarette and for mixtures with some of the additives, which can be considered representative of the rest. As can be seen, when the proposed additives are used, reductions in generated CO of about 24-88% were obtained with respect to the reference cigarette while the reduction in CO₂ formation can reach 0-84%. On the other hand, according to the data listed in table 3, and as has been explained, the studied materials also reduce the total amount of liquid and gaseous products generated. For example, reductions of around 37-97% are observed in the TMP while the solid residue generated increases. By way of example, table 4 lists the results obtained for the production of some of the toxic and cancerous compounds that appear in tobacco smoke. As can be seen in most cases, the use of proposed additives provides a reduction of more than 50% in most of the compounds. For example, when Na-MCM-41 is used as an additive, the following reductions with respect to the reference cigarette are observed. CO₂, 81.4%; CO, 84.4%; TPM, 97.1%; glycerin, 32.5%; neofitadieno, 72.1%; nicotine, 79.1%; acetone, 57.5%; acetaldehyde, 70.3%; hydroquinone, 79.7%; propionaldehyde, 49.3%; acrolein, 69.1%; crotonaldehyde, 62.2%; isobutiraldehyde, 66.7%; furane, 63.8% and benzene, 62.2%.

[0052] All the described mixtures can also be prepared using quick mixers, fluidized and entrained beds or any other type of equipment that helps to mix the tobacco fiber with the additive. Sieves can also be used for separating and recirculating the additive that has not stuck to the tobacco fibers. On the other hand, for other preparations different than conventional cigarettes where the preparation of tobacco-additive mixtures must be performed manually by the smoker,

a dispenser can be used that provides the right amount of catalyst for preparing the soft, black, leaf, fine cut, hand rolling, pipe tobacco and for any other item capable of being smoked. This dispenser can consist of a blister, where each cavity contains the selected amount (between 5 and 70 mg, in order to obtain between 0.5 and 7 % with respect to tobacco, which will usually be consumed in portions of around 1 g of tobacco), individual capsules that contain these quantities, a container that includes a calibrated or graduated spoon or any other type of calibrated dispenser. To prepare the ready to smoke product (MYO, RYO, pipe or other forms), the content of the calibrated dispenser is poured over the tobacco fiber and is carefully mixed by hand. This procedure guarantees excellent results as good as the ones listed in tables 2 through 4.

Obtained results: b) Examples corresponding to tobacco-additive mixtures with different additive concentration.

[0053] The influence of additive concentration in the additive-tobacco mixtures has also been studied. To accomplish this, mixtures with a catalyst nominal percentage between 1 and 10% were prepared using the above mentioned procedure. By way of example, tables 5 and 6 show the results obtained when Na-Fe-MCM-41 is used as an additive. As can be seen, the best results are achieved when the maximum concentration of additive is used even though the mixtures with 3-7% also obtain excellent results and can be adjusted depending on the reduction of toxic compounds that is desired.

Table 1. Typical values for the different properties of some of the additives studied in this patent (^aBJH; ^bmethod BET, adsorption isotherms for N₂; ^cmethod t, adsorption isotherms for N₂; ^dmeasured at P/P₀=0.995, adsorption isotherms for N₂; ^eXRF, ^fTPD for NH₃, ^gNMR).

PROPERTY	BETA	H-ZSM-5	H-USY	H-MCM-41	Na-MCM-41	Na-Fe-MCM-41
Pore size (nm) ^a	0.66x0.67 0.56x0.56	0.55	0.74	1.9	1.9	1.8
BET area (m ² /g) ^b	510	341	614	956	1174	1142
External surface area (m ² /g) ^c	183	38	28	115	120	234
Pore volume (cm ³ /g) ^d	0.17	0.18	0.35	0.62	0.78	0.70
Si/Al ^e Ratio	25	22	4.8	18	21	88
Acidity (mmol/g) ^f	2.1	2.0	2.1	0.75	0.43	0.40
Acidity associated to weak centers ^f	1.1	1.2	2.1	0.75	0.43	0.25
Acidity associated to strong centers ^f	0.97	0.88	-	-	-	0.15
T _{distortion} NH ₃ (°C) ^f weak acid centers	190	166	154	380	380	251
T _{distortion} NH ₃ (°C) ^f strong acid centers	370	416	-	-	-	490

Table 1.- Continued.

PROPERTY	H-MCM-22	Na-MCM-22	Na-Fe-MCM-22
Pore size (nm) ^a	0.71x0.71x1.8 1	0.71x0.71x1.8 1	0.71x0.71x1.8 1
BET area (m ² /g) ^b	410	440	400
External surface area (m ² /g) ^c	75	79	76
Pore volume (cm ³ /g) ^d	0.34	0.37	0.33
Si/Al ^e Ratio	18	18	18
Acidity (mmol/g) ^f	1.2	0.95	1.2
Acidity associated to weak centers ^f	0.82	0.79	0.82
Acidity associated to strong centers ^f	0.38	0.16	0.41
T _{distortion} NH ₃ (°C) ^f weak acid centers	300	300	300
T _{distortion} NH ₃ (°C) ^f strong acid centers	500	500	500

Table 2. Contains CO₂ and CO in tobacco smoke generated under controlled conditions.

Sample	CO ₂ (mg/cigarette)	CO (mg/cigarette)
Tobacco	29.08	4.74
Tobacco + H-MCM-22 10%	9.79	1.49
Tobacco + H-MCM-41 10%	4.74	0.57
Tobacco + Na-MCM41 10%	5.41	0.74
Tobacco + Na-Fe-MCM41 10%	7.02	1.10
Tobacco + Na-Fe-MCM-41 +CeO ₂	19.55	3.62

(continued)

<i>Sample</i>	<i>CO₂</i> <i>(mg/cigarette)</i>	<i>CO (mg/cigarette)</i>
Tobacco + H-USY 10%	19.24	1.90
Tobacco + H-ZSM-5 10%	30.00	2.99
Tobacco + H-Beta 10%	10.0	1.0
Tobacco + Na-Beta 10%	20.25	2.52

Table 3. TMP obtained when smoking tobacco under controlled conditions.

<i>Sample</i>	<i>TPM</i> <i>(mg/cigarette)</i>
Tobacco	6.88
Tobacco + H-MCM-22 10%	0.40
Tobacco + H-MCM-41 10%	0.82
Tobacco + Na-MCM41 10%	0.20
Tobacco + Na-Fe-MCM41 10%	1.12
Tobacco + Na-Fe-MCM-41 +CeO ₂	3.75
Tobacco + H-USY 10%	3.00
Tobacco + H-ZSM-5 10%	3.95
Tobacco + H-Beta 10%	4.31
Tobacco + Na-Beta 10%	3.30

Table 4. Generation (mg compound/cigarette) of different toxic compounds present in the gases and in the condensable products retained in the filter's rear trap when tobacco is smoked under controlled conditions.

Sample	Phenol	Glycerine	p-Cresol	Hydroquinone	Nicotine	Neofitaldine	Acetone	Propionaldehyde	Acrolein
Tobacco	0.0026	0.0120	0.0029	0.0158	0.3979	0.0280	0.0920	0.0144	0.0136
Tobacco + H-MCM-22 10%	---	---	---	---	0.0238	0.0014	0.0075	---	---
Tobacco + H-MCM-41 10%	0.0001	0.0010	0.0004	0.0007	0.0316	0.0018	0.0029	---	---
Tobacco + Na-MCM41 10%	---	0.0081	<0.0001	0.0032	0.0814	0.0078	0.0391	0.0073	0.0042
Tobacco + Na-Fe-MCM41 10%	---	---	---	0.0019	0.0583	0.0038	0.0457	0.0077	0.0070
Tobacco + Na-Fe-MCM-41 +CeO ₂	0.0013	0.0020	0.0014	0.0077	0.2270	0.0164	0.0491	0.0075	0.0073
Tobacco + H-USY 10%	---	0.0251	0.0010	0.0057	0.1460	0.0188	0.0587	0.0123	0.0079
Tobacco + H-ZSM-5 10%	0.0024	0.0347	0.0019	0.0110	0.3059	0.0244	0.0968	0.0336	0.0191
Tobacco + Beta 10%	0.0026	0.0402	0.0014	0.0108	0.2324	0.0173	0.0419	0.0097	0.0090
Tobacco + Na-Beta	---	0.0299	0.0003	0.0046	0.1453	0.0107	0.0295	0.0057	0.0059

Table 4.- Continued.

Sample	Crotonaldehyde	Isobutiraldehyde	Toluene	Benzene	Acetonitrile	Acetaldehyde	Furane
Tobacco	0.0045	0.0060	0.0013	0.0037	0.0156	0.1225	0.0116
Tobacco + H-MCM-22 10%	0.0012	---	<0.0001	0.0002	---	0.0107	0.0040
Tobacco + H-MCM-41 10%	---	---	---	0.0026	---	0.0069	0.0048
Tobacco + Na-MCM41 10%	0.0017	0.0020	0.0002	0.0014	---	0.0364	0.0042
Tobacco + Na-Fe-MCM41 10%	0.0027	0.0025	0.0004	0.0018	0.0023	0.0436	0.0052
Tobacco + Na-Fe-MCM-41 +CeO ₂	0.0019	0.0025	0.0004	0.0017	0.0056	0.0478	0.0053
Tobacco + H-USY 10%	0.0017	0.0030	0.0005	0.0024	0.0041	0.0578	0.0086
Tobacco + H-ZSM-5 10%	0.0045	0.0068	0.0013	0.0047	0.0175	0.1237	0.0124
Tobacco + Beta 10%	0.0029	0.0039	0.0006	0.0024	0.0067	0.0764	0.0082
Tobacco + Na-Beta	0.0018	0.0018	0.0005	0.0024	0.0050	0.0621	0.0099

Table 5. TMP obtained when smoking tobacco under controlled conditions.

<i>Sample</i>	<i>TPM (mg/cigarette)</i>
Tobacco	6.88
Tobacco+Na-Fe-MCM-41 1%	6.39
Tobacco+Na-Fe-MCM-41 4%	4.75
Tobacco+Na-Fe-MCM-41 7%	1.57
Tobacco+Na-Fe-MCM-41 10%	1.12

Table 6. Generation (mg compound/cigarette) of different toxic compounds present in the gases and in the condensable products retained in the filter's rear trap when tobacco is smoked under controlled conditions.

Sample	Phenol	Glycerine	p-Cresol	Hydroquinone	Nicotine	Neofitadieno	Acetone
Tobacco	0.0026	0.0120	0.0029	0.0158	0.3979	0.0280	0.0920
Tobacco + Na-Fe-MCM41 1%	0.0025	0.0083	0.0046	0.0140	0.3900	0.0280	0.0900
Tobacco + Na-Fe-MCM41 4%	0.0021	0.0047	0.0024	0.0103	0.3000	0.0217	0.0588
Tobacco + Na-Fe-MCM41 7%	0.0008	0.0031	0.0004	0.0040	0.0905	0.0078	0.0260
Tobacco + Na-Fe-MCM41 10%	---	---	---	0.0019	0.0583	0.0038	0.0257

Table 6.- Continued.

Sample	Propionaldehyde	Acrolein	Crotonaldehyde	Isobutir-aldehyde	Toluene	Benzene
Tobacco	0.0144	0.0136	0.0045	0.0060	0.0013	0.0037
Tobacco + Na-Fe-MCM41 1%	0.0085	0.0072	0.0028	0.0039	0.0006	0.0019
Tobacco + Na-Fe-MCM41 4%	0.0077	0.0067	0.0018	0.0032	0.0007	0.0019
Tobacco + Na-Fe-MCM41 7%	0.0050	0.0045	0.0013	0.0024	0.0006	0.0012
Tobacco + Na-Fe-MCM41 10%	0.0057	0.0040	0.0010	0.0020	0.0004	0.0012

Claims

1. The use of an additive that is mixed in with tobacco **characterized in that** this additive is selected from the following group formed by:

- a) zeolites in their acid, sodium or exchanged with iron forms;
- b) mesoporous aluminosilicates in their acid, sodium or interchanged with iron forms;
- c) mixtures of the above mentioned materials with iron oxides, cerium or zirconium; and
- d) a mixture of the materials mentioned above

for reducing the toxic and cancerous substances present in tobacco smoke

2. Use according to the previous claim **characterized in that** the additive is selected from a group formed by:

- a) zeolites in their acid, sodium and exchanged with iron forms of BETA zeolite: H-BETA, Na-BETA, Na-Fe-BETA;
- b) acid, sodium and exchanged with iron forms of zeolite: H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5;
- c) acid, sodium and exchanged with iron forms of USY zeolite: H-USY, Na-USY, Na-Fe-USY;
- d) acid, sodium and exchanged with iron forms of mesoporous aluminosilicate MCM-41: Na-MCM-41, Na-Fe-MCM-41;
- e) acid, sodium and exchanged with iron forms of aluminosilicate MCM-22: Na-MCM-22, Na-Fe-MCM-22;
- f) mixture of Fe, Ce or Zr oxides with any of the above mentioned materials;
- g) mixtures of the above mentioned materials.

3. Use according to the prior claim 2, **characterized in that** the additive used is selected among the group formed by H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5, Na-Ce-ZSM-5, Na-Zr-ZSM-5, H-USY, Na-USY, Na-Fe-USY, Na-Ce-USY, Na-Zr-USY, Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, Na-MCM-22, Na-Fe-MCM-22, Na-Ce-MCM-22, Na-Zr-MCM-22, mixture of these with Fe, Ce or Zr oxides; and mixtures of these materials.

4. Use according to any of the prior claims 1 through 3 **characterized in that** the additive is selected from the group formed by the sodium and exchanged with iron zeolites or aluminosilicate forms, Fe, Ce or Zr oxides mixed with any of the above mentioned materials, and their mixtures.

5. Use according to any of the prior claims 1 through 4 **characterized in that** the additive is selected between the group formed by Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, its mixtures with Fe, Ce or Zr oxides and mixtures of these materials.

6. Use of additive according to any of the prior claims 1 through 5 **characterized in that** the toxic and cancerous compounds are reduced in the main and secondary streams of tobacco smoke.

7. Composition that uses any form of tobacco i.e. soft, black, leaf, fine cut, hand rolling (RYO), pipe tobacco (MYO) or any other item capable of being smoked with at least one additive from the group formed by:

- e) zeolites in their acid, sodium and exchanged with iron forms;
- f) mesoporous aluminosilicates in their acid, sodium or exchanged with iron forms;
- g) mixtures of the above mentioned materials with iron oxides, cerium or zirconium;
- h) a mixture of the materials mentioned above.

8. Composition according to claim 7 **characterized in that** the additive is selected from a group formed by:

- h) zeolites in their acid, sodium and exchanged with iron forms of BETA zeolite: H-BETA, Na-BETA, Na-Fe-BETA;
- i) acid, sodium and exchanged with iron forms of zeolite ZSM-5: H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5;
- j) acid, sodium and exchanged with iron forms of USY zeolite: H-USY, Na-USY, Na-Fe-USY;
- k) acid, sodium and exchanged with iron forms of mesoporous aluminosilicate MCM-41: Na-MCM-41, Na-Fe-MCM-41;
- l) acid, sodium and exchanged with iron forms of aluminosilicate MCM-22: Na-MCM-22, Na-Fe-MCM-22;
- m) mixture of Fe, Ce or Zr oxides with any of the above mentioned materials;

n) mixtures of the above mentioned materials.

- 5 **9.** The composition according to claim 8 **characterized in that** the additive used is selected among the group formed by H-ZSM-5, Na-ZSM-5, Na-Fe-ZSM-5, Na-Ce-ZSM-5, Na-Zr-ZSM-5, H-USY, Na-USY, Na-Fe-USY, Na-Ce-USY, Na-Zr-USY, Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, Na-MCM-22, Na-Fe-MCM-22, Na-Ce-MCM-22, Na-Zr-MCM-22, mixture of these with Fe, Ce or Zr oxides; and mixtures of these materials.
- 10 **10.** The composition according to any of the prior claims 7 through 9 **characterized in that** the additive is selected from the group formed by the sodium and exchanged with iron zeolites or aluminosilicate forms, Fe, Ce or Zr oxides mixed with any of the above mentioned materials, and their mixtures.
- 15 **11.** The composition according to any of the prior claims 7 through 10 **characterized in that** the additive is selected between the group formed by Na-MCM-41, Na-Fe-MCM-41, Na-Ce-MCM-41, Na-Zr-MCM-41, its mixtures with Fe, Ce or Zr oxides; and mixtures of these materials.
- 20 **12.** The composition according to any of the prior claims 7 through 11 **characterized by** the additive being found in concentrations between 0.5 and 15% of the weight with respect to tobacco.
- 25 **13.** The composition according to claim 12 above **characterized by** the additive being found in concentrations between 2 and 7% of the weight with respect to tobacco.
- 30 **14.** The composition according to any of the prior claims 6 through 13 **characterized in that** the additive has a particle size between 0.1-2 μm .
- 35 **15.** Composition preparation procedure according to any of the prior claims 6 through 14 **characterized in that** it places the tobacco in contact with the right amount of additive and mixes both components.
- 40 **16.** The procedure according to previous claim 15 **characterized in that** water, ethanol, glycerin or a mixture of these is also added.
- 45 **17.** The procedure according to any of the previous claims 15 through 16 **characterized in that** quick mixers, fluidized and entrained beds or any other type of equipment is used to help mix the tobacco fiber and the additive; and sieves for separating and recirculating the additive that has not stuck to the tobacco fibers.
- 50 **18.** Kit for composition preparation according to any of the prior claims 6 through 14 **characterized in that** it has separate compartments for tobacco and additives in the right proportions as well as instructions for preparing the mixture.
- 55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/ ES 2007/000628

A. CLASSIFICATION OF SUBJECT MATTER

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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

A24B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CIBEPAT, EPODOC, WPI, CAS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 740907 A (F.J.BURRUS, SA) 06.11.1996; page 11, line 11 - page 12, line 25; tablas XI, XII.	1, 2, 6-8, 12-18
A	US 2005133054 A (FOURNIER et al.) 23.06.2005; the whole document.	1-18
A	US 3572348 A (NORMAN, VELLO et al.) 23.03.1971; the whole document.	1-18

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/ ES 2007/000628

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REFERENCES CITED IN THE DESCRIPTION

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