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(54) **Tobacco product carrying catalytically active material, its use in a smokers' article and a process for preparing it**

(57) The tobacco product carries on its surface catalytically active material for improving the burning process. The catalytically active material is selected from the group of crystalline and non-crystalline oxides and hydroxides of aluminium, e.g. gibbsite, having a particle size of 1 to 100 µm and a specific surface of 75 to 250 m^2/g. With the use of the catalyst in the tobacco, the amount of noxious compounds in the mainstream and sidestream smoke can be considerably reduced in the combustion process of the smokers' article during its consumption.

The said tobacco product is useful for smoker's articles comprising a filter, a tobacco rod and a wrapper. In such articles the tobacco rod consists of the tobacco product.

The process for preparing the tobacco product carrying catalytically active materials on its surface consists in treating tobacco with any of the above-mentioned catalytically active materials, without the use of binding agents, by the steps of distributing the catalytically active material on tobacco particles and pressing the catalytically active material on the tobacco particles, preferably with a defined degree of moisture. The treated tobacco product is useful for manufacturing smokers' articles, particularly cigarettes, having a reduced amount of toxic components in the smoke.

For carrying out the process, a device (1) comprising the following means is proposed:

a) at least one conveyor belt (11, 12) for carrying the tobacco T
b) a device (7) for supplying and distributing tobacco on the conveyor belt
c) at least one device (9; 10) for supplying and distributing catalytically active material (C1, C2) on the tobacco on the conveyor belt
d) at least one driving means for driving simultaneously the conveyor belt(s) (11, 12) and the devices (7, 9, 10) for supplying and distributing tobacco and catalytically active material.

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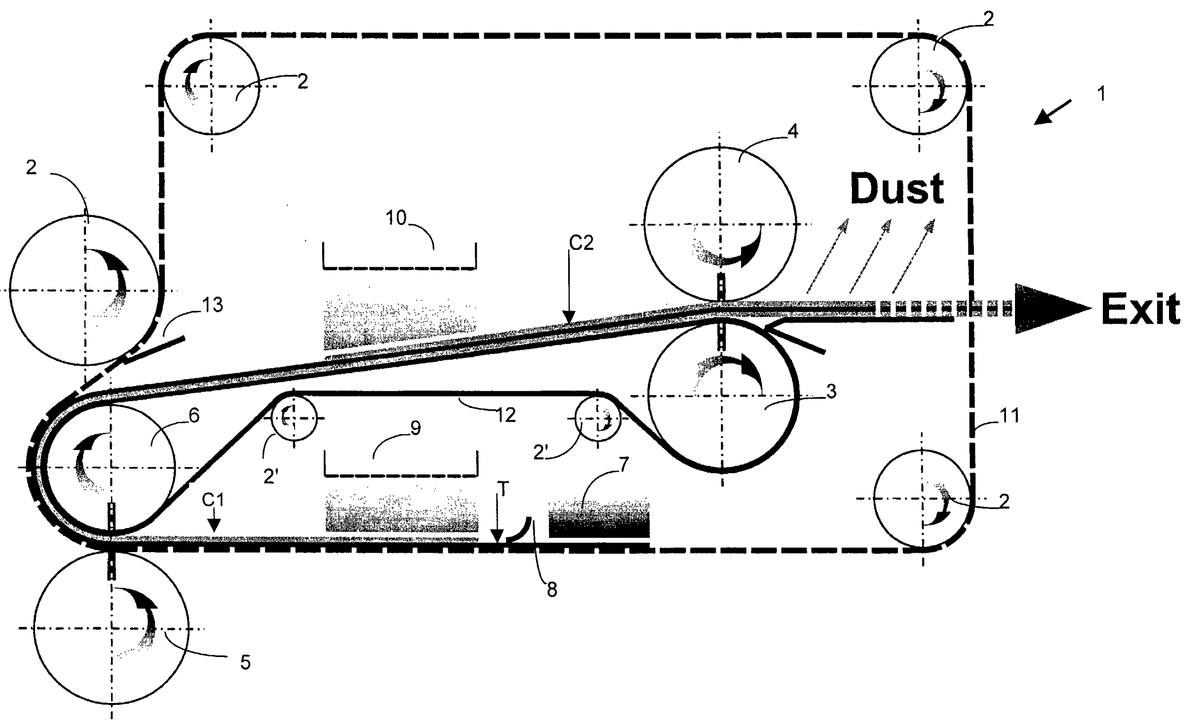

Fig. 1

Description

[0001] This invention relates to a tobacco product carrying catalytically active material, to articles for smoking containing such a tobacco product and more particularly to cigarettes which contain non-zeolitic catalysts in the tobacco rod, and to a process for treating tobacco with catalytically active material for reducing toxic components in tobacco smoke of smokers' articles, particularly of cigarettes.

[0002] As is well known, two kinds of smoke arise during the smoking of a cigarette, the mainstream smoke and the sidestream smoke. The mainstream smoke is the smoke which enters the mouth of the smoker when he draws on the cigarette through the filter part, while the sidestream smoke is the smoke which is released by the smouldering combustion of the cigarette in the interim phases. From technical literature it can be learned that approximately twice as much tobacco is burned during the glowing of a cigarette between the puffs than during the puffs.

[0003] Although in the prior art many — albeit unsatisfactory — means of reducing the mainstream smoke of noxious substances have been proposed, there has been no solution so far which makes it possible to remove the noxious substances from the sidestream smoke in sufficient manner.

[0004] Large pore zeolites were the first catalysts to be found to reduce significant amounts of undesirable compounds in sidestream as well as mainstream smoke (US-A-5,727,537, EP-A-0 740 907). However, zeolites have an inherent disadvantage in that larger PAH molecules like benzo(a)pyrine, one of the worst carcinogenic smoke constituents, are not reduced in the mainstream. The overall PAH reduction values are less than a 25 % in the mainstream compared to over 50 % in the sidestream. The disappointing performance in the mainstream has been assigned to the sieving effect of the pore openings in the zeolite framework structure (W.M.Meier and K.Siegmann, *Microporous and Mesoporous Materials*, 33 (1999) 307-310).

[0005] US-A-3,572,348 and US-A-3,703,901 suggest the use of zeolites for incorporating in tobacco material for reducing toxic compounds in the smoke. However, the proposed zeolite compounds contain substantial amounts of zinc besides palladium or platinum which are not suitable for several reasons for a product which cannot be recycled. These typical preparations known in petrochemistry of those days were heated in nitrogen (rather than burned in the presence of oxygen) and have little to do with a burning cigarette, and the process was pyrolysis rather than combustion. Mainstream and sidestream could not be distinguished in the set-up used. Moreover, the use of zinc is not permissible in open systems by environmental laws.

[0006] Described in EP-A-0 740 907 are smokers' articles wherein the tobacco comprises a catalyst of a zeolite compound. It is proposed that the catalyst in the tobacco be bound to the tobacco with or without a binding agent, such as silica gel or attapulgite, a meerschaum-like clay mineral. Attempts to fix catalyst particles on the tobacco by electrostatic deposition failed. The catalyst particles were observed to discharge on the tobacco fibers within seconds and sputtered. It was found that the use of binding agents has serious drawbacks because the catalytic activity of the material which is bound by the agent is affected. Without binding agent, the binding strength of the catalytically active material to the tobacco is not sufficient, and therefore a separation of the catalyst from the material can occur easily during the manufacturing process of smokers' articles or during transportation.

[0007] Zeolitic materials, both natural and synthetic, in appropriate form, can have catalytic capabilities for various kinds of organic reactions. Zeolites are microporous crystalline aluminosilicates which have definite crystal structures having a large number of cavities connected to each other by channels. These cavities and channels are absolutely uniform in size, and their dimensions can be determined by probe molecules as well as by crystal structure analysis. In most cases these data are known and do not have to be determined further. Since the dimensions of these pores are such that they sorb molecules of particular dimensions while rejecting those of larger dimensions, these materials have come to be known as "molecular sieves" and are utilized in a variety of ways to take advantage of these properties.

[0008] Such molecular sieves comprise a large variety of structural types (nearly 100; cf. W.M. Meier, D.H. Olson and Ch. Baerlocher, *Atlas of Zeolite Structure Types,* 4rd Edition, 1996, Elsevier) of crystalline aluminosilicates and isostructural materials with free pore diameters in the range of 0.3 to 1.3 nm or 3 to 13 Å. These aluminosilicates can be described as a rigid three-dimensional network of SiO_4 and AlO_4, wherein the tetrahedra are cross-linked by sharing of oxygen atoms, the ratio of all aluminium and silicon atoms to oxygen being 1:2. Such a network containing aluminium is negatively charged, and requires for charge balance one monovalent cation (e.g. Na or K) or half a divalent cation (e.g. Ca) for each Al in the network. These cations can be exchanged either completely or partially using standard ion exchange techniques. Cation exchange is a possible means of fine tuning the critical pore diameter in a particular application.

[0009] The pore volume of a typical zeolite is occupied by water molecules before dehydration. Dehydrated or activated zeolites are excellent sorbents for molecules which are small enough to pass through the apertures of the sieve. Syntheses using organic cations (such as tetrapropylammonium) have led to "high silica zeolites", which contain only few Al in the network, if any at all, and the composition approaches that of SiO_2. High silica zeolites are not unanimously considered to be zeolites; although they have the same kind of structure, their exchange capacities are comparatively low, their selectivities very different, and these materials are hydrophobic. Consequently they are referred to as zeolite-like molecular sieves in this specification, following widespread usage.

[0010] The sieving effect of the molecular sieve is based on the pore size. Sorption is also controlled by electrostatic interactions. Many of the chemical and physical properties are dependent upon the Al content of the zeolite. A rising Si/Al ratio means an increased temperature stability, up to 1000 °C in the case of silicalite, which is a molecular sieve with a pure SiO_2 framework structure. The selectivity of the inner surfaces changes from strongly polar and hydrophilic in the case of the molecular sieves rich in aluminium to a polar and hydrophobic in the case of a zeolite with a modulus > 400.

[0011] It has been discovered that the object of the present invention can be achieved by incorporating certain zeolites or zeolite-like molecular sieves or other catalytically active material, which fulfil the necessary catalytic criteria, into tobacco by distributing the catalytically active material regularly on conditioned tobacco and by pressing the catalytically active material on the tobacco. When incorporated into the tobacco rod of a cigarette, the catalytic properties of the material which is pressed on the tobacco can develop its catalytic activity completely. The advantage is that the pores of the material remain open. Moreover the method assures an even distribution of catalyst particles on the tobacco which is all-important.

[0012] Consequently there is a demand for smokers' articles, especially filter cigarettes, whose mainstream as well as sidestream smoke is significantly lower in noxious substances than with smokers' articles of prior art.

[0013] A first object of the present invention is therefore to provide a tobacco product having a considerably lower content of noxious compounds such as PAHs and nitrosamines in its smoke than known products and which is free of the above-mentioned drawbacks.

[0014] To overcome the shortcomings of large pore zeolites like NaY in the mainstream other catalyst materials have been investigated. Good results were obtained with oxides and hydroxides of aluminium. These materials should have a particle size of around 1 μm (not smaller and be dusty) and a surface of some 100 m^2/g or more.

[0015] A second object of the present invention is therefore to propose a method for binding catalytically active material to tobacco without the above mentioned drawbacks. The aim is therefore to provide a method for binding catalytically active material to tobacco without adhesive or other additives affecting the catalytically activity at least partially.

[0016] In a first aspect, one subject matter of the present invention is thus a tobacco product carrying on its surface catalytically active material for improving the burning process, wherein the catalytically active material is selected from the group of crystalline and non-crystalline oxides and hydroxides of aluminium

[0017] In a second aspect, a further subject matter of the present invention is a smokers' article comprising a filter, a tobacco rod and a wrapper in which the tobacco rod contains a catalyst selected from the group of oxides or hydroxides of aluminium. They are preferably acid or slightly acidic. The catalyst may contain Fe or Si in minor amounts (0 to 3 %). The catalyst can comprise particles consisting of single crystals or particles consisting of agglomerates of smaller crystals which are bound with a binder as kaolinite ("granulate"). Normally the catalyst is not highly crystalline. Typically the catalyst is selected from the compounds of the group alumina (Al-oxide), diaspore, natural or synthetic boehmite, natural or synthetic gibbsite, natural or synthetic doylite, natural or synthetic nordstrandite, natural or synthetic bayerite and hydrargillite. Typically the particle size of the catalyst is in the range of 1 to 100 μm (e.g. 3, 5 or 10 μm) and its specific surface is in the range of 75 to 250 m^2/g (e.g. 100 or 150 m^2/g).

[0018] In a third aspect a further subject matter of this invention is a process for treating of tobacco with catalytically active materials, e.g. zeolites as well as non-zeolites, like oxides of aluminium and silicon having a surface area of around 100 m^2/g or more, consisting of the steps of

a) distributing catalytically active material on tobacco,

b) pressing the catalytically active material on the tobacco.

[0019] Advantageously the catalytically active material is distributed evenly on the smoking tobacco. The tobacco can consist of leaves or reconstituted tobacco sheets, cut or uncut.

[0020] The method can be used with all types of suitable catalytically active material (including zeolitic catalysts or catalyst based on alumina) is suitable for reducing noxious compound in tobacco smoke.

[0021] Advantageously the tobacco is made reasonably soft by conditioning it, i.e. it has a defined degree of moisture. If the tobacco is too dry it is brittle and not suitable for receiving the catalytic material.

[0022] Preferably the catalyst is pressed on the tobacco by a single or double layer cylinder press. For a continuous working process such a press can work in combination with a conveyor belt. The process can be carried out with two or more distributing and pressing steps, e.g. on the upper and lower side of the tobacco. Normally the catalyst content in relation to the tobacco is about 4 - 8 % (wt/wt).

[0023] The following table lists a representative number of compounds which are suitable in the first aspect of the present invention.

Table A:

Aluminium oxides and hydroxides and characteristic lines according to Powder Diffraction File (PDF)					
Material		d-values (in A) of the 3 strongest lines			PDF#
Alumina (Al-oxide)	α-Al_2O_3	2.07	2.52	1.59	48-366
	β-Al_2O_3	1.40	11.97	2.68	10-414
	γ-Al_2O_3	1.98	1.40	2.39	10-425
		1.40	2.41	2.12	13-373
		1.40	1.98	2.39	29-63
	δ-Al_2O_3	1.39	2.60	2.46	46-1215
	Θ-Al_2O_3	1.39	2.84	2.73	23-1009
Diaspore	α-AlO(OH)	3.99	232	2.13	5-355
Boehmite, syn.	γ-AlO(OH)	6.32	1.85	3.16	49-133
Gibbsite, syn.	$Al(OH)_3$	4.85	4.37	2.39	33-18
Doylite	$Al(OH)_3$	4.79	437	2.39	38-376
Nordstrandite, syn.	$Al(OH)_3$	4.79	2.27	4.32	24-6
Bayerite, syn.	α-$Al(OH)_3$	2.22	4.71	4.35	20-11
	δ-$Al(OH)_3$	3.62	2.27	1.80	37-1377
Hydrargillite (see gibbsite)					

[0024] If not purely synthetic, these compounds frequently contain significant amounts of Si, Fe, Na and/or other elements. β-Alumina, widely listed as such, is not a true aluminium oxide, but at least in part a Na-aluminate. Many Al-compounds listed in Table A are alteration products, and are thus not highly crystalline. As indicated by the names, most of these compounds are also known minerals. They are environmentally safe, which is an important aspect in the present context.

[0025] In all these compounds Al is octahedrally coordinated by oxygen whereas in aluminosilicates (like felspars and zeolites) Al is in tetrahedral coordination.

Preparation and testing of cigarettes containing aluminium-based catalysts

[0026] For initial testing, the cigarettes were hand-rolled and the tobacco was loaded with 5 % of the catalyst. This was done by using a procedure wherein the tobacco is treated with catalytically active materials, consisting of the steps of

a) distributing catalytically active material on tobacco,

b) pressing the catalytically active material on the tobacco.

[0027] For PAH (polycyclic aromatic hydrocarbons) analyses, the method described by W.M.Meier and K.Siegmann [*Microporous and Mesoporous Materials,* 33 (1999) 307-310] was applied using a smoking machine. This method is based on a photoelectric PAH sensor in combination with a commercially available light scattering instrument which determines the total mass of particles smaller than 10 μm (PM-10). The signal of the photoelectric aerosol sensor is proportional to the amount of particle bound PAH. Light scattering reflects the number and size of particles, independently of chemical composition, and was found to agree with the results obtained with conventional methods in numerous tests. The method allows the simultaneous measurement of tar and PAH values.

Example 1

[0028] The tobacco blend (American blend type) was received from a tobacco lot and kept in a humidifier at 60% relative humidity. 5 % by weight of synthetic gibbsite (obtained from Fluka, Switzerland) was evenly distributed over the tobacco, and then pressed on by a heavy cylinder on a rubber belt.

[0029] Hand-rolled cigarettes of 1 g tobacco each were then prepared without filter tips, i.e. using tobacco with catalyst and without catalyst (reference). The measurements gave reductions of

48-53 % PAH (40-45 % tar) in the mainstream

44-46 % PAH in the sidestream

Example 2

[0030] Following the same procedure as described in example 1, but using α-alumina (supplied by Dr. Markus Meier, Sierre, Switzerland) and tested by X-ray diffraction. These gave the following results

in mainstream 49% reduction in PAH (50 % in tar)

in sidestream 45 % reduction in PAH (43 % in tar)

[0031] Note that the PAH reduction values in the mainstream are very much higher than those recorded for zeolite type catalysts (less than 20 % overall measured by the same method).

[0032] A smoking panel noted a smoother taste without off-taste in the products of the above examples.

[0033] The method of the second aspect of the present invention is illustrated by the accompanying drawing showing a double layer cylinder press adapted to the method according to the present invention.

[0034] Figure 1 shows a double layer cylinder press 1 equipped with conveyor belts 11,12 and devices 7, 8, 9, 10 which are adapted to the present method. A first conveyor belt 11 is carried by the cylinders 2 and 6. Tobacco is distributed on the belt 11 by the tobacco dispenser 7. A flattener 8 is responsible for regularizing the distributed tobacco T. A suitable amount of catalytically active compound C1 is layered on the tobacco layer T by a catalyst supply device 9. After this step the belt 11 moves into a first cylinder press formed by the cylinders 5 and 6. These cylinders exercise an adjustable pressure on the tobacco/catalyst layer T, C1 for binding the catalyst on the soft tobacco particles. In the first cylinder press, a second conveyor belt joins to the tobacco/catalyst layer at the catalyst side. The two conveyor belts carry the tobacco layer around the cylinder 6: the layer is now turned, i.e. the catalyst layer C1 is on the lower side of the layer and directly on the second conveyor belt 12, and is supported by this belt, whereas the first belt 11 is moving away from the tobacco layer. A scraper 13 cleans the first belt of tobacco particles, which fall back on the tobacco layer T. Then this layer moves on the second belt 12, passing a second catalyst supply 10, where a further layer C2 of catalytically active material is put on the tobacco layer T. Subsequently the layers C1, T, C2 are introduced into a second cylinder press, formed by the cylinders 3 and 4, which exercise again a suitable pressure on the tobacco layer, carrying on both sides a catalyst layer. In this step the loose catalyst is also bound on the tobacco particles of the layer on the belt 12. After the passage of the second cylinder press, the dust of catalyst not bound is removed, and the tobacco carrying a catalytically active compound exits, and is ready for direct use or storage. Simpler devices based on the same principle may also be applied.

[0035] For example, acidic and hydrophilic zeolites, saturated with water, including zeolites X, Y, L, mordenite and BETA, are used in the tobacco and are bound to the tobacco, without a binding agent, according to the present invention. At higher temperatures, these molecular sieves function as catalysts and, with respect to the noxious components of the smoke, have positive effects during combustion of the tobacco without a residue being left in the ashes which is harmful to the environment. During the smoking of tobacco articles which are equipped in the aforementioned way, the noxious substances, such as lower aldehydes, nitrosamines and the like, are considerably reduced in the mainstream smoke and in the sidestream smoke, without affecting the taste.

Example 3

[0036] The tobacco blend type (Amercan blend Type) was received from a tobacco lot ready for cigarette manufacture and kept in a humidifier. 5% by weight of synthetic faujasite in powder form (obtained from CU Uetikon, Switzerland) were pressed on the tobacco in using a cylinder press rolled on a rubber belt. Hand rolled cigarettes of 1 g each were then prepared. In the sidestream a reduction of 50 % of PAH was observed using the method described by Meier and Siegmann, Microporous an Mesoporous Materials, 33 (1999) 307.

Example 4

[0037] Following the same procedure as described in Example 1 but using synthetic gibbsite (obtained from Fluka, Switzerland) instead of faujasite was also tried. In the sidestream a reduction of 44 % of PAH was observed in this instance. In both instances the amount of loosely attached catalyst was found to be significantly below 10 % of the total amount of catalyst.

Claims

1. Tobacco product carrying on its surface catalytically active material for improving the burning process, wherein the catalytically active material is selected from the group of crystalline and non-crystalline oxides and hydroxides of aluminium.

2. Tobacco product according to claim 1 wherein the catalytically active material is bound to the surface, wherein the catalytically active material is preferably pressed into the tobacco surface so as to be bound without an adhesive in order to prevent the catalytically active material from being partially or completely inactivated by closed pores.

3. Tobacco product according to claim 1 or 2, wherein the oxides and hydroxides of aluminium are acid or slightly acidic.

4. Tobacco product according to one of the claims 1 to 3, wherein the oxides and hydroxides of aluminium contain Fe in an amount of less than 3 %.

5. Tobacco product according to one of the claims 1 to 3, wherein the oxides and hydroxides of aluminium contain silicon in an amount of less than 3 %.

6. Tobacco product according to one of the claims 1 to 5, wherein the catalyst is not highly crystalline, or it comprises particles consisting of single crystals, or it comprises a granulate consisting of agglomerates of crystals which are bound to each other with a binder, e.g. kaolinite.

7. Tobacco product according to one of the claims 1 to 6, wherein the catalyst is selected from the compounds of the group alumina (Al-oxide), diaspore, natural or synthetic boehmite, natural or synthetic gibbsite, natural or synthetic doylite, natural or synthetic nordstrandite, natural or synthetic bayerite and hydrargillite.

8. Tobacco product according to one of the claims 1 to 7, wherein the particle size of the catalyst is in the range of 1 - 100 µm, and its specific surface is in the range of 75 to 250 m^2/g.

9. Tobacco product according to one of the claims 1 to 8, wherein the tobacco consists of cut or uncut tobacco leaves or reconstituted tobacco sheets.

10. A smokers' article comprising a filter, a tobacco rod and a wrapper, wherein the tobacco rod consists of a tobacco product according to one of the claims 1 to 9.

11. Use of a catalytically active material comprising an oxide or hydroxide of aluminium for adding to the tobacco of a tobacco rod of a smokers' article for reducing the amount of noxious compounds in the mainstream and side-stream smoke in the combustion process of the smokers' article during its consumption.

12. Use according to claim 11, wherein the catalytically active material is selected from the group consisting of alumina, diaspore, natural or synthetic boehmite, natural or synthetic gibbsite, natural or synthetic doylite, natural or synthetic nordstrandite, natural or synthetic bayerite and hydrargillite.

13. Use according to claim 12 wherein the catalytically active materials comprise finely ground natural counterparts of oxides and hydroxides of aluminium and granulated using a binder such as kaolinite.

14. A process for preparing a tobacco product according to one of the claims 1 to 8 having bound catalytically active materials on its surface, consisting in treating of tobacco with catalytically active materials without the use of binding agents by the steps of

a) distributing catalytically active material on tobacco

b) pressing the catalytically active material on the tobacco.

15. The process of claim 14, wherein the tobacco consists of cut or uncut tobacco leaves or reconstituted tobacco sheets.

16. The process of claim 14 or 15, wherein the catalytically active material is selected from a group consisting of zeolites and acidic oxides of aluminium and silicon.

17. The process of one of the claims 14 to 16, wherein the tobacco is made reasonably soft by conditioning it, i.e. by conferring a defined degree of moisture.

18. The process of one of the claims 14 to 17, wherein the catalyst is pressed on the tobacco by a single or double layer cylinder press.

19. The process of claim 18, wherein the tobacco and the catalytically active material are moved with a conveyor belt into the cylinder press.

20. The process of one of the claims 14 to 19, wherein additional distributing and pressing steps are carried out.

21. The process of one of the claims 14 to 20, wherein the surface area of the catalytically active compound is at least 100 m^2/g.

22. The process of one of the claims 14 to 21, wherein the content of catalytically active compound in relation to the tobacco is about 4 -8 % (wt/wt).

23. A device (1) for carrying out the process of one of the claims 14 to 22 comprising the following means:

a) at least one conveyor belt (11, 12) for carrying the tobacco T
b) a device (2) for supplying and distributing tobacco on the conveyor belt (11)
c) at least one device (9, 10) for supplying and distributing catalytically active material (C1, C2) on the tobacco on the conveyor belt
d) at least one driving means for driving simultaneously the conveyor belt(s) and the devices for supplying and distributing tobacco and catalytically active material.

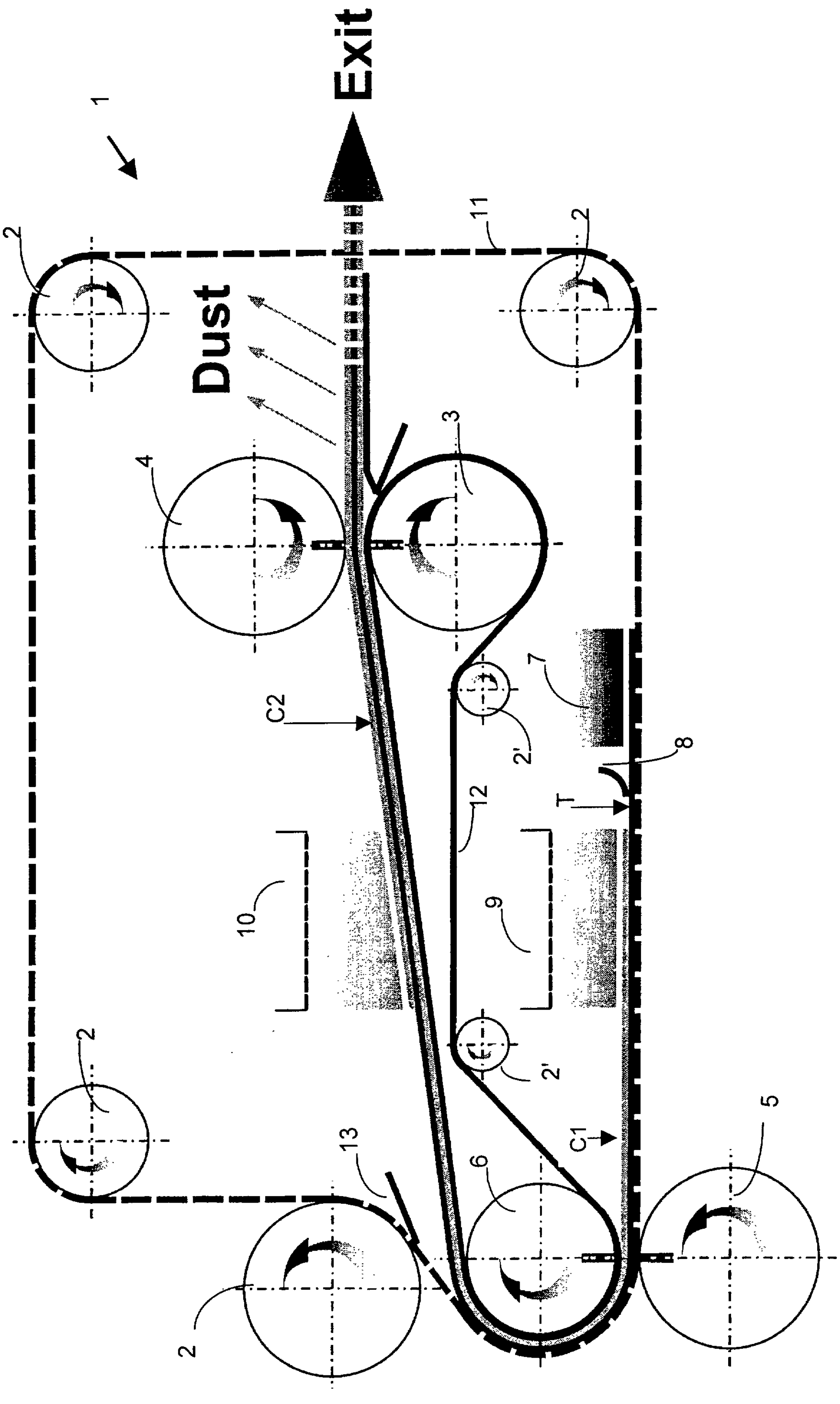

Fig. 1