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(54) **FILTER FOR SMOKING ARTICLE, SMOKING ARTICLE, AND PROCESS FOR PRODUCING FILTER FOR SMOKING ARTICLE**

(57) A filter for a smoking article, comprising composite particles made of core particles having an average particle diameter of 200 μm to 1000 μm , and nanoparticles supported on at least a part of a surface of each of the core particles, the nanoparticles being made of a hydrotalcite compound and having an average particle diameter of 200 nm or less.

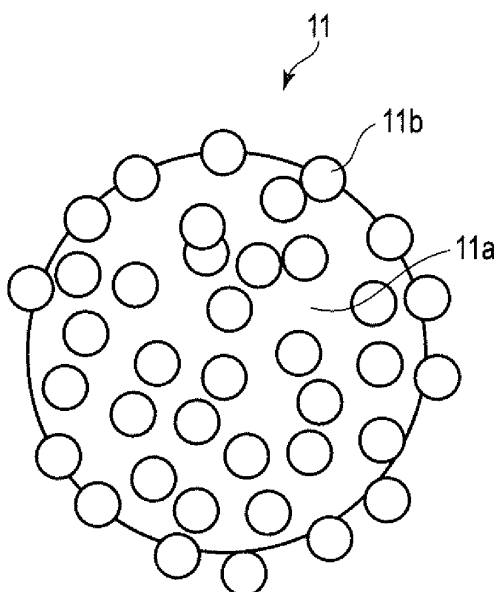


FIG. 1

Description

FIELD

5 **[0001]** The present invention relates to a filter for a smoking article, a smoking article, and a method of preparing a filter for a smoking article.

BACKGROUND

10 **[0002]** In smoking articles such as a cigarette, adsorbent particles are added to a filter to adsorb and remove chemical components in mainstream smoke. Activated carbon particles are typically used as the adsorbent particles, but attempts have been made to use various adsorbent particles. For example, it has been reported that hydrotalcite particles having an average particle diameter of 200 to 800 μm are added to a cigarette filter to selectively remove formaldehyde in mainstream smoke (Patent Document 1).

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Prior Art Document

Patent Document

20 **[0003]** Patent Document 1: International Publication No. WO 2003/056947

SUMMARY

TECHNICAL PROBLEM

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[0004] It is generally known that when the particle diameter of the adsorbent particles is reduced to increase the specific surface area, the adsorption ability is improved. The present inventors have attempted to improve the adsorption ability by reducing the particle diameter of hydrotalcite particles to the nano level and adding the hydrotalcite particles to a cigarette filter. As a result, they have found a problem that the particles are not suitable for use as an adsorbent of a cigarette filter due to the remarkable increase in airflow resistance.

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[0005] Therefore, it is an object of the present invention to provide a filter for a smoking article which enables more effective removal of formaldehyde in mainstream smoke without excessively increasing airflow resistance.

SOLUTION TO PROBLEM

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[0006] According to one aspect of the present invention, there is provided a filter for a smoking article, comprising composite particles made of:

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core particles having an average particle diameter of 200 μm to 1000 μm , and nanoparticles supported on at least a part of a surface of each of the core particles, the nanoparticles being made of a hydrotalcite compound and having an average particle diameter of 200 nm or less.

[0007] According to another aspect, there is provided a smoking article comprising:

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the above-mentioned filter for a smoking article; and a tobacco rod connected to one end of the filter for a smoking article.

[0008] According to still another aspect, there is provided a method of preparing a filter for a smoking article, comprising:

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stirring an aqueous suspension containing core particles having an average particle diameter of 200 μm to 1000 μm and nanoparticles made of a hydrotalcite compound and having an average particle diameter of 200 nm or less, and then drying the suspension to prepare composite particles made of the core particles and the nanoparticles supported on at least a part of a surface of each of the core particles, and incorporating the composite particles into a filter for a smoking article.

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ADVANTAGEOUS EFFECTS

[0009] According to the present invention, it is possible to more effectively remove formaldehyde in mainstream smoke

without excessively increasing airflow resistance.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010]

FIG. 1 is a view schematically showing an example of a composite particle made of a core particle and nanoparticles.

FIG. 2 is an exploded perspective view showing an example of a filter of the present invention.

FIG. 3 is a graph showing filter airflow resistance of a composite particle-containing filter and a nanoparticle-containing filter.

FIG. 4 is a graph showing filter airflow resistance of a composite particle-containing filter and a core particle-containing filter.

FIG. 5 is a view schematically showing a cigarette prepared in the Examples.

Fig. 6 is a view showing an apparatus for measuring formaldehyde in cigarette mainstream smoke.

FIG. 7 is a graph showing the formaldehyde reduction rate of cigarettes.

FIG. 8 is a graph showing the adhesion strength of hydrotalcite particles to core particles.

FIG. 9 is a graph showing the relationship between the particle diameter of hydrotalcite particles and the formaldehyde adsorption rate.

FIG. 10 is a graph showing the relationship between the particle diameter of hydrotalcite particles and the airflow resistance.

DETAILED DESCRIPTION

[0011] Hereinafter, the present invention will be described, but the following description is for the purpose of detailed explanation of the present invention and is not intended to limit the present invention.

[0012] A filter for a smoking article of the present invention comprises composite particles made of:

core particles having an average particle diameter of 200 μm to 1000 μm , and
nanoparticles supported on at least a part of a surface of each of the core particles, the nanoparticles being made
of a hydrotalcite compound and having an average particle diameter of 200 nm or less.

[0013] FIG. 1 schematically shows an example of a composite particle 11 made of a core particle 11a and nanoparticles 11b. As shown in FIG. 1, the nanoparticles 11b are supported on at least a part of the surface of the core particle 11a.

[0014] The core particle preferably has a function as an adsorbent particle. When the core particle has a function as an adsorbent particle, it is preferable that the nanoparticles do not cover the entire surface of the core particle. When the core particle has a function as an adsorbent particle and has pores on the surface thereof, the nanoparticles may penetrate into the pores, but at least a part of the nanoparticles are preferably supported on the surface of the core particle excluding the surface of the pores.

[0015] In order for the core particle to efficiently adhere the nanoparticles to the surface thereof, it is preferable that the core particle has a water retention property. The water retention property refers to the property of retaining water on the surface of the core particle. Specifically, the water retention property refers to the property of retaining water on the surface of the core particle because the surface of the core particle is hydrophilic and/or porous.

[0016] The water retention property of the core particle can be quantified by the water retention rate defined below.

[0017] 1 g of core particles are immersed in 10 mL of water, and after 1 minute has passed, the mixture is filtered using a metal mesh (0.1 mm) to separate the core particles and water. The weight of the separated core particles is measured. From the measured weight, the water retention rate of the core particles is obtained by the following equation.

[0018] Water retention rate (%) = $\{[(\text{Weight of core particles after filtration through metal mesh}) - (\text{Weight of core particles before immersion in water})] / (\text{Weight of core particles before immersion in water})\} \times 100$

[0019] The core particles preferably have a water retention rate of 70% or more, more preferably 70 to 150%, and even more preferably 70 to 100%.

[0020] As the core particles, for example, porous particles can be used. More specifically, as the porous particles, porous particles used as an adsorbent in a filter for smoking articles, such as activated carbon particles, silica particles, hydrotalcite particles, calcium phosphate particles, or zeolite particles can be used. Preferably, activated carbon particles are used as the porous particles. The activated carbon particles preferably have a BET specific surface area of 400 to 2800 m^2/g . As the core particles, non-porous particles can also be used, for example, calcium carbonate particles, saccharide particles (e.g., particles made of monosaccharide, disaccharide, oligosaccharide, polysaccharide, or any combination thereof), cellulose particles, cellulose triacetate particles, and the like can be used.

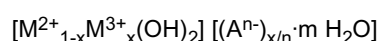
[0021] The core particles have an average particle diameter of 200 μm to 1000 μm , preferably an average particle

diameter of 300 μm to 700 μm , more preferably an average particle diameter of 400 μm to 600 μm . In the present specification, the average particle diameter of the core particles refers to a value measured using a digital image of the particles photographed with a CCD camera, for example, a value measured using an image analysis type particle size distribution measuring apparatus (Camsizer, Retsch technology). The average particle diameter of the nanoparticles refers to a value measured using a transmission electron microscope (TITAN 80-300, FEI Co.). The average particle diameter of the core particles and the nanoparticles can be obtained by randomly selecting a statistically sufficient number of particles (for example, 30 particles), measuring the particle diameter, and obtaining the arithmetic mean. The average particle diameter of the composite particles can be measured in the same manner as the core particles.

[0022] The nanoparticles have an average particle diameter of 1 to 200 nm, preferably 10 nm to 150 nm, more preferably 10 nm to 50 nm. The nanoparticles are made of a hydrotalcite compound.

[0023] The hydrotalcite compound constituting the nanoparticles has a layered structure in which a large number of octahedral layers of a metal hydroxide are laminated, and an anion is intercalated between these layers. The octahedral layer is called a host and exhibits basicity. The removal of formaldehyde achieved by the hydrotalcite compound is believed to result from the basicity of the host and from ion exchange action performed by the intercalated anion. The hydrotalcite compound may be natural or synthetic.

[0024] The hydrotalcite compound is represented by the following general formula:



wherein M^{2+} is a divalent metal ion selected from the group consisting of Mg, Zn, Ni and Ca ions; M^{3+} is Al ion; A^{n-} is an n-valent anion selected from the group consisting of CO_3 , SO_4 , OOC-COO , Cl, Br, F, NO_3 , $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, alkenyl acid and a derivative thereof, malic acid, salicylic acid, acrylic acid, adipic acid, succinic acid, citric acid and sulfonic acid anions; x satisfies $0.1 < x < 0.4$; and m satisfies $0 < m < 2$.

[0025] In the above general formula, it is preferable that M^{2+} is an Mg ion, M^{3+} is an Al ion, A^{n-} is CO_3^{2-} or SO_4^{2-} , x satisfies $0.1 < x < 0.4$, and m satisfies $0 < m < 2$. The Mg-Al based hydrotalcite compound is stable in the case where the value of x falls within the range of 0.20 to 0.33. The above general formula is most preferably represented by $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$.

[0026] The Mg-Al based hydrotalcite compound can be prepared by adding an alkali carbonate or both an alkali carbonate and a caustic alkali to an aqueous solution containing a water-soluble magnesium salt and either a water-soluble aluminum salt selected from aluminum sulfate, aluminum acetate and alum or aluminic acid, and carrying out the reaction while maintaining the pH of the reaction mixture at 8.0 or more. The obtained hydrotalcite compound can be pulverized and classified, thereby preparing nanoparticles having an average particle diameter of 200 nm or less.

[0027] For both the core particles and the nanoparticles, those prepared according to a known method may be used, or commercially available products may be used.

[0028] Composite particles made of the core particles and the nanoparticles can be prepared as described below. A suspension containing the nanoparticles and the core particles in water can be stirred and then dried, thereby preparing composite particles in which the nanoparticles are supported on the surface of each of the core particles.

[0029] As the core particles and the nanoparticles, those described above can be used. The core particles preferably have a water retention rate of 70% or more, more preferably 70 to 150%, and even more preferably 70 to 100%. The higher the water retention rate of the core particles (i.e., the higher the ability to retain water on the surface), the higher the rate of supporting the nanoparticles. This is because the core particles and the nanoparticles are bound mainly by the liquid bridge adhesion force in the suspension, and thus a higher water retention rate of the core particles leads to a higher liquid bridge adhesion force. On the other hand, when the water retention rate is too high, aggregation of the composite particles occurs and it becomes difficult to uniformly add the composite particles to a filter. Therefore, a water retention rate of 70 to 100% is particularly desirable from the viewpoint of production suitability. Also, after drying the suspension, the nanoparticles are supported on the surface of the core particles mainly by the Van der Waals force, and the adhesion is maintained.

[0030] In preparing the composite particles, the core particles and the nanoparticles are mixed in a weight ratio of, for example, 1000 : 1 to 1 : 1, preferably in a weight ratio of 100 : 1 to 2 : 1. When mixing 20 mg of core particles and 10 mg of nanoparticles, these particles can be added to, for example, 30 to 1000 μL of water to prepare a suspension. Such a suspension can be dried at 80 to 200°C for 5 to 120 minutes to obtain a sample containing the composite particles. The drying is preferably carried out until the entire amount of moisture is removed.

[0031] When all of the used nanoparticles are not supported on the core particles, the sample contains nanoparticles not supported on the core particles. In this case, the composite particles and the nanoparticles may be separated using a sieve.

[0032] When the rate (supporting rate) of the nanoparticles supported on the core particles is low, the treatment for supporting the nanoparticles on the core particles may be repeated. Specifically, after preparing the composite particles,

the composite particles and the nanoparticles are separated using a sieve, the separated nanoparticles are suspended in water, and the obtained suspension is mixed with the separated composite particles and then dried. This enables additional nanoparticles to be further adhered to the composite particles. By repeating this operation, the supporting rate can be increased.

[0033] The composite particles can be added in an amount of generally 10 to 100 mg, preferably 15 to 40 mg, to a filter having a size of 7.7 mm in diameter and 27 mm in length. The composite particles can generally be added to account for 3 to 33% of the total volume of the filter, preferably 5 to 13% of the total volume of the filter.

[0034] The composite particles can be incorporated into a filter for smoking articles to prepare a filter for a smoking article in various forms as follows.

(1) A filter in which the composite particles are dispersed in a filter material, for example, a fiber tow such as cellulose acetate, or nonwoven fabric.

(2) A filter shaped from a paper sheet obtained by making a paper from a paper raw material containing the composite particles.

(3) A filter composed of two or more segments wherein at least one of the segments is the filter of (1) or (2). In this case, the other segment(s) can be conventional cellulose acetate filter(s) or charcoal filter(s).

(4) A filter in which the composite particles are filled in a space (filter cavity portion) between two or more filter plugs arranged to be separated from each other. In this case, the filter plug may be a conventional cellulose acetate filter or a charcoal filter, or it may be the filter of (1) or (2). When there are two or more spaces, it is sufficient to fill the composite particles in at least one space, and activated carbon particles can be filled in other spaces. An example of this filter is shown in FIG. 2

[0035] In the filter 10 shown in FIG. 2, the composite particles 11 are arranged in a space (filter cavity portion) between two filter plugs 12 arranged to be separated from each other, and plug wrapping paper 13 is wound around the two filter plugs 12.

[0036] In the following description, a filter incorporating the composite particles is also referred to as a composite particle-containing filter. The composite particle-containing filter can be incorporated into any smoking article, in particular a combustion type smoking article that burns the tobacco filler, such as a cigarette, or a non-combustion type inhalation article that does not burn the tobacco filler, such as a heating type inhalation article. For the heating type inhalation article, reference can be made, for example, to WO 2006/073065 or WO 2010/110226. For example, a combustion type smoking article, such as a cigarette, can be prepared by connecting a tobacco rod containing a tobacco filler to one end of a composite particle-containing filter. Alternatively, for example, a non-combustion type smoking article, such as a heating type inhalation article, can be prepared by disposing a composite particle-containing filter at one end or both ends of a tubular member forming a cavity inside, and arranging a flavor source in the cavity.

[0037] The composite particle-containing filter is less likely to increase the filter airflow resistance compared to a filter with the nanoparticles directly added (see Experiment 1 below). When the composite particles are added in an amount of 10 to 100 mg to a filter having a diameter of 7.7 mm and a length of 27 mm, the composite particle-containing filter can exhibit a filter airflow resistance of 40 to 80 mmH₂O, for example. Thereby, when the composite particle-containing filter showing the above filter airflow resistance is incorporated into a cigarette, the obtained cigarette can exhibit cigarette airflow resistance of 80 to 120 mmH₂O, for example.

[0038] In addition, when the composite particle-containing filter is incorporated into a cigarette, the obtained cigarette can more effectively remove formaldehyde in mainstream smoke (see Experiment 2 below).

Examples

Experiment 1: Filter airflow resistance

(1-1) Preparation of composite particle-containing filter

[0039] Hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$; average particle diameter: 50 nm; BET specific surface area: 111.5 m²/g) were supported on activated carbon particles (average particle diameter: 400 μm; BET specific surface area: 1252 m²/g) to prepare hydrotalcite-supported activated carbon (hereinafter also referred to as composite particles). Specifically, the supporting of the hydrotalcite particles on the activated carbon particles was carried out as follows. 40 μL of water was added to a mixture of 20 mg of the activated carbon particles and 10 mg of the hydrotalcite particles and stirred until the activated carbon particles and the hydrotalcite particles were uniformly mixed to obtain a slurry sample. The obtained slurry sample was dried in an oven (100°C, 60 minutes) and then conditioned under conditions of 22°C and 60% humidity for 48 hours to obtain composite particles.

[0040] The obtained composite particles were placed in a space (filter cavity portion) between two filter plugs (filter

material: acetate tow; diameter: 7.7 mm; length: 5 mm) arranged to be separated from each other, and then a plug wrapping paper was wound around the filter plugs, thereby preparing a composite particle-containing filter (see FIG. 5).

(1-2) Preparation of nanoparticle-containing filter

[0041] Hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$; average particle diameter: 50 nm; BET specific surface area: $111.5 \text{ m}^2/\text{g}$) were placed in a space (filter cavity portion) between two filter plugs (filter material: acetate tow; diameter: 7.7 mm; length: 5 mm), and then a plug wrapping paper was wound around the filter plugs, thereby preparing a nanoparticle-containing filter (Comparative example 1).

(1-3) Preparation of core particle-containing filter

[0042] Activated carbon particles (average particle diameter: $400 \text{ }\mu\text{m}$; BET specific surface area: $1252 \text{ m}^2/\text{g}$) were placed in a space (filter cavity portion) between two filter plugs (filter material: acetate tow; diameter: 7.7 mm; length: 5 mm), and then a plug wrapping paper was wound around the filter plugs, preparing a core particle-containing filter (Comparative Example 2).

(1-4) Measurement of filter airflow resistance

[0043] Measurement of filter airflow resistance was carried out in accordance with ISO 6565: 2015 Draw resistance of cigarettes and pressure drop of filter rods.

(1-5) Results

[0044] FIG. 3 shows filter airflow resistance of the composite particle-containing filter and the nanoparticle-containing filter. Fig. 4 shows filter airflow resistance of the composite particle-containing filter and the core particle-containing filter.

[0045] In FIG. 3, the addition amount on the horizontal axis indicates the addition amount (mg) of the hydrotalcite particles (nanoparticles). Further, in FIG. 3, the filter airflow resistance of the composite particle-containing filter shows a value calculated by the following equation.

$$\begin{aligned} & (\text{Filter airflow resistance of a composite particle-} \\ & \text{containing filter}) = (\text{Filter airflow resistance measured} \\ & \text{using the composite particle-containing filter}) - (\text{Filter} \\ & \text{airflow resistance measured using a filter containing} \\ & \text{activated carbon particles in the same amount as the} \\ & \text{activated carbon particles used in the composite particle-} \\ & \text{containing filter}) \end{aligned}$$

[0046] Further, in FIG. 3, the filter airflow resistance of the nanoparticle-containing filter shows a value calculated by the following equation.

$$\begin{aligned} & (\text{Filter airflow resistance of a nanoparticle-} \\ & \text{containing filter}) = (\text{Filter airflow resistance measured} \\ & \text{using the nanoparticle-containing filter}) - (\text{Filter airflow} \\ & \text{resistance measured using a filter not containing the} \\ & \text{nanoparticles}) . \end{aligned}$$

[0047] In FIG. 4, the addition amount on the horizontal axis indicates the addition amount (mg) of the composite particles or the activated carbon particles. Further, in FIG. 4, the filter airflow resistance of the composite particle-containing filter shows a value calculated by the following equation.

(Filter airflow resistance of a composite particle-containing filter) = (Filter airflow resistance measured using the composite particle-containing filter) - (Filter airflow resistance measured using a filter not containing the composite particles)

[0048] Further, in FIG. 4, the filter airflow resistance of the core particle-containing filter shows a value calculated by the following equation.

(Filter airflow resistance of a core particle-containing filter) = (Filter airflow resistance measured using the core particle-containing filter) - (Filter airflow resistance measured using a filter not containing the core particles).

[0049] From the results in FIG. 3, the following can be seen. When hydrotalcite particles having an average particle diameter of 50 nm are directly added to a filter, the filter airflow resistance increases markedly according to the addition amount of the hydrotalcite particles. On the other hand, when hydrotalcite particles having an average particle diameter of 50 nm are added to a filter in the form of hydrotalcite-supported activated carbon (composite particles), the presence of the hydrotalcite particles does not significantly increase the filter airflow resistance.

[0050] From the results in FIG. 4, the following can be seen. When hydrotalcite particles having an average particle diameter of 50 nm are added to a filter in the form of hydrotalcite-supported activated carbon (composite particles), such a filter exhibits a filter airflow resistance equivalent to that of a filter to which the same amount of activated carbon particles are added. This indicates that the presence of the hydrotalcite particles does not significantly increase the filter airflow resistance.

[0051] These results show that when hydrotalcite particles having an average particle diameter of 50 nm are added to a filter in the form of hydrotalcite-supported activated carbon (composite particles), the presence of the hydrotalcite particles is less likely to increase the filter airflow resistance, compared to the case where the hydrotalcite particles are directly added thereto.

Experiment 2: Formaldehyde reduction rate

(2-1) Preparation of cigarette of the present invention

[0052] A composite particle-containing filter was prepared in the same manner as Experiment 1. The prepared composite particle-containing filter was connected to a tobacco rod (diameter: 7.7 mm; length: 57 mm; tobacco filler: 605 mg) to prepare a cigarette of the present invention. The connection was made so as to cover the connection part with a tipping paper (not shown). FIG. 5 schematically shows the prepared cigarette of the present invention.

[0053] In FIG. 5, a filter 10 is composed of two filter plugs 12 arranged apart from each other, a plug wrapping paper 13 wound around the filter plugs 12, and composite particles 11 arranged between the filter plugs 12. A tobacco rod 20 is composed of a tobacco filler 21 and a cigarette paper 22 wound around the tobacco filler 21.

(2-2) Preparation of cigarette of comparative example

[0054] A cigarette of a comparative example was prepared in the same manner as the cigarette of the present invention, except that 10 mg of hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$; average particle diameter: 700 μm ; BET specific surface area: 103.8 m^2/g) were used in place of the hydrotalcite-supported activated carbon (composite particles). The Hydrotalcite particles having an average particle diameter of 700 μm correspond to adsorbent particles used in the prior art document (WO 2003/056947).

(2-3) Measurement of amount of formaldehyde in mainstream smoke

[0055] The amount of formaldehyde in mainstream smoke was measured by the Canadian official method (2,4-DNPH-HPLC method), and the formaldehyde reduction rate was determined.

[0056] First, 9.51 g of 2,4-dinitrophenylhydrazine (DNPH) was dissolved in 1 L of acetonitrile by heating, then 5.6 mL of 60% perchloric acid was added, and ultrapure water was added to prepare 2 L of a trapping solution.

[0057] An outline of the measuring apparatus will be described with reference to FIG. 6. As shown in FIG. 6, a DNPH trapping solution 32 is placed in a gas washing bottle 31 for trapping gas. The volume of the gas washing bottle 31 is 100 mL, and the amount of the DNPH trapping solution 32 is 80 mL. The gas washing bottle 31 is put in an ice water bath 33 and cooled with ice. The lower end of a glass tube 34 for attaching a cigarette 30 is immersed in the trapping solution 32 contained in the gas washing bottle 31. A glass tube 35 and a Cambridge pad 36 are attached so as to communicate with the dead volume of the gas washing bottle 31, and then an automatic smoking device 37 is connected to the Cambridge pad 36.

[0058] The cigarette 30 is attached to the glass tube 34, and the cigarette 30 is automatically smoked under the ISO-compliant standard smoking condition. That is, for each cigarette, an empty puff is taken once and the operation of puffing of 35 mL for 2 seconds is repeated at 58 second intervals. While mainstream smoke is bubbling, formaldehyde is derivatized by DNPH. Two cigarettes were used for measurement. At this time, any cigarette using any type of adsorbent particles was adjusted so that the pressure loss became the same.

[0059] The derivative (derivatized formaldehyde) thus produced is measured by high performance liquid chromatography (HPLC). First, after filtering the trapping solution, it is diluted with Trizma Base solution (4 mL of the trapping solution and 6 mL of Trizma Base solution). The obtained solution is measured by HPLC. The HPLC measurement conditions are as follows.

Column: HP LiChrospher 100RP-18 (5 μ) 250 $\times$ 4 mm

Guard column: HP LiChrospher 100RP-18 (5 μ) 4 $\times$ 4 mm

Column temperature: 30°C

Detection wavelength: DAD 356 nm

Injection volume: 20 μ L

Mobile phase: three phase gradient (Solution A: an ultrapure water solution containing 30% acetonitrile, 10% tetrahydrofuran and 1% isopropanol, Solution B: an ultrapure water solution containing 65% acetonitrile, 1% tetrahydrofuran and 1% isopropanol, Solution C: 100% acetonitrile).

[0060] As a control experiment, the amount of formaldehyde in mainstream smoke was measured for a cigarette (hereinafter referred to as a control cigarette) equipped with a filter not containing either the hydrotalcite-supported activated carbon (composite particles) or the hydrotalcite particles (average particle diameter: 700 μ m).

[0061] The formaldehyde reduction rate was determined by substituting the measured formaldehyde amount into the following equation.

$$\begin{aligned}
 & \text{(Formaldehyde reduction rate)} = [\{ (\text{Formaldehyde amount} \\
 & \text{measured using a control cigarette}) - (\text{Formaldehyde amount} \\
 & \text{measured using a cigarette of the present invention or a} \\
 & \text{cigarette of the comparative example}) \} / (\text{Formaldehyde} \\
 & \text{amount measured using the control cigarette})] \times 100
 \end{aligned}$$

(2-4) Results

[0062] FIG. 7 shows the formaldehyde (FA) reduction rate of the cigarette of the present invention and the cigarette of the comparative example.

[0063] From the results shown in FIG. 7, it can be seen that the hydrotalcite-supported activated carbon (composite particles) can effectively remove formaldehyde in mainstream smoke, as compared with the hydrotalcite particles having an average particle diameter of 700 μ m.

Experiment 3: Adhesion strength of hydrotalcite particles to core particles

(3-1) Preparation of hydrotalcite-supported particles

[0064] The following Core particles A to C were used as core particles.

Core Particle A: Activated carbon particles (average particle diameter: 400 μm ; BET specific surface area: 1252 m^2/g)

Core Particle B: Hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$; average particle diameter: 700 μm ; BET specific surface area: 103.8 m^2/g)

Core particle C: Cellulose triacetate granules (average particle diameter: 400 μm ; particles described in Japanese Patent No. 5786038)

[0065] The Core particle A and the Core particle B are porous particles.

[0066] 100 mg of hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, average particle diameter: 50 nm; BET specific surface area: 111.5 m^2/g) were suspended in 500 μL of water, mixed with 1 g of core particles, and stirred until the hydrotalcite particles and the core particles were uniformly mixed, thereby preparing a slurry sample. The obtained slurry sample was dried in an oven (100°C, 60 minutes) to prepare hydrotalcite-supported particles (composite particles). The hydrotalcite-supported particles obtained using the Core particle A are referred to as Composite particle A, the hydrotalcite-supported particles obtained using the Core particle B are referred to as Composite particle B, and the hydrotalcite-supported particles obtained using the Core particle C are referred to as Composite particle C.

[0067] Further, 100 mg of hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, average particle diameter: 50 nm; BET specific surface area: 111.5 m^2/g) were thoroughly mixed with 1 g of Core particle A using a shaker, thereby preparing hydrotalcite-supported particles (composite particles). The composite particles are referred to as Composite particle D.

(3-2) Measurement of water retention rate

[0068] 1 g of core particles were immersed in 10 mL of water, and after 1 minute had passed, the mixture was filtered using a metal mesh (0.1 mm) to separate the core particles and water. The weight of the separated core particles was measured. From the measured weight, the water retention rate of the core particles was determined by the following equation.

[0069] Water retention rate (%) = $\{[(\text{Weight of core particles after filtration through metal mesh}) - (\text{Weight of core particles before immersion in water})] / (\text{Weight of core particles before immersion in water})\} \times 100$

(3-3) Measurement of adhesion strength

[0070] The adhesion strength of hydrotalcite particles to core particles was measured as follows.

[0071] The case of Composite particles A to C

100 mg of hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, average particle diameter: 50 nm; BET specific surface area: 111.5 m^2/g) were suspended in 500 μL of water, mixed with 1 g of core particles, and stirred until the hydrotalcite particles and the core particles were uniformly mixed, thereby preparing a slurry sample. The obtained slurry sample was dried in an oven (100°C, 60 minutes). The dried sample was passed through a 0.15 mm mesh sieve.

[0072] The fine powder that passed through the sieve was suspended in 500 μL of water, added to the particles that did not pass through the sieve, mixed, and then dried in an oven (100°C, 60 minutes). The dried sample was again passed through the sieve. This operation (mixing, drying and sieving operations) was repeated three times in total. Finally, the weight of the fine powder that passed through the sieve was measured.

[0073] The case of Composite particle D

100 mg of hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$, average particle diameter: 50 nm; BET specific surface area: 111.5 m^2/g) were thoroughly mixed with 1 g of Core particle A using a shaker. The obtained mixture was passed through a 0.15 mm mesh sieve.

[0074] The fine powder that passed through the sieve was added to the particles that did not pass through the sieve, and mixed. The obtained mixture was again passed through the sieve. This operation (mixing and sieving operations) was repeated three times in total. Finally, the weight of the fine powder that passed through the sieve was measured.

[0075] The adhesion strength of the hydrotalcite particles (average particle diameter: 50 nm) to the core particles was determined by the following equation.

$$\text{Adhesion strength (\%)} = \{(100 \text{ (mg)} - \text{Weight of fine powder}) / 100\} \times 100$$

powder that passed through the sieve (mg)) / 100 (mg)) $\times$ 100

(3-4) Results

[0076] The water retention rates of the Core particles A to C are shown below.

Core particle A: water retention rate 95%

Core particle B: water retention rate 74%

Core particle C: water retention rate 34%

[0077] The adhesion strength (%) of the hydrotalcite particles (average particle diameter: 50 nm) to the core particles is shown in FIG. 8.

[0078] From the result of the water retention rate and the result of FIG. 8, the following can be seen. When composite particles are prepared by mixing nanoparticles and core particles having a water retention rate in the presence of water and drying the mixture, the nanoparticles can be supported (attached) on the core particles (see Composite particles A to C). On the other hand, when composite particles are prepared by mixing nanoparticles and core particles having a water retention rate in the absence of water, the attachment rate of the hydrotalcite particles decreases (see Composite particle D). From the results of the Composite particles A to C, it can be seen that the higher the water retention rate of the core particles (i.e., the higher the ability to retain water on the surface), the higher the rate of attaching the hydrotalcite particles.

Experiment 4: Reference Example

[0079] The relation between the particle diameter of hydrotalcite particles and the formaldehyde adsorption rate, and the relationship between the particle diameter of hydrotalcite particles and the airflow resistance were investigated.

(4-1) Preparation of hydrotalcite particles

[0080] Hydrotalcite particles ($\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) were pulverized and classified to prepare hydrotalcite particles having a particle diameter of 100 to 300 μm , hydrotalcite particles having a particle diameter of 300 to 500 μm , hydrotalcite particles having a particle diameter of 500 to 700 μm , and hydrotalcite particles having a particle diameter of 700 μm or more.

(4-2) Preparation of cigarette

[0081] The obtained hydrotalcite particles were placed in a space (filter cavity portion) between two filter plugs (filter material: acetate tow; diameter: 7.7 mm; length: 5 mm) arranged to be separated from each other, and then a plug wrapping paper was wound around the filter plugs, thereby preparing an adsorbent particle-containing filter.

[0082] The prepared adsorbent particle-containing filter was connected to a tobacco rod (diameter: 7.7 mm; length: 57 mm; tobacco filler: 605 mg) to prepare a cigarette (see FIG. 5). The connection was made so as to cover the connecting part with a tipping paper.

(4-3) Measurement of formaldehyde adsorption rate

[0083] The amount of formaldehyde in mainstream smoke was measured in the same manner as described in Experiment 2, and the formaldehyde adsorption rate was determined by substituting the measured formaldehyde amount into the following equation.

$$(\text{Formaldehyde adsorption rate}) = \left[\frac{(\text{Formaldehyde amount measured using a control cigarette}) - (\text{Formaldehyde amount measured})}{(\text{Formaldehyde amount measured using the control cigarette})} \right]$$

[0084] The control cigarette has the same configuration as the cigarette prepared above, except that the adsorbent particles were not added.

(4-4) Measurement of filter airflow resistance

[0085] Filter airflow resistance was measured by the same method as described in Experiment 1.

(4-5) Results

[0086] The results of formaldehyde adsorption rate and cigarette airflow resistance are shown in FIGS. 9 and 10, respectively. The horizontal axis in FIG. 9 represents the amount of the hydrotalcite particles added to the filter in volume. The horizontal axis in FIG. 10 represents the amount of the hydrotalcite particles added to the filter by weight.

[0087] From the results shown in FIG. 9, it can be seen that when the particle diameter of the adsorbent particles is decreased, the formaldehyde adsorbing ability is improved. From the results shown in FIG. 10, it can be seen that when the particle diameter of the adsorbent particles is decreased, the airflow resistance increases.

Reference Signs List

[0088] 10: Filter, 11: Composite particle, 11a: Core particle, 11b: Nanoparticle, 12: Filter plug, 13: Plug wrapping paper, 20: Tobacco rod, 21: Tobacco filler, 22: Cigarette paper, 30: Cigarette, 31: Gas washing bottle, 32: Trapping solution, 33: Ice water bath, 34: Glass tube, 35: Glass tube, 36: Cambridge pad, 37: Automatic smoking device

Claims

1. A filter for a smoking article, comprising composite particles made of:

core particles having an average particle diameter of 200 μm to 1000 μm , and nanoparticles supported on at least a part of a surface of each of the core particles, the nanoparticles being made of a hydrotalcite compound and having an average particle diameter of 1 to 200 nm.

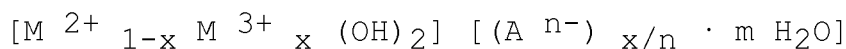
2. The filter for a smoking article according to claim 1, wherein the core particles have a water retention property.

3. The filter for a smoking article according to claim 2, wherein the core particles have a water retention rate of 70% or more.

4. The filter for a smoking article according to claim 2 or 3, wherein the core particles are porous particles.

5. The filter for a smoking article according to claim 4, wherein the porous particles are activated carbon particles.

6. The filter for a smoking article according to any one of claims 1 to 5, wherein the nanoparticles are made of a hydrotalcite compound represented by the general formula:



wherein M^{2+} is a divalent metal ion selected from the group consisting of Mg, Zn, Ni and Ca ions; M^{3+} is Al ion; A^{n-} is a n-valent anion selected from the group consisting of CO_3 , SO_4 , $OOC-COO$, Cl, Br, F, NO_3 , $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, phthalic acid, isophthalic acid, terephthalic acid, maleic acid, alkenyl acid and a derivative thereof, malic acid, salicylic acid, acrylic acid, adipic acid, succinic acid, citric acid and sulfonic acid anions; x satisfies $0.1 < x < 0.4$; and m satisfies $0 < m < 2$.

7. The filter for a smoking article according to claim 6, wherein M^{2+} is Mg ion, M^{3+} is Al ion, A^{n-} is CO_3^{2-} or SO_4^{2-} , x satisfies $0.1 < x < 0.4$, and m satisfies $0 < m < 2$.

8. The filter for a smoking article according to claim 6, wherein the general formula is represented by $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$.

9. The filter for a smoking article according to any one of claims 1 to 8, wherein the average particle diameter of the core particles is 300 μm to 700 μm , preferably 400 μm to 600 μm .

10. The filter for a smoking article according to any one of claims 1 to 9, wherein the average particle diameter of the nanoparticles is 10 nm to 150 nm, preferably 10 nm to 50 nm.

11. A smoking article comprising:

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the filter for a smoking article according to any one of claims 1 to 10; and
a tobacco rod connected to one end of the filter for a smoking article.

12. A method of preparing a filter for a smoking article, comprising:

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stirring an aqueous suspension containing core particles having an average particle diameter of 200 μm to 1000 μm and nanoparticles made of a hydrotalcite compound and having an average particle diameter of 1 to 200 nm, and then drying the suspension to prepare composite particles made of the core particles and the nanoparticles supported on at least a part of a surface of each of the core particles, and

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incorporating the composite particles into a filter for a smoking article.

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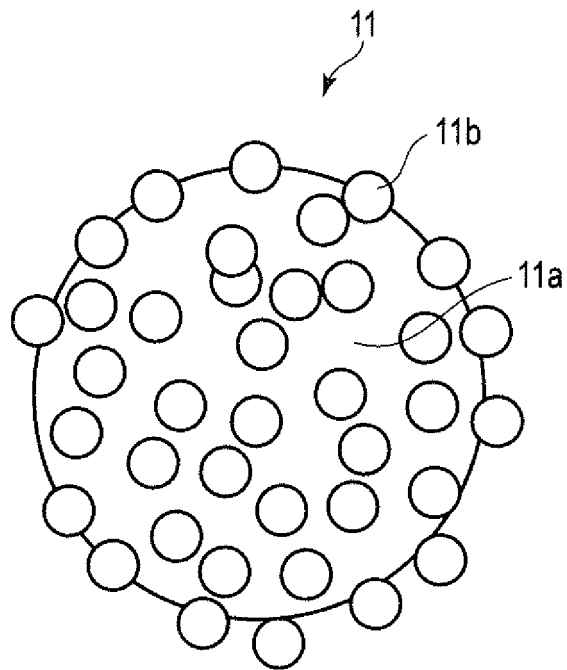


FIG. 1

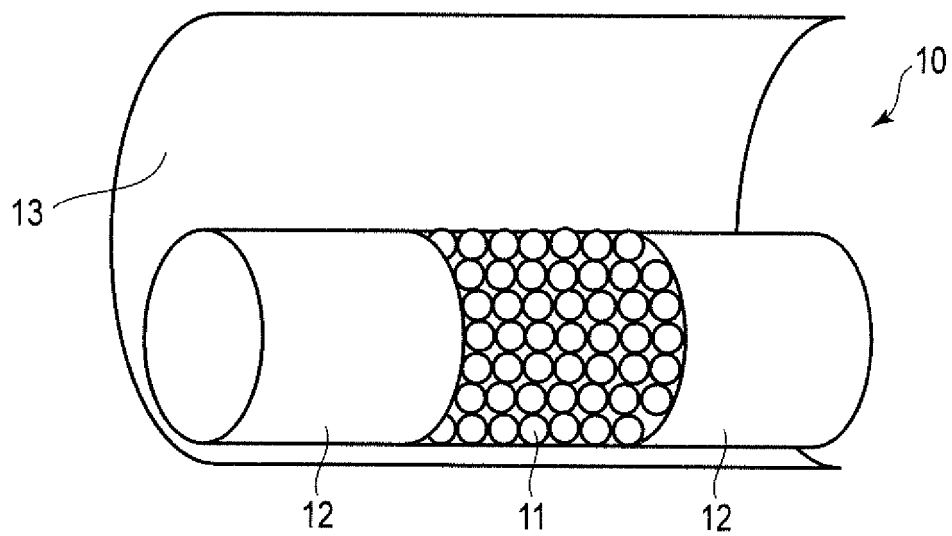


FIG. 2

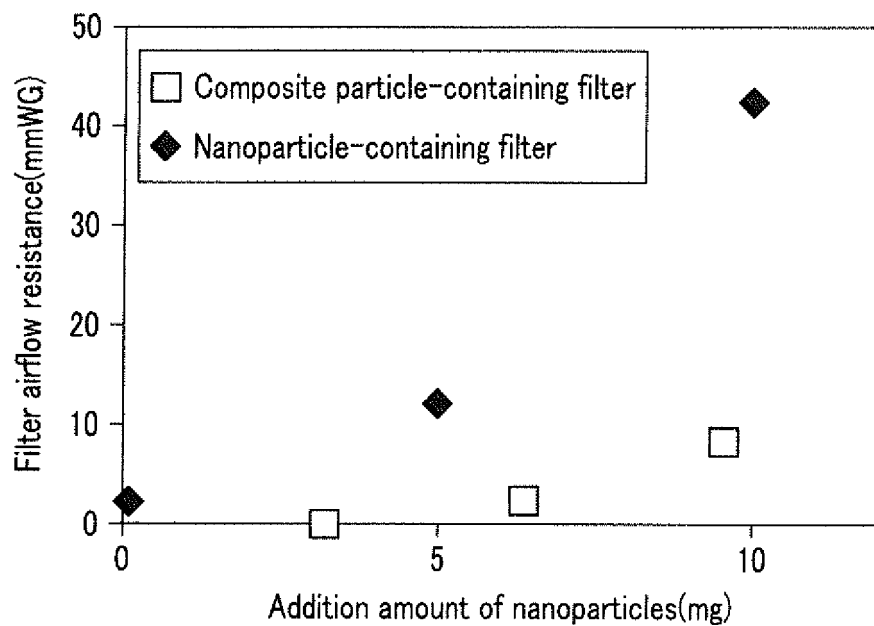


FIG. 3

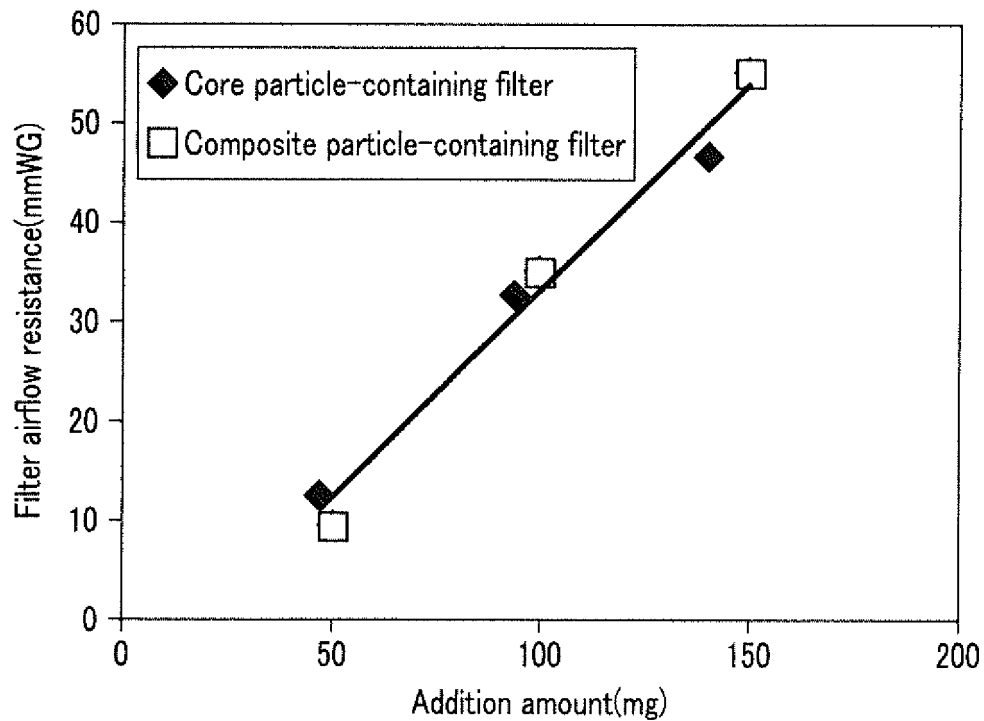


FIG. 4

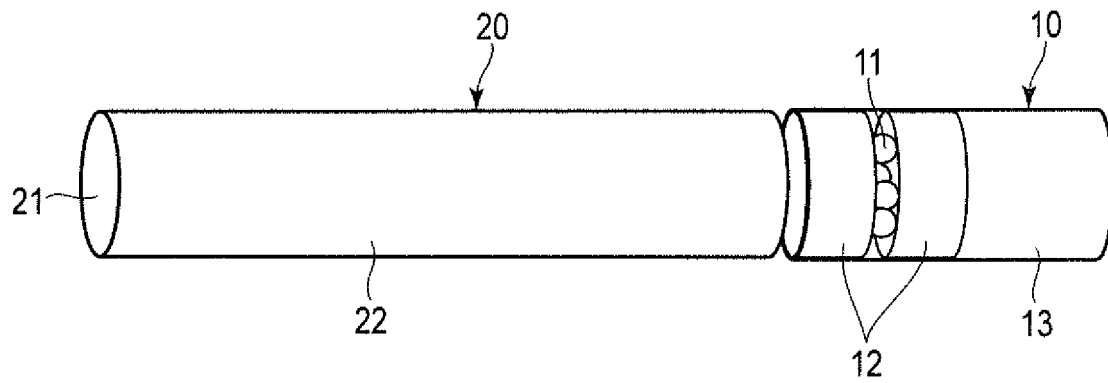


FIG. 5

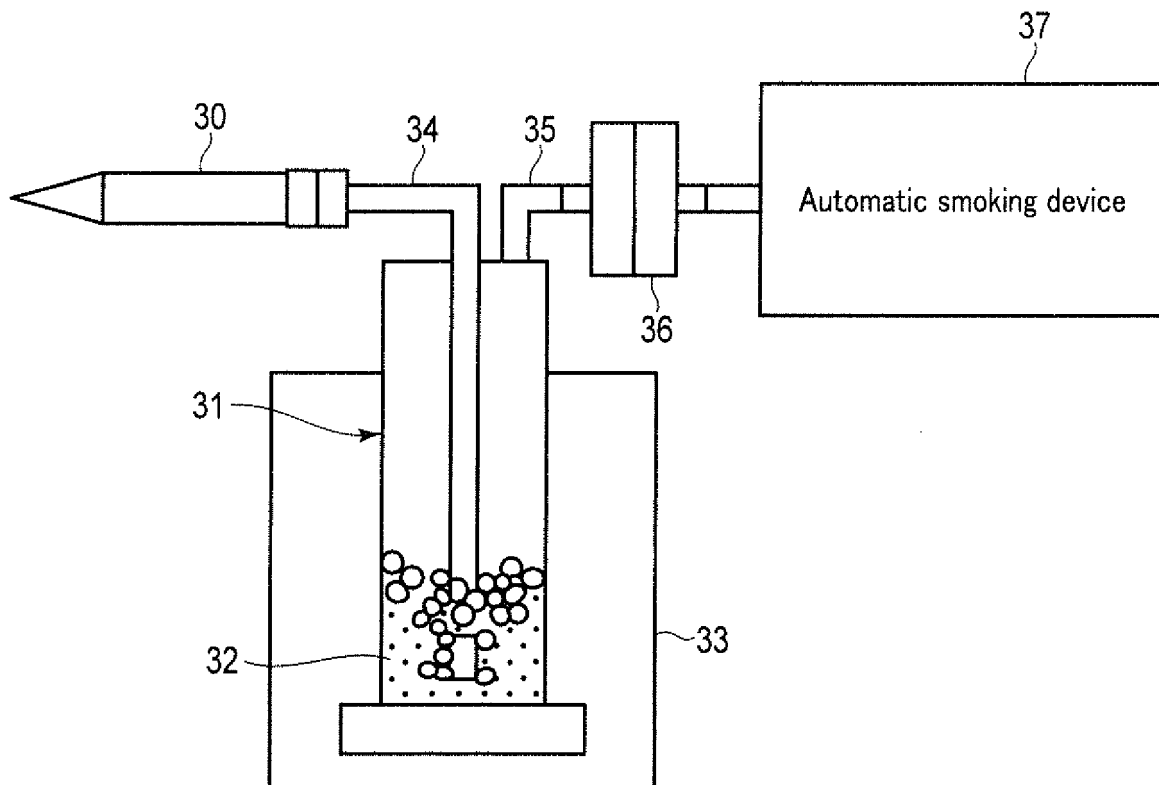


FIG. 6

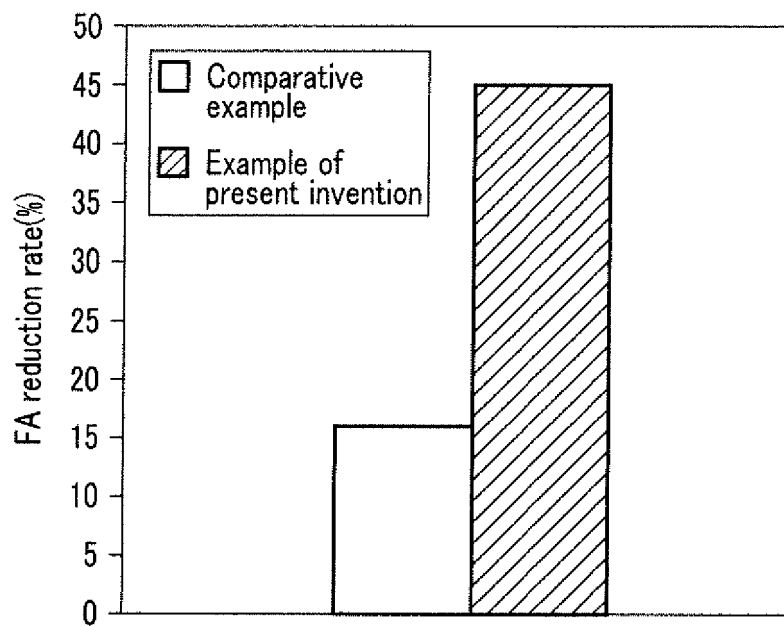


FIG. 7

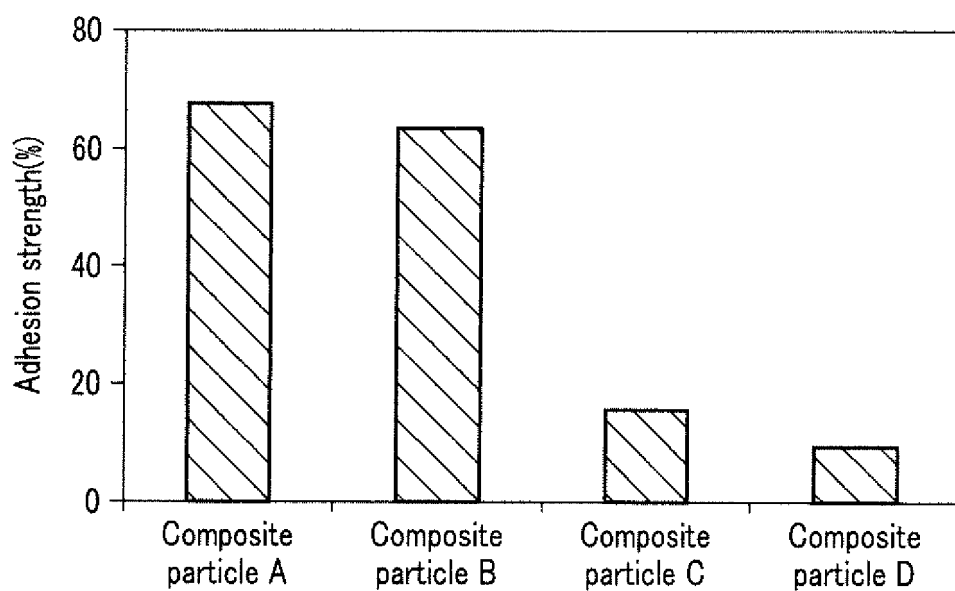


FIG. 8

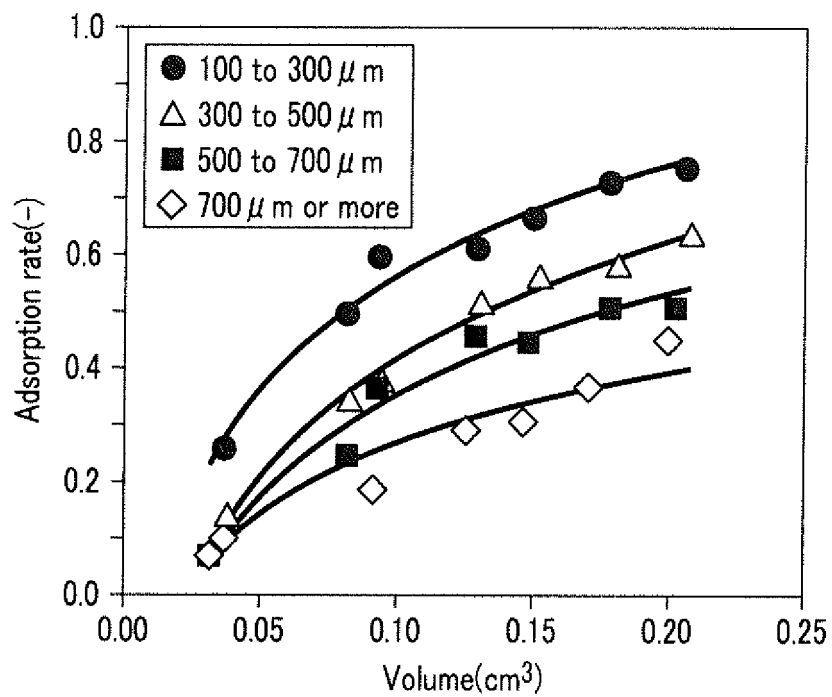


FIG. 9

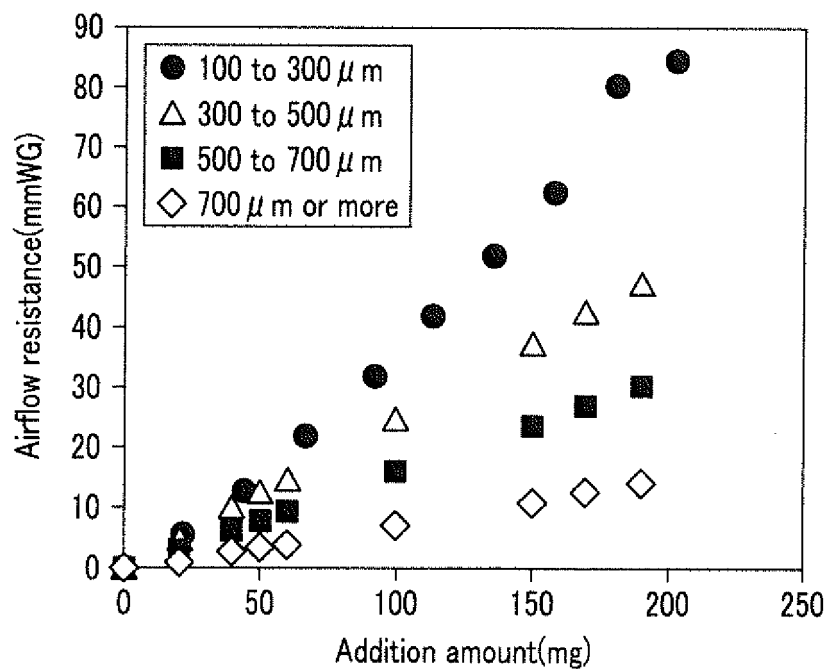


FIG. 10

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/059916

A. CLASSIFICATION OF SUBJECT MATTER

A24D3/16(2006.01) i, A24D3/12(2006.01) i

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)

A24D3/00

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 03/056947 A1 (Japan Tobacco Inc.), 17 July 2003 (17.07.2003), description, page 4, line 7 to page 6, line 18	1-12
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A	WO 2006/092962 A1 (Japan Tobacco Inc.), 08 September 2006 (08.09.2006), paragraph [0029]	1-12

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

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Date of the actual completion of the international search
17 June 2016 (17.06.16)Date of mailing of the international search report
28 June 2016 (28.06.16)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/059916

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Form PCT/ISA/210 (continuation of second sheet) (January 2015)

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REFERENCES CITED IN THE DESCRIPTION

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- WO 2006073065 A [0036]
- WO 2010110226 A [0036]
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