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(54) **CIGARETTE AND METHOD FOR TREATING CIGARETTE MATERIAL**

(57) A cigarette includes a shredded tobacco rod and a cigarette paper that wraps the outer peripheral surface

of the shredded tobacco rod. The shredded tobacco and/or the cigarette paper contains a transition metal salt of an organic acid.

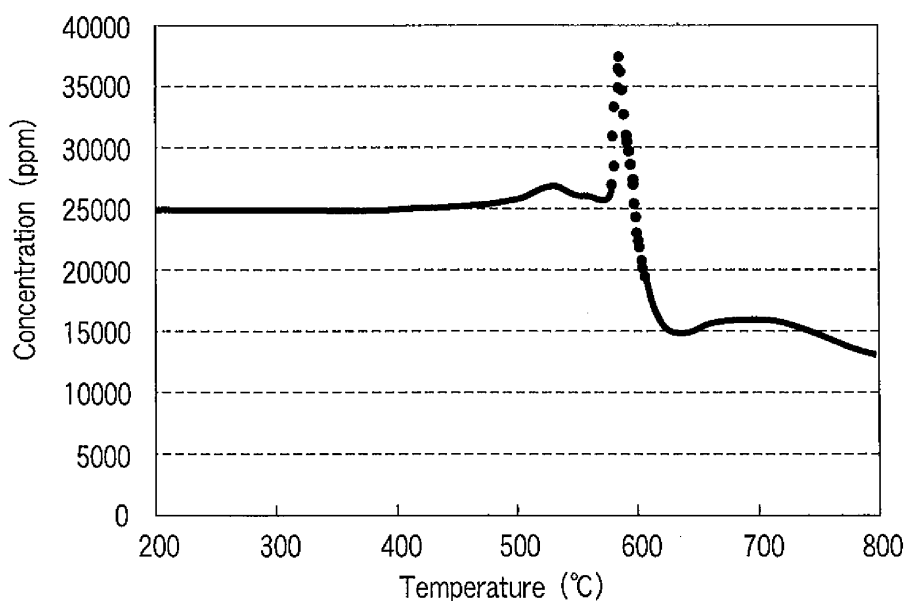


FIG. 2

Description

Technical Field

5 **[0001]** The present invention relates to a cigarette and a method for treating a cigarette material.

Background Art

10 **[0002]** There have been proposed that, in order to remove carbon monoxide present in cigarette mainstream smoke, a noble metal catalyst or a transition metal oxide catalyst is added to shredded tobacco, a cigarette paper or a filter to convert carbon monoxide into carbon dioxide.

15 **[0003]** For example, Patent Literature 1 discloses that a catalyst made of Fe_2O_3 nano-particles is added to a tobacco cut filler. However, a complicated process is required to prepare the finely divided metal oxide nano-particles. Patent Literature 2 discloses that high-surface area carrier particles carrying nano-scale metal particles or metal oxide particles are added to a tobacco cut filler. However, in order to make high-surface area carrier particles that carry nano-scale metal particles or metal oxide particles, more complicated processes, for example, a process of deriving the high-surface area carrier particles from a colloidal solution, are required.

20 **[0004]** Patent Literature 3 discloses that a metal oxyhydroxide is added to a cigarette paper, tobacco cut filler, filter or the like. Patent Literature 3 shows in Table 1 that the CO reduction rate when the metal oxyhydroxide is added is 29%. This is lower than the CO reduction rate of 33% obtained when a metal oxide and calcium carbonate are added from the start as shown in Table 1.

Citation List

25 Patent Literatures

[0005]

30 Patent Literature 1: Jpn. PCT National Publication No. 2005-522206
Patent Literature 2: Jpn. PCT National Publication No. 2007-527698
Patent Literature 3: U.S. Patent Application Publication No. 2005/0155616

Summary of Invention

35 Technical Problem

[0006] It is an object of the present invention to provide a cigarette more reduced in carbon monoxide in mainstream smoke and a method for treating a cigarette material.

40 Solution to Problem

[0007] According to a first aspect of the present invention, there is provided a cigarette, comprising a shredded tobacco rod and a cigarette paper that wraps the outer peripheral surface of the shredded tobacco rod, wherein the shredded tobacco and/or the cigarette paper contains a transition metal salt of an organic acid.

45 **[0008]** According to a second aspect of the present invention, there is provided a method for treating a cigarette material, comprising treating shredded tobacco and/or cigarette paper with a transition metal salt of an organic acid.

Advantageous Effects of Invention

50 **[0009]** According to the present invention, carbon monoxide in cigarette mainstream smoke can be reduced significantly.

Brief Description of Drawings

55 **[0010]**

FIG. 1 is a block diagram of a device used to analyze the carbon monoxide reduction capability by using a model gas.
FIG. 2 is a graph showing a heating temperature of a reaction tube filled with a transition metal salt of an organic

acid and a concentration of carbon monoxide in the gas which has passed through the reaction tube.

Description of Embodiments

[0011] The present invention will be explained in detail below.

[0012] A cigarette according to the present invention comprises a shredded tobacco rod and a cigarette paper that wraps the outer peripheral surface of the rod.

[0013] The shredded tobacco is cut or shredded tobacco material and may contain adequate additives. As the tobacco material, tobacco leaves or stem of Burley tobaccos, flue-cured tobaccos or orient tobaccos, fermented tobacco, dark cured tobaccos or reconstituted tobacco materials or their combinations may be used. Examples of the additives may include natural or synthetic flavors; polyhydric alcohols such as glycerol and propylene glycol; sugar alcohols such as erythritol, xylitol and sorbitol; and hyaluronic acid.

[0014] The cigarette paper that wraps the shredded tobacco rod is itself a cigarette paper used in ordinary cigarettes. As the raw material of the cigarette paper, agricultural byproduct fibers such as bagasse, non-wood fibers such as bamboos and the like besides flax and wood may be used. Further, the cigarette paper may contain any one or more of aluminum hydroxide, aluminum sulfate, aluminum oxide, magnesium oxide, talc and titanium dioxide, and sodium, potassium, calcium or magnesium salts of carbonic acid, formic acid, acetic acid, malic acid, citric acid, tartaric acid, lactic acid or nitric acid as a white incineration agent and a burn adjusting agent.

[0015] In the present invention, a transition metal salt of an organic acid is contained in the shredded tobacco and/or cigarette paper. As the organic acid, there may be exemplified, for example, fumaric acid, citric acid, oxalic acid, formic acid, benzoic acid, lactic acid and stearic acid. Among these acids, organic acids having a total of 2 to 7 carbon atoms are preferable, fumaric acid, citric acid and oxalic acid are more preferable and fumaric acid is particularly preferable.

[0016] As the transition metal, at least one metal selected from the group consisting of Ti, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Ce, Ir, Pt and Au may be used. Fe, Cu and Mn are preferable, and Fe is particularly preferable.

[0017] It is considered that the organic acid transition metal salt added to the shredded tobacco and/or the cigarette paper is decomposed when tobacco is burned and converted into a transition metal oxide which exerts a catalytic action, leading to reduction in carbon monoxide in mainstream smoke. In other words, according to the present invention, a catalyst is automatically produced by the combustion heat of a tobacco. The organic acid transition metal salt functions as a precursor of the carbon monoxide reduction catalyst and produces the catalyst by burning of the cigarette.

[0018] The above organic acid transition metal salt is preferably contained in an amount of 1 to 50% by weight based on shredded tobacco. When the amount is less than 1% by weight, the carbon monoxide reduction capability tends not to be exerted sufficiently. An amount exceeding 50% by weight makes it difficult to treat shredded tobacco and is therefore undesirable.

[0019] When the organic acid transition metal salt is contained in the cigarette paper, the organic acid transition metal salt is preferably contained in an amount of 0.1 to 50 g/m² in the cigarette paper. When the amount is less than 0.1 g/m², the carbon monoxide reduction capability tends not to be exerted sufficiently. An amount exceeding 50 g/m² makes it difficult to treat cigarette paper.

[0020] When the organic acid transition metal salt is contained in the cigarette paper, it preferably has a particle diameter of 0.05 to 5 μ m from the viewpoint of the smoothness of the cigarette paper and retainability in the cigarette paper.

[0021] Further, the present invention relates to a method for treating a cigarette material, comprising treating shredded tobacco and/or cigarette paper with the above organic acid transition metal salt.

[0022] The method for treating a cigarette material according to the present invention may be carried out, for example, by spreading a solution in which the above organic acid transition metal salt is dispersed in an organic solvent (which does not dissolve the organic acid transition metal salt) onto the shredded tobacco and/or the cigarette paper. As the organic solvent, any organic solvent may be used, and alcohols such as ethanol may be mentioned. An aqueous solvent dissolves the above organic acid transition metal salt, making it difficult to spread the salt in an amount exceeding the amount to be absorbed in the cigarette paper. When the organic acid transition metal salt is dispersed in an organic solvent, it is more preferable to further add an emulsifier to use it in a slurry state. The emulsifier may be a known one which is used as a food additive, for example, lecithin. The emulsifier may be used in an amount of 1 to 50% of the weight of the organic acid transition metal salt. When the amount is less than 1%, only insufficient dispersing effect is developed, whereas when the amount exceeds 50%, this is a hindrance to the decomposition of the organic acid transition metal salt.

[0023] Moreover, the organic acid transition metal salt may be kneaded into the shredded tobacco or may be coated to the cigarette paper. Moreover, the organic acid transition metal salt may be furnished in the papermaking of cigarette paper.

[0024] As mentioned above, the method for treating a cigarette material of the present invention is such a very simple method that a cigarette material (shredded tobacco and/or cigarette paper) is treated with the organic acid transition metal salt. As will be explained later, such a simple method can more reduce carbon monoxide in mainstream smoke

than an iron oxide nano-powder which is conventionally regarded as an excellent material.

Example 1

[0025] Using a model gas, the carbon monoxide reduction capabilities of various transition metal salts of organic acids added to the cigarette of the present invention were investigated. Iron was used as the transition metal in Example 1.

[0026] As the iron salt of an organic acid salt, iron citrate manufactured by Nacalai Tesque, Inc., and other iron salts of organic acids manufactured by Wako Pure Chemical Industries, Ltd. were used. As the iron salt of the organic acid, particles which passed through a 75 μm screen diameter were used.

[0027] FIG. 1 shows a device for analyzing the carbon monoxide reduction capability of an organic acid transition metal salt. The iron salt of the organic acid of Example 1 containing iron in the amount shown in the Table 1 below was filled in a reaction tube 9 disposed in a heating furnace 8. Carbon monoxide (CO) gas and carbon dioxide (CO₂) were supplied from gas cylinders 3 and 5 through mass flowmeters 4 and 6 respectively and water was weighed by an electronic balance 1 and supplied by a metering pump 2. The above water was made to flow through an evaporator 7 (200°C) together with the CO gas and CO₂ gas. The water was vaporized into water vapor. Thus, a model gas (CO concentration: 4 mol%, CO₂ concentration: 8 mol%, H₂O concentration: 10 mol%, nitrogen: balance) was prepared in the evaporator 7. The flow rate of the model gas was set such that its space velocity (SV) was 500,000 h⁻¹ and the model gas was made to flow through the layer of the iron salt of the organic acid filled in the reaction tube 9. The model gas was made to flow for 3.5 hours while heating the layer in the reaction tube 9 from 200 to 900°C. In FIG. 1, PG is a pressure gauge, TIC is a temperature gauge used to measure the temperature of the tube wall of the reaction tube 9 and TI is a temperature gauge used to measure the temperature of the filled layer. The temperature measured by the temperature gauge TIC was used as a control monitor temperature when heating the reaction tube 9 by the furnace 8. The gas flowed out of the reaction tube 9 was made to flow through a cooling trap 10 and then, the carbon monoxide was quantitatively measured by an infrared gas analyzer 11 manufactured by Horiba Ltd. (VIA-510, according to the nondispersive infrared absorption method).

[0028] The carbon monoxide oxidation amount of each organic acid iron salt, carbon monoxide oxidation amount of each organic acid iron salt per mol of an iron element and carbon monoxide removal rate of each organic acid iron salt were measured. The results are shown in Table 1. In the Table, the organic acid iron salt is indicated as "Additive".

Comparative Example 1

[0029] The carbon monoxide removal rate was measured under the same conditions as in Example 1 except that an iron oxide (triiron tetraoxide) powder (manufactured by Sigma-Aldrich Corporation) was added in place of the organic acid iron salt. The results are shown in Table 1.

Table 1

Temp. °C	Gas flow rate NL/h	Space velocity h ⁻¹	Additive	Filled additive amount ^{a)}		CO oxidation amount ^{b)} % mmol-CO	CO/Fe ^{c)} %	CO removal rate ^{d)} (highest value)	
				g-Fe	Mmol-Fe			%	Temp. °C
Ex. 1									
200→900 (temp. increase)	100	500,000	Iron (II) oxalate	0.23	69.97	53.90	77.0	27.7	634
			Iron (II) fumarate	0.27	86.90	88.06	101.3	51.9	673
			Iron (II) citrate	0.16	35.35	25.23	71.4	27.2	668
			Iron (II) lactate	0.12	23.03	19.47	84.5	19.9	648
			Iron (II) stearate	0.05	4.39	0.91	20.7	4.6	646

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(continued)

Comp. Ex. 1									
200→900 (temp. increase)	100	500.000	Iron oxide powder (triiron tetraoxide)	0.15	108.54	81.56	75.1	37.2	668
a) Filled additive amount Mass or mol of iron contained in the organic acid iron filled as an additives. b) CO oxidation amount A value obtained by multiplying a difference (mol%) between the concentration of carbon monoxide in the model gas and the concentration of carbon monoxide in the gas discharged from the reaction tube by the flow rate (amount by mol per hour) of the model gas to integrate the obtained value with respect to time (3.5 hours). c) CO/Fe Co oxidation amount per mol of iron element. d) CO removal rate Conversion rate of CO into CO ₂ .									

Examples 2 and 3

[0030] The carbon monoxide reduction capability was investigated under the same conditions as in Example 1 except that organic acid copper salts or organic acid manganese salts were used in place of the organic acid iron salts. The results are shown in Tables 2 and 3. In these Examples, as the organic acid transition metal salts, ones manufactured by Wako Pure Chemical Industries, Ltd., were used.

Table 2

Ex.2									
Temp. °C	Gas flow rate NL/h	Space velocity h ⁻¹	Additive	Filled additive amount ^{a)}		CO oxidation amount ^{b)} mmol-CO	CO/Cu ^{c)} %	CO removal rate ^{d)} (highest value)	
				g-Cu	mmol-Cu			%	Temp. °C
200→900 (temp. increase)	100	500,000	Copper (II) oxalate	0.28	108.83	18.70	17.2	14.4	460
			Copper (II) tartarate	0.17	47.04	10.68	22.7	15.5	619
			Copper (II) citrate	0.22	38.81	0.28	0.7	0.1	742
			Copper (II) phthalate	0.15	41.87	5.19	12.4	17.2	645
a) Filled additive amount Mass or mol of copper contained in the organic acid iron filled as an additive. b) CO oxidation amount A value obtained by multiplying a difference (mol%) between the concentration of carbon monoxide in the model gas and the concentration of carbon monoxide in the gas discharged from the reaction tube by the flow rate (amount by mol per hour) of the model gas to integrate the obtained value with respect to time (3.5 hours). c) CO/Fe Co oxidation amount per mol of copper element d) CO removal rate Conversion rate of CO into CO ₂ .									

Table 3

Ex.3									
Temp. °C	Gas flow rate NL/h	Space velocity h ⁻¹	Additive	Filled additive amount ^{a)}		CO oxidation amount ^{b)} mmol-CO	CO/Mn ^{c)} %	CO removal rate ^{d)} (highest value)	
				g-Mn	mmol-Mn			%	Temp. °C
200→900 (temp. increase)	100	500,000	Manganese (II) oxalate	0.22	67.53	11.08	16.4	9.3	858
			Manganese (II) formate	0.20	60.71	16.23	26.7	10.9	754
			Manganese (II) benzoate	0.17	25.29	5.21	20.6	2.7	765
a) Filled additive amount Mass or mol of manganese contained in the organic acid iron filled as an additive. b) CO oxidation amount A value obtained by multiplying a difference (mol%) between the concentration of carbon monoxide in the model gas and the concentration of carbon monoxide in the gas discharged from the reaction tube by the flow rate (amount by mol per hour) of the model gas to integrate the obtained value with respect to time (3.5 hours). c) CO/Fe Co oxidation amount per mol of manganese element. d) CO removal rate Conversion rate of CO into CO ₂ .									

[0031] As is clear from Tables 1 to 3, it was found that carbon monoxide was oxidized. It was found from the results of Examples 1 to 3 that excellent carbon monoxide reduction capability was developed when iron was used as the transition metal. The CO oxidation amount per mol of an iron element in Example 1 was equal to or more than that in Comparative Example 1 though the number of moles of an iron element contained in the additives of Example 1 was smaller than that contained in the conventional iron oxide catalyst of Comparative Example 1. When iron fumarate was used in particular, it was found that it was superior to Comparative Example 1 in all of the carbon monoxide oxidation amount, carbon monoxide oxidation amount per mol of an iron element and carbon monoxide removal rate. Further, it was found that because the carbon monoxide removal rate and the like were largely deteriorated when iron stearate was used, it was preferable to use, as the organic acid, one having a total of about 2 to 7 carbon atoms.

Example 4

[0032] 145 g of iron fumarate as an organic acid transition metal salt and 15 g of flax pulp (manufactured by Rinsel Company) were dispersed in 2000 g of a mixture solution of ethanol and lecithin (weight ratio of ethanol : lecithin = 90 : 0.5) to prepare a slurry. This slurry was cast into a sheet form, or made to flow on a manual paper making tool having a 16-mesh stainless wire gauge superposed on a 200-mesh stainless wire gauge to manufacture cigarette paper having a basis weight of 50 g/m².

[0033] Here, it was found that if the particle diameter of iron fumarate was too large, the smoothness of the cigarette paper was deteriorated and iron fumarate particles were not uniformly dispersed, whereas if the particle diameter was too small, the iron fumarate particles passed through the manual paper making tool, so that the iron fumarate particles could not be carried on the cigarette paper. The particle diameter of the iron fumarate particles is preferably 0.05 to 5 μm.

[0034] Further, iron fumarate was dispersed in 30 ml of the above-noted mixture solution of ethanol and lecithin to prepare a slurry. It was found that iron fumarate can be added to shredded tobacco by spraying the above slurry by an atomizer such that the amount of iron fumarate was 10% by weight based on the weight of the shredded tobacco.

Example 5

[0035] In this Example, the action mechanism of the organic acid transition metal salt will be discussed.

[0036] 100 mg of shredded tobacco (2R4F) was mixed with 10 mg of iron fumarate and the mixture was filled in a sample tube. This sample tube was set to a catalyst analyzer (BELCAT, manufactured by BEL Japan, Inc.). A model gas (CO: 3.39 mol%, O₂: 2.19 mol%, He: balance) was made to flow through the sample tube and heated to raise its temperature at a rate of 40°C/minute from 200 to 800°C to measure the concentration of CO. The results are shown in FIG. 2. As is clear from FIG. 2, it was found that after the shredded tobacco was oxidized/burned at about 600°C with

temporary increase in carbon monoxide, carbon monoxide tended to decrease. This allows to infer that the heat treatment of iron fumarate at a temperature close to 600°C caused iron fumarate to be decomposed into iron oxide, which functioned as a catalyst.

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Claims

1. A cigarette comprising a shredded tobacco rod and a cigarette paper that wraps the outer peripheral surface of the shredded tobacco rod, wherein the shredded tobacco and/or the cigarette paper contains a transition metal salt of an organic acid.
2. The cigarette according to Claim 1, wherein the organic acid is fumaric acid, citric acid, oxalic acid, formic acid, benzoic acid, or lactic acid.
3. The cigarette according to Claim 1, wherein the transition metal is at least one metal selected from the group consisting of Ti, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Ce, Ir, Pt and Au.
4. The cigarette according to Claim 1, wherein the transition metal salt of the organic acid is contained in an amount of 1 to 50% by weight in the shredded tobacco.
5. The cigarette according to Claim 1, wherein the transition metal salt of the organic acid is contained in an amount of 0.1 to 50 g/m² in the cigarette paper.
6. A method for treating a cigarette material, comprising treating shredded tobacco and/or cigarette paper with a transition metal salt of an organic acid.
7. The method according to Claim 6, wherein the organic acid is fumaric acid, citric acid, oxalic acid, formic acid, benzoic acid, or lactic acid.
8. The method according to Claim 6, wherein the transition metal is at least one metal selected from the group consisting of Ti, Mn, Fe, Co, Ni, Cu, Y, Zr, Nb, Mo, Ru, Rh, Pd, Ag, Ce, Ir, Pt and Au.
9. The method according to Claim 6, wherein a solution in which the transition metal salt of the organic acid dispersed in an organic solvent is spread onto the shredded tobacco and/or the cigarette paper.
10. The method according to Claim 9, wherein the solution further contains an emulsifier.

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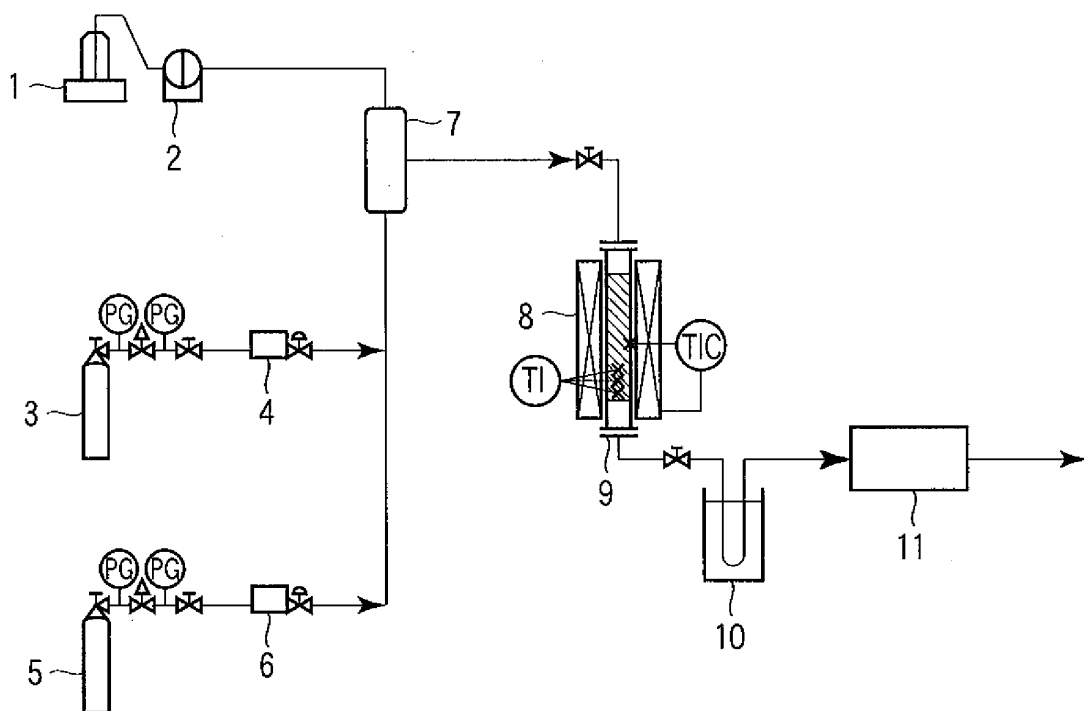


FIG. 1

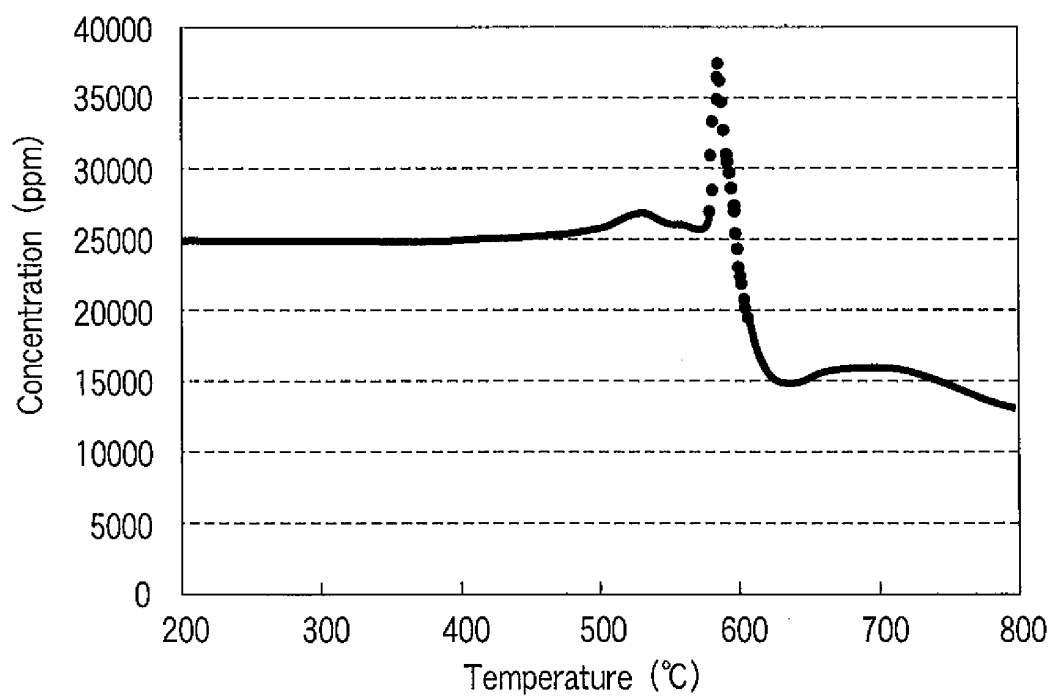


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/056020

A. CLASSIFICATION OF SUBJECT MATTER

A24B15/28(2006.01) i, A24D1/02(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)

A24B15/28, A24D1/02, B01J23/00

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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

WPI

C. 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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Y	JP 9-86928 A (Nissan Motor Co., Ltd.), 31 March 1997 (31.03.1997), paragraph [0037] & JP 2003-175337 A & US 6060420 A & US 6129862 A	1-10



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

09 July, 2010 (09.07.10)

Date of mailing of the international search report

20 July, 2010 (20.07.10)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/056020

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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REFERENCES CITED IN THE DESCRIPTION

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