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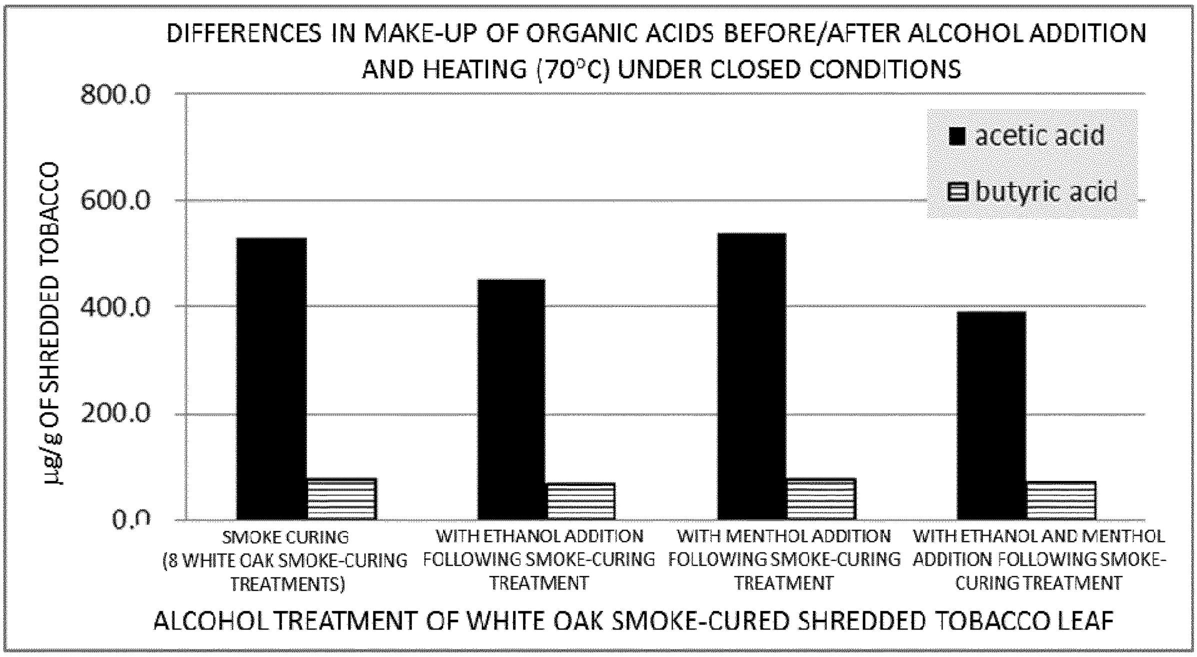
## (54) PROCESS FOR PRODUCING RAW TOBACCO MATERIAL

(57) Provided is a method of producing a tobacco raw material, the method comprising: a step of smoke-processing dried tobacco leaf; a step of adding an alcohol to the smoke-processed dried tobacco leaf; and a step of storing the tobacco leaf to which the alcohol has been added.

[Fig.3]



EP 2 965 637 A1

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## Description

## TECHNICAL FIELD

**[0001]** The present invention relates to a method of producing a tobacco raw material.

## BACKGROUND ART

**[0002]** Attempts have hitherto been made to improve the flavor of raw leaf tobacco. For example, Patent Document 1 describes a method in which ethyl alcohol is added to the leaf tobacco before a leaf tobacco barrel-aging step.

**[0003]** According to this art, chemical actions by the ethyl alcohol adsorbed onto the leaf tobacco enliven oxidation reactions, decomposition, deamination, etc. of protein-based macromolecular compounds, nitrogen-containing compounds and sugars in the leaf tobacco, so that aging of the tobacco proceeds while releasing a large amount of carbon dioxide. The smoke emitted when cigarettes that use the leaf tobacco obtained by such fermentation are smoked reportedly contains high levels of organic acids such as formic acid and acetic acid. Mention is also made that levels of substances such as acetaldehyde, acetone, acrolein and acetol which cause off-flavors and irritation during smoking are reduced.

**[0004]** Patent Document 1: Japanese Patent Application Laid-open No. S56-51976

## DISCLOSURE OF THE INVENTION

**[0005]** Although Patent Document 1 states that the method described therein, by applying ethyl alcohol to leaf tobacco, is able to increase the content of organic acids included in the smoke emitted when cigarettes using this leaf tobacco are smoked, the only compounds that are increased are organic acids.

**[0006]** By contrast, the present invention focuses on ester compounds as ingredients that impart flavor to leaf tobacco, providing a method for enhancing the flavor of a tobacco raw material by increasing the level of such flavor ingredients in the tobacco raw material.

**[0007]** The inventors have conducted extensive investigations, as a result of which they have discovered that, in a tobacco raw material obtained by a production method that includes: a step of smoke-processing dried tobacco leaf; a step of adding an alcohol to the smoke-processed dried tobacco leaf; and a step of storing the tobacco leaf to which the alcohol has been added, the content of flavor-enhancing esters is increased.

**[0008]** The invention is recited below.

[1] A method of producing a tobacco raw material, the method including: a step of smoke-processing dried tobacco leaf; a step of adding an alcohol to the smoke-processed dried tobacco leaf; and a step of storing the tobacco leaf to which the alcohol has been added.
[2] The production method according to [1], further including, after the storage step, the step of adding a polyol to the tobacco leaf.
[3] The production method according to [1] or [2], wherein the storage step is carried out at from room temperature to 70°C for a period of one week or more.
[4] The production method according to any one of [1] to [3], wherein the storage step is carried out under closed conditions.
[5] The production method according to any one of [1] to [4], wherein smoke-processing is carried out by cold smoking.
[6] A tobacco product containing the tobacco raw material produced by the production method according to any one of [1] to [5].

**[0009]** The invention provides a method of producing a tobacco raw material which has an increased content of ester compounds as flavor ingredients.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0010]**

FIG. 1 presents graphs illustrating the relationship between the number of times tobacco leaves are smoke-processed and the organic acid content of the tobacco leaf, with FIG. 1A showing the acetic acid content, and FIG. 1B showing the contents of isobutyric acid, butyric acid, isovaleric acid, 2-methylbutyric acid and valeric acid.
FIG. 2 is a graph showing differences in the organic acid make-up when the type of wood used during the smoke-processing of tobacco leaves was varied.
FIG. 3 is a graph showing the organic acid make-up in the respective tobacco raw materials obtained by carrying out only a smoke-processing step, by carrying out a smoke-processing step followed by an ethanol addition step, by carrying out a smoke-processing step followed by a menthol addition step, and by carrying out a smoke-processing step followed by an ethanol and menthol addition step.
FIG. 4 presents graphs showing the amount of change in organic acid esters in tobacco raw material, to which propylene glycol was added at various concentrations, after a step in which an alcohol was added to smoke-processed dried tobacco leaf (horizontal axis 1 in the graphs), and after a step in which tobacco leaves obtained by the addition of an alcohol were stored for one week (horizontal axes 2 to 4 in the graphs).

## MODE FOR CARRYING OUT THE INVENTION

**[0011]** The invention is described in detail below by way of embodiments, examples and the like. However, the invention is not limited to the following embodiments and examples, and may be practiced using any modifications thereto insofar as they do not depart from the spirit and scope of the invention.

**[0012]** The present method of producing a tobacco raw material includes the steps of smoke-processing dried tobacco leaf, adding an alcohol to the smoke-processed dried tobacco leaf, and storing the tobacco leaf to which the alcohol has been added.

**[0013]** The tobacco leaf subjected to smoke-processing treatment in the production method of the invention is tobacco leaf that has been subjected to drying treatment. The drying treatment is exemplified by methods that are publicly known. In this invention, "dried tobacco leaf" refers to tobacco leaves that have been dried to a moisture content of generally less than 15 wt%.

**[0014]** Drying treatment may be carried out using a known method without particular limitation.

**[0015]** The tobacco leaves used, although not particularly limited, are exemplified by the following genus *Nicotiana* varieties: the flue-cured and burley varieties of *N. tabacum,* and the brasilia variety of *N. rustica.*

**[0016]** These tobacco leaves are cut by a known method to produce shredded tobacco.

<Smoke-processing Step>

**[0017]** The method of smoke-processing the tobacco leaf is exemplified by known methods such as hot smoke-processing, warm smoke-processing and cold smoke-processing.

**[0018]** Hot smoke-processing is treatment in which the tobacco leaf is smoke-processed at a leaf temperature of from about 60°C to about 120°C. The treatment time may be set as desired based on the required amount of organic acids to be imparted to the tobacco leaf, and is typically from about 10 minutes to about 1 hour.

**[0019]** Warm smoke-processing is treatment in which the tobacco leaf is smoke-processed at a leaf temperature of from about 30°C to about 60°C. The treatment time may be set as desired based on the required amount of organic acids to be imparted to the tobacco leaf, and is typically from about 10 minutes to about 1 day.

**[0020]** Cold smoke-processing is treatment in which the tobacco leaf is smoke-processed at a leaf temperature of from about 15°C to about 30°C. The treatment time may be set as needed based on the required amount of organic acids to be imparted to the tobacco leaf, and is typically from about 10 minutes to about 4 weeks.

**[0021]** The type of wood used to generate the curing smoke is not particularly limited and includes, for example, white oak, cherry, walnut, apple, beech, oak and hickory. The curing smoke may be generated either by burning or by heating the wood. The heating temperature may be set to from 350°C to 650°C, and is preferably from 450°C to 500°C.

**[0022]** All of these smoke-processing treatments can be carried out using a known smoker.

**[0023]** By subjecting the tobacco leaf to smoke-processing treatment, organic acids such as acetic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid and 2-methylbutyric acid are imparted to the tobacco leaves.

**[0024]** Organic acids can be imparted to the tobacco leaf using any of the above smoke-processing treatments. By way of illustration, in one embodiment, from the standpoint of handling of the production equipment (ease of washing), smoke-processing treatment is carried out by cold smoke-processing. The smoke-processing treatment time in this case is preferably from 10 minutes to 1 day, and more preferably from 1 hour to 3 hours.

<Alcohol Addition Step>

**[0025]** The alcohol added to the tobacco leaf obtained by smoke-processing treatment, although not particularly limited, is exemplified by monovalent aliphatic alcohols such as ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-1-propanol, 2,2-dimethylethanol and cyclohexanol; monovalent alcohols having an aromatic substituent, such as benzyl alcohol and phenylethyl alcohol; and sugar alcohols such as sorbitol, maltitol, xylitol, erythritol, lactitol, sorbitan, xylose, arabinose, mannose and trehalose.

**[0026]** These alcohols may be used singly or two or more may be used in combination.

**[0027]** Storing the smoke-processed tobacco leaf to which organic acids were imparted and to which alcohol was subsequently added allows the organic acids and alcohol to react, giving rise to esterification. As a result, the content of ester compounds in the resulting tobacco raw material increases.

**[0028]** The alcohol added to the tobacco leaf may be added in a ratio of from 0.000001 to 0.1 parts by weight per part by weight of tobacco leaf.

**[0029]** Addition of the alcohol is carried out using an ordinary method such as spraying in order to apply the alcohol as uniformly as possible to the shredded tobacco leaf.

**[0030]** In the alcohol addition step, other flavors may be added together with the alcohol. Examples of such flavors include one or more selected from among essential oils and flavor extracts such as menthol, rum, peppermint oil, spearmint oil, menthe oil, rosemary oil, licorice extract, St. John's extract and cocoa.

**[0031]** The flavors added to the tobacco leaf may be added in a ratio of from 0.000001 to 0.1 parts by weight per part by weight of tobacco leaf.

<Storage Step>

**[0032]** The step of storing the tobacco leaf to which alcohol has been added is preferably carried out under conditions where the ester compounds that form during storage do not volatilize off. Such conditions are exemplified by closed conditions.

**[0033]** The closed conditions may be the conditions formed using a closed vessel. Alternatively, the closed conditions may be conditions of a degree where volatile ingredients such as low-molecular-weight ester compounds do not volatilize off.

**[0034]** The storage period is not particularly limited so long as it is a period sufficient for ester compounds to form, although a period of one week or more is preferred for allowing sufficient reactions to arise.

**[0035]** No particular upper limit is imposed on the storage period. Taking into account the period up until the tobacco raw material being produced is shipped out, the storage period may be up to, for example, about 30 weeks.

**[0036]** The temperature during storage is preferably a temperature at which ester compound formation fully arises.

**[0037]** This temperature is preferably a temperature at which the enzymes that are present in the tobacco leaf and promote esterification reactions are activated, and also a temperature at which chemical esterification reactions readily arise.

**[0038]** In one embodiment, the temperature may be suitably adjusted in the range of from room temperature to 70°C. In another embodiment, the temperature may be suitably set in the range of from 30°C to 80°C.

**[0039]** In addition to the organic acids imparted to the tobacco leaf by smoke-processing treatment, the tobacco leaf may also include organic acids already present therein, such as myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid and linolenic acid. As a result, by having the production process pass through the alcohol addition step and the storage step described above, esters of the organic acids already present in the tobacco leaf and the added alcohol also form.

**[0040]** The tobacco leaf also includes the following alcohols: methanol, benzyl alcohol and phenylethyl alcohol. By having the inventive production process pass through the above steps, it is thought that these alcohols also contribute to ester formation.

**[0041]** Illustrative examples of the organic acid esters whose levels are increased in the tobacco raw material obtained by the production method of the invention include ethyl acetate, ethyl valerate, ethyl crotonate, ethyl hexanoate, ethyl myristate, ethyl palmitate, ethyl stearate, ethyl oleate and ethyl succinate.

**[0042]** The production method of the invention may also include, after the storage step, the step of adding a polyol to the shredded tobacco leaf. Propylene glycol, glycerol, or a mixture thereof may be used as the polyol. The polyol may be added to the shredded tobacco leaf in an amount of from 0.1 wt% to 5 wt%.

**[0043]** Polyol addition is preferably carried out by spraying or some other ordinary method used in tobacco production processes, such that the polyol pervades all the shredded tobacco leaf.

**[0044]** As shown in the subsequently described experiments, polyols serve to suppress the esterification reactions between the alcohol that was added and organic acids. Hence, by adding a polyol after the storage step, the formation of ester compounds due to additional reactions elicited by the alcohol that was added can be suppressed. As a result, in this invention, the makeup of the ester compounds that have formed in the storage step is less likely to change over time.

**[0045]** The reason appears to be that, compared with alcohols, the polyol that was added preferentially forms esters with the organic acids.

**[0046]** After the production process has passed through the polyol addition step, to fully suppress esterification reactions between the alcohol that was added and the organic acids, storage for about one week or more is preferred. Such storage is preferably carried out under closed conditions.

**[0047]** Additives such as the above-mentioned essential oils and flavor extracts may be added in any amount and in any step in the production method of the invention.

## <Tobacco Product>

**[0048]** The tobacco raw material of the invention may be rendered into, for example, an oral tobacco product such as snus. In this case, the tobacco raw material produced by the above production method is packed by a known method in a packaging medium made of nonwoven fabric or the like. For example, snus is obtained by filling the packaging medium with a controlled amount of the tobacco raw material, then sealing the packaging medium by means such as heat sealing.

**[0049]** The packaging medium is not subject to any particular limitation, although the use of a cellulose-based nonwoven fabric is preferred.

**[0050]** In cases where the oral tobacco product is gum, the gum can be obtained by using a known method to mix the tobacco raw material produced by the above production method with a known gum base. Chewing tobacco, snuff and compressed tobacco as well, apart from using the tobacco raw material obtained by the production method of the invention, may be obtained by known methods. Likewise, edible films too, apart from using the tobacco raw material obtained by the inventive production method, may be obtained in use of a known material or method.

**[0051]** The tobacco raw material of the invention may be mixed in any ratio with conventional shredded tobacco, and the resulting mixture used to manufacture cigarettes. Alternatively, the tobacco raw material of the invention may be placed within the filter portion of known cigarettes. Placement in the filter portion may entail, for example, disposing the tobacco raw material within the cavity or dispersing the tobacco raw material among the filter fibers.

**[0052]** The tobacco raw material of the invention may also be used in warming or non-heating type cigarette substitutes.

**[0053]** The production method of the invention enables the supply of tobacco raw materials containing an enhanced level of flavor ingredients. Also, the tobacco raw material produced by the method of the invention may be used as all of the tobacco raw material in a tobacco product or may be used as part of the tobacco raw material in a tobacco product. In cases where the tobacco raw material obtained by this invention is used as part of the tobacco raw material in a tobacco product, it may be used in any proportion.

## EXAMPLES

**[0054]** The invention is described more fully below by way of examples. However, the invention, insofar as it does not depart from the spirit and scope thereof, is not limited to the following examples.

### <Experiment 1>

### Application of Short-Chain Fatty Acids by Smoke-processing Treatment of Tobacco Leaves

(Details of Smoke-processing Treatment)

**[0055]** Wood chips of white oak, 20 g, were weighed out onto aluminum foil, then spread over the bottom of a smoker.

**[0056]** Next, 20 g of shredded tobacco was placed on a screen within the smoker. The smoker lid was shut and the heater was turned on (600 W). Once smoke began to emerge, heating was continued at 600 W for another 5 minutes, after which the power supply for the heater was turned off. The length of time until smoke began to emerge was about 6 minutes to about 7 minutes. The smoker was then left to stand for 30 minutes with the lid remaining shut (cooling).

**[0057]** In cases where the treated shredded tobacco was subjected to additional smoke-processing treatment, the above operations were repeated.

**[0058]** In the foregoing treatment, the temperature of the tobacco was about 100°C and the temperature of the wood chips was about 600°C.

(Method of Analysis)

**[0059]** The concentration of acetic acid included in the tobacco leaf on which smoke-processing treatment had been carried out was measured as follows.

**[0060]** Ultrapure water, 10 mL, was added to 0.5 g of the smoke-processed shredded tobacco, and extraction was carried out by 30 minutes of shaking.

**[0061]** The extract was ultrafiltered (molecular weight cutoff, 3000), and the filtrate was collected. The filtrate was diluted with ultrapure water so as to fall within the range of a working curve, and quantitative analysis by capillary electrophoresis (DAD detector) was performed.

**[0062]** Next, the analysis of other organic acids was carried out by solid phase-extraction gas chromatography-mass spectrometry (SPE-GCMS).

**[0063]** Ultrapure water, 50 mL, was added to 0.5 g of the smoke-processed shredded tobacco, and extraction was carried out by 30 minutes of shaking.

**[0064]** The extract was filtered and recovered, then adjusted to a pH of 2 by the addition of hydrochloric acid.

**[0065]** The extract was passed through a solid phase extraction cartridge (Oasis HLB) conditioned with about 20 mL each of diethyl ether, methanol and an aqueous 0.01 N hydrochloric acid solution, following which the cartridge was dried using a stream of nitrogen. The organic acids that had adsorbed to the cartridge were eluted with diethyl ether and quantitatively determined by GCMS analysis.

**[0066]** FIG. 1 shows comparative data on the analytic values for organic acids before and after smoke-processing treatment.

**[0067]** From the results in FIG. 1, it was confirmed that the content of organic acids included in the tobacco leaf increased as a result of subjecting the tobacco leaf to smoke-processing treatment. In addition, it was also confirmed that increasing the number of smoke-processing treatments raises the amount of organic acids imparted to the tobacco leaves.

**[0068]** In addition, differences in the acetic acid concentrations obtained when using various types of wood in smoke-processing were examined.

**[0069]** The procedure carried out for each type of wood was the same as that described above for white oak.

**[0070]** The results are shown in FIG. 2.

**[0071]** It is apparent from the results in FIG. 2 that, even when the type of wood used in smoke-firing treatment was varied, the content of organic acids in the tobacco leaves increased.

### <Experiment 2>

### Changes in Organic Acid Composition Accompanying Esterification Treatment

<Esterification Treatment Operations>

**[0072]** Ten grams of shredded tobacco subjected to 8 smoke-processing treatments with white oak was placed, together with alcohol (0.5 g of ethanol, 0.5 g of menthol, or 0.5 g of ethanol + 0.5 g of menthol), in a 50 mL of a screw neck vial, which was then sealed. The sealed tube was stored in a closed vessel under warming at a given temperature (70°C) for a given period of time (one week).

**[0073]** Concerning such esterification treatment, the organic acid concentrations for smoke-processing treatment (8 smoke-processing treatments with white oak) alone, for ethanol addition following smoke-processing treatment, for menthol addition following smoke-processing treatment, and for ethanol and menthol addition following smoke-processing treatment were each investigated. The results are presented in FIG. 3.

**[0074]** Measurement of the organic acid contents was carried out by the same method as in Experiment 1 above.

**[0075]** It can be assumed from the results in FIG. 3 that, in smoke-processed tobacco leaf to which alcohol was added and which was warmed in a closed vessel, the content of organic acids decreased and esterification reactions arose.

<Experiment 3>

Formation of Various Esters Accompanying Esterification Treatment

<Quenching of Smoke-processed Shredded Tobacco by Ethyl Esterification and Polyol Addition>

Esterification and Quenching Conditions

**[0076]** Ethanol (5%, based on the weight of the shredded tobacco leaf following smoke-processing treatment) was added to the smoke-processed tobacco leaf, following which the tobacco leaf was placed within a screw neck vial, which was then sealed at 40°C for one week. After one week of storage in this manner, propylene glycol was added to the tobacco leaf in predetermined concentrations (1 wt%, 2 wt% or 5 wt%, based on the tobacco leaf).

**[0077]** The organic acid esters were each analyzed by the operations indicated below when 0 weeks had elapsed (untreated), when one week had elapsed following ethanol addition (before propylene glycol addition), and at one-week intervals thereafter (following propylene glycol addition).

**[0078]** Analysis of the ester compounds was carried out as follows.

**[0079]** After precisely weighing out 0.5 g of shredded tobacco into a solid phase microextraction (SPME) vial (20 mL capacity), the vial was sealed by attaching the vial cap and analysis was carried out with a gas chromatograph-mass spectrometer (GCMS) equipped with an SPME automated injection system.

**[0080]** In addition, a sample obtained by adding 25 μL of an acetonitrile solution of p-bromophenethyl alcohol (1 mg/mL) to another SPME vial was similarly analyzed, the ratio of the peak surface areas for the analyte and the p-bromophenethyl alcohol was determined and, based on the calculated values, the amounts of the analyte contained in the respective tobacco samples were compared.

<Analysis Conditions>

Equipment: Agilent gas chromatograph (6890A)

Agilent mass detector (5973N)

**[0081]** Injection volume: 1 μL (injected in pulsed splitless mode)

Column: INNOWAX
Oven: 40°C → 250°C (3°C/min)
Mass detector: TIC mode (mass number, 29 to 550)

<Analytes>

**[0082]** Ester compounds: ethyl acetate, ethyl valerate, ethyl hexanoate, ethyl crotonate, ethyl hexanoate, ethyl myristate, ethyl palmitate, ethyl stearate, ethyl oleate.

**[0083]** The results of Experiment 3 are shown in FIGS. 4A to 4H. The numerical values on the vertical axes in FIG. 4 represent not the concentrations of the organic acid esters, but the peak surface areas obtained in GCMS analysis. The numerical values on the horizontal axes in FIG. 4 represent the number of weeks that have elapsed.

**[0084]** As is apparent from FIG. 4, following one week of storage, organic acid esters were found to have formed in the tobacco leaves to which alcohol was added. In tobacco leaves to which propylene glycol was subsequently added, compared with tobacco leaves to which propylene glycol was not added, the formation of organic acid esters was found to be suppressed with the passage of time.

## INDUSTRIAL APPLICABILITY

**[0085]** The production method of the invention enables a tobacco raw material containing an increased level of flavor ingredients such as organic acid esters to be provided.

## Claims

1. A method of producing a tobacco raw material, the method comprising:

    a step of smoke-processing dried tobacco leaf;
    a step of adding an alcohol to the smoke-processed dried tobacco leaf; and
    a step of storing the tobacco leaf to which the alcohol has been added.

2. The production method according to claim 1, further comprising a step of, after the storage step, adding a polyol to the tobacco leaf.

3. The production method according to claim 1 or 2, wherein the storage step is carried out at from room temperature to 70°C for a period of one week or more.

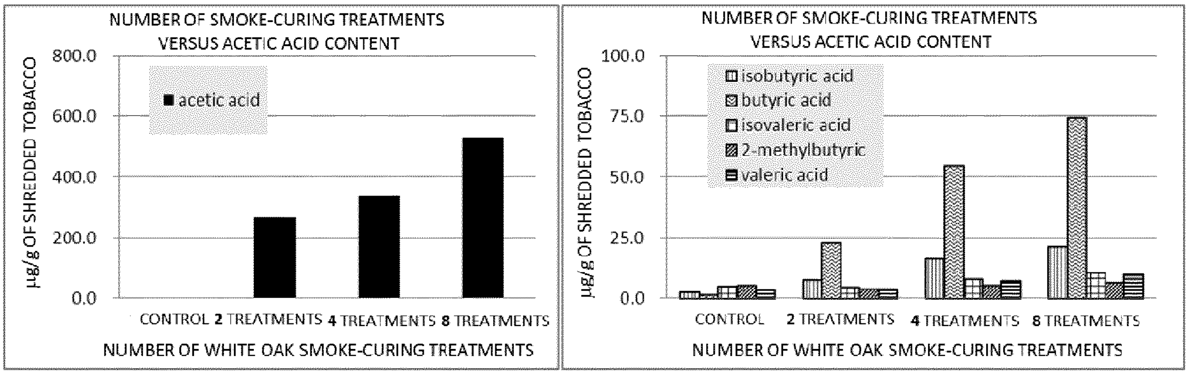
4. The production method according to any one of claims 1 to 3, wherein the storage step is carried out under closed conditions.

5. The production method according to any one of claims 1 to 4, wherein smoke-processing is carried

out by cold smoking.

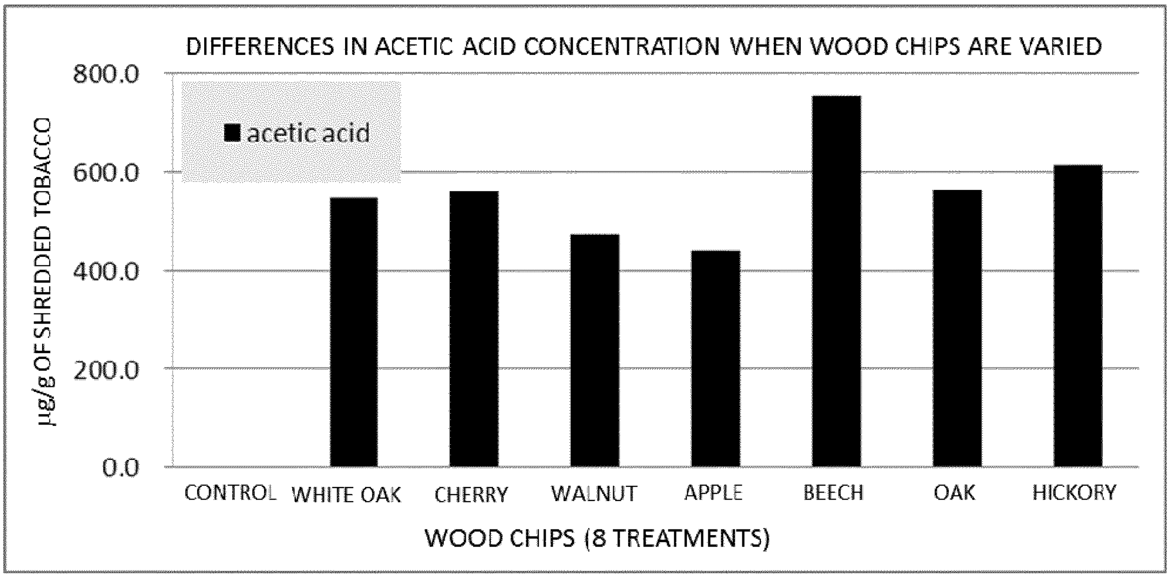
**6.** A tobacco product containing the tobacco raw material produced by the production method according to any one of claims 1 to 5.

[Fig.1]

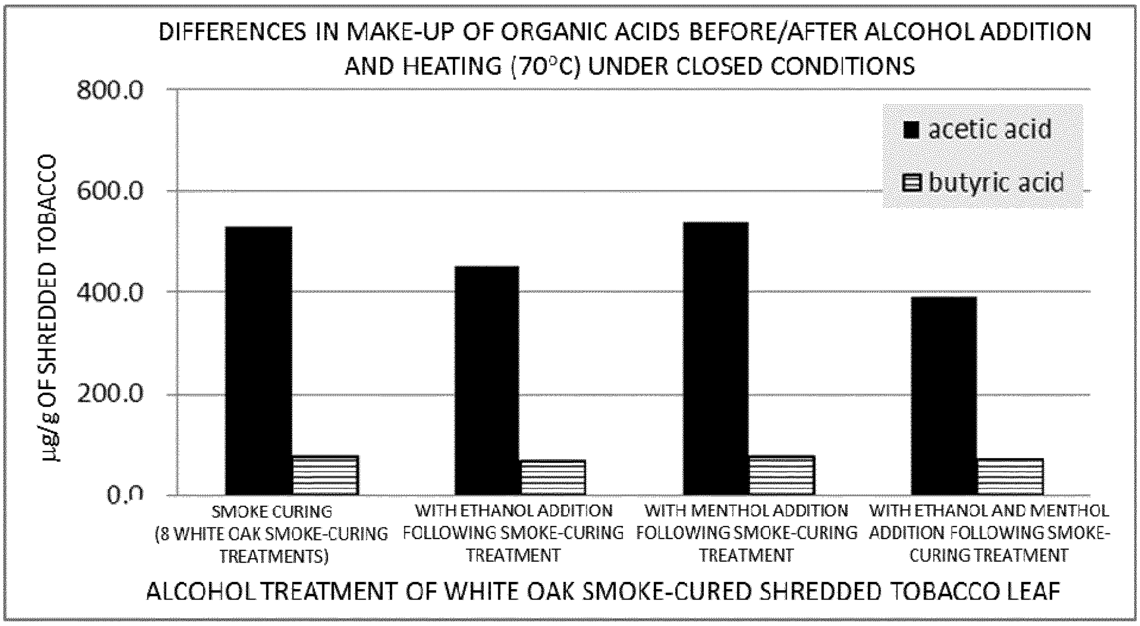

NUMBER OF SMOKE-CURING TREATMENTS VERSUS ACETIC ACID CONTENT
µg/g OF SHREDDED TOBACCO
800.0
600.0
400.0
200.0
0.0
■ acetic acid
CONTROL
2 TREATMENTS
4 TREATMENTS
8 TREATMENTS
NUMBER OF WHITE OAK SMOKE-CURING TREATMENTS
NUMBER OF SMOKE-CURING TREATMENTS VERSUS ACETIC ACID CONTENT
µg/g OF SHREDDED TOBACCO
100.0
75.0
50.0
25.0
0.0
isobutyric acid
butyric acid
isovaleric acid
2-methylbutyric
valeric acid
CONTROL
2 TREATMENTS
4 TREATMENTS
8 TREATMENTS
NUMBER OF WHITE OAK SMOKE-CURING TREATMENTS

(A) (B)

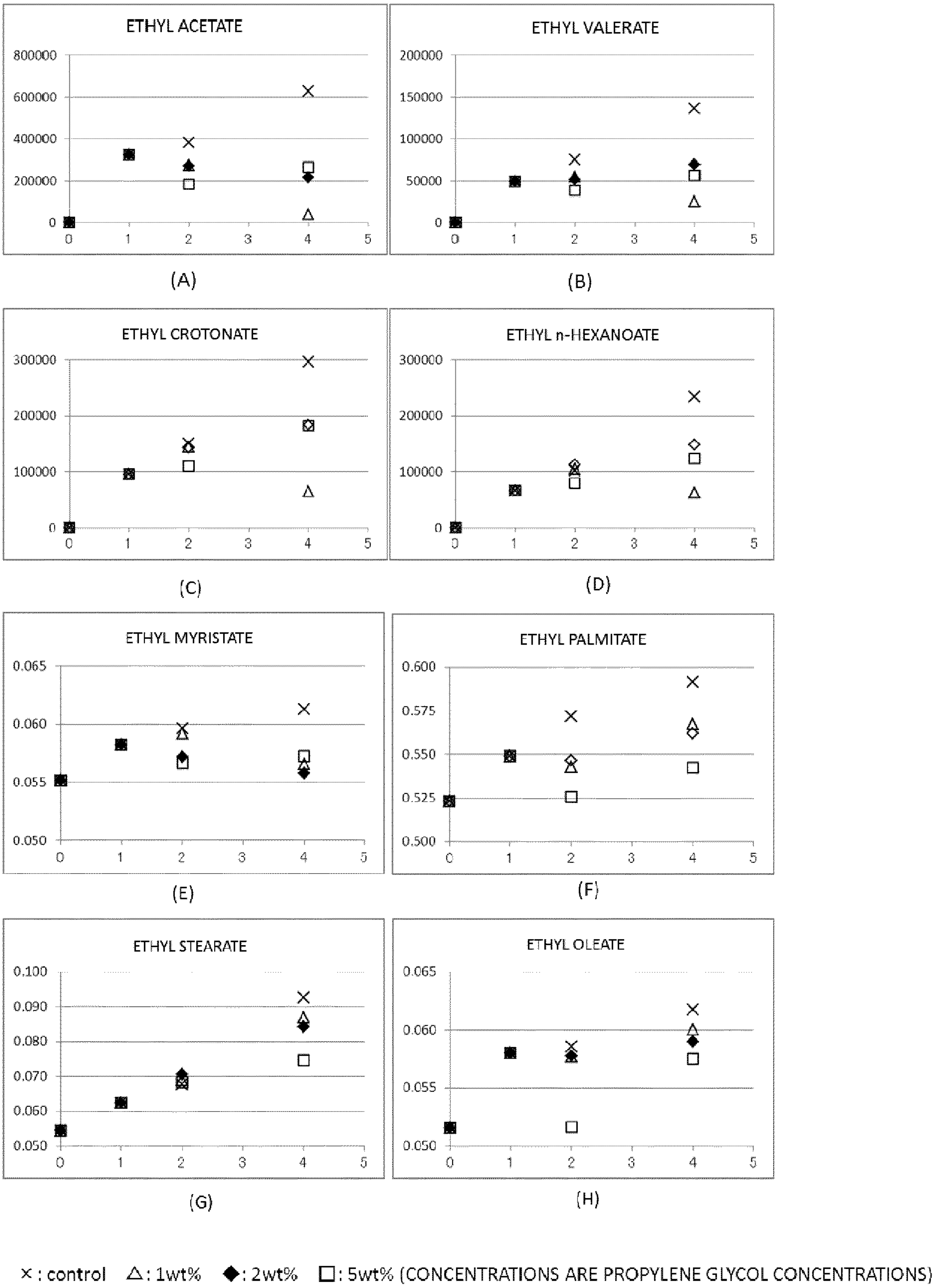
[Fig.2]


DIFFERENCES IN ACETIC ACID CONCENTRATION WHEN WOOD CHIPS ARE VARIED
µg/g OF SHREDDED TOBACCO
800.0
600.0
400.0
200.0
0.0
■ acetic acid
CONTROL
WHITE OAK
CHERRY
WALNUT
APPLE
BEECH
OAK
HICKORY
WOOD CHIPS (8 TREATMENTS)

[Fig.3]


DIFFERENCES IN MAKE-UP OF ORGANIC ACIDS BEFORE/AFTER ALCOHOL ADDITION AND HEATING (70°C) UNDER CLOSED CONDITIONS
800.0
600.0
400.0
200.0
0.0
μg/g OF SHREDDED TOBACCO
■ acetic acid
▤ butyric acid
SMOKE CURING (8 WHITE OAK SMOKE-CURING TREATMENTS)
WITH ETHANOL ADDITION FOLLOWING SMOKE-CURING TREATMENT
WITH MENTHOL ADDITION FOLLOWING SMOKE-CURING TREATMENT
WITH ETHANOL AND MENTHOL ADDITION FOLLOWING SMOKE-CURING TREATMENT
ALCOHOL TREATMENT OF WHITE OAK SMOKE-CURED SHREDDED TOBACCO LEAF

[Fig.4]


ETHYL ACETATE
800000
600000
400000
200000
0
0 1 2 3 4 5
(A)
ETHYL VALERATE
200000
150000
100000
50000
0
0 1 2 3 4 5
(B)
ETHYL CROTONATE
300000
200000
100000
0
0 1 2 3 4 5
(C)
ETHYL n-HEXANOATE
300000
200000
100000
0
0 1 2 3 4 5
(D)
ETHYL MYRISTATE
0.065
0.060
0.055
0.050
0 1 2 3 4 5
(E)
ETHYL PALMITATE
0.600
0.575
0.550
0.525
0.500
0 1 2 3 4 5
(F)
ETHYL STEARATE
0.100
0.090
0.080
0.070
0.060
0.050
0 1 2 3 4 5
(G)
ETHYL OLEATE
0.065
0.060
0.055
0.050
0 1 2 3 4 5
(H)
× : control △: 1wt% ◆: 2wt% □: 5wt% (CONCENTRATIONS ARE PROPYLENE GLYCOL CONCENTRATIONS)

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2013/066806

A. CLASSIFICATION OF SUBJECT MATTER
*A24B3/12*(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)
A24B3/12

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 | 1996-2013 |
| Kokai Jitsuyo Shinan Koho | 1971-2013 | Toroku Jitsuyo Shinan Koho | 1994-2013 |

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. |
|---|---|---|
| Y | JP 57-022545 B2 (Nippon Senbai Kosha),<br>13 May 1982 (13.05.1982),<br>entire text; all drawings<br>& JP 56-51976 A | 1-4,6 |
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☒ 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<br>09 September, 2013 (09.09.13) | Date of mailing of the international search report<br>17 September, 2013 (17.09.13) |
| Name and mailing address of the ISA/<br>Japanese Patent Office<br>Facsimile No. | Authorized officer<br>Telephone No. |

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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2013/066806

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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| Y | JP 59-033345 B2 (R.J. Reynolds Tobacco Co.), 15 August 1984 (15.08.1984), entire text; all drawings<br>& JP 57-208977 A & US 4449541 A<br>& EP 67601 A1 & DE 3272008 D<br>& AU 8283982 A & BR 8202891 A<br>& CA 1179568 A & AT 20697 T<br>& AU 549327 B & AT 20697 E | 2 |
| Y | JP 2003-000219 A (Japan Tobacco Inc.), 07 January 2003 (07.01.2003), paragraphs [0015] to [0016]; fig. 1<br>(Family: none) | 2 |
| A | JP 124767 C2 (Chosen Sotokufu Senbai Kyokucho), 18 May 1938 (18.05.1938), entire text<br>& JP 13-000479 B1 | 1-5 |
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