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2,995,476

ORGANOLEPTIC MATERIALS AND METHOD OF PRODUCTION THEREOF

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This invention relates to organoleptic materials derived from tobacco, methods for their preparation, and tobacco products embodying such materials. The term "organoleptic materials" as used herein includes substances prepared in accordance with our invention, which are pleasing to the senses of taste and smell.

It is an object of this invention to provide novel and useful flavoring materials.

It is also an object of this invention to provide tobacco and tobacco products with enhanced qualities of flavor and aroma.

It is a further object of this invention to provide tobacco with novel and pleasing characteristics of flavor and aroma.

Another object of this invention is to provide means for deriving economic value from tobacco leaf or stems or other portions of the tobacco plant which are commonly considered inferior or waste.

It is an additional object of this invention to provide organoleptic materials derived from natural tobacco sources which are pleasing to the taste and smell organs, before and during combustion of tobacco products in which such organoleptic materials are incorporated.

Other objects of this invention will be apparent or will appear hereinafter.

It has long been common to alter, enhance, and improve the flavor and aroma of tobacco products by incorporating therein, by various methods, a host of flavoring and other ingredients. Sugars, licorices, and other condiments have frequently been used for this purpose, and it has also been suggested to incorporate more uncommon flavorings on the leaf or even to inject them within the living plant. Our invention, however, centers around substances native to the tobacco itself to produce organoleptic products which usefully enhance the smoking product.

We have now discovered that novel and useful organoleptic materials are formed by the reaction of tobacco with lower alkyl alcohols in the presence of a mineral acid catalyst. It is believed that the organoleptic materials obtained are in large part esters formed by reaction of the alcohols with the complex organic acids naturally present in the tobacco leaf, although it is recognized that other alcoholysis products will also be present.

The characteristic flavors and aromas of the organoleptic products obtained in accordance with this invention may be varied according to the alcohols or mixtures thereof which are employed. Lower alkyl alcohols containing up to 8 carbon atoms have been found to give pleasing and useful products, although alcohols of higher molecular weight may also be employed. Lower alkyl alcohols containing from 1 to 6 carbon atoms are generally preferred. Alcohols useful in the practice of our invention include methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-amyl, isoamyl, 2-pentyl, 2-methyl butyl, 3-pentyl, cyclopentyl, n-hexyl, other primary hexyl alcohols, sec-hexyl, cyclohexyl, heptyl, octyl, and other primary and secondary monofunctional alcohols up to at least C₈.

The mineral acid catalyst is essential in the practice of our invention. In its absence any reaction which may occur is at a rate so slow as to be substantially useless.

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The attributes and amount of catalyst have been found to vary according to the mode of practice of our invention, as will appear hereinafter, but it may generally be stated that a highly acid reaction medium is desired.

Among the many advantages of our invention is the number of modes in which it may suitably be practiced. These include exposure of the tobacco to gaseous alcohol and acid, conveniently termed the vapor phase; the application of liquid alcohol and catalyst to tobacco, or liquid phase reaction; and the preparation of a solvent extract of tobacco, which extract may then be reacted with the alcohol and catalyst.

In the vapor phase mode of reaction the organoleptic materials are formed directly in and on the leaf or other part of the plant. In this mode of practicing the invention the tobacco leaf may be suspended or otherwise exposed to the atmosphere of a room or chamber and lower alkyl alcohol vapors introduced therein. In order to maintain the alcohol in vapor phase an appropriately high temperature or low pressure, depending on the particular reagents used, must be maintained. Selection of proper reaction conditions to maintain the alcohol in vapor phase will be routine to those skilled in the art. Temperatures in the range of 20° to 70° C. are preferred. The amount of alcohol employed is not critical but a ratio of 4 to 16 parts by weight of tobacco to 1 part of alcohol has been found satisfactory. The novelty and desirability of the enhanced tobacco flavorings may be improved by employing mixtures of such alcohols as the reagent.

In order to assure that the optimum pH conveniently attained is reached, a substantial amount of mineral acid should be employed, limited principally by a concentration of acid vapor which would char or discolor the leaf. A preferred amount of acid is about 0.03 to about 0.20 gram equivalent per 100 grams of tobacco.

The reaction will be promoted by circulating the atmosphere within the reaction chamber to increase the exposure of the surface of the tobacco to the alcohol and acid vapors. The leaves or other portions of the plant should be disposed so as to permit the greatest contact with the vapors within the chamber. The reaction may proceed for three hours or less to three weeks or more, depending upon the concentration of reagents, temperature, flavor or aroma desired, and other variables apparent to one skilled in the art.

Upon conclusion of reaction in the vapor phase the alcohol and acid vapors may be removed from the tobacco by exposure to a current of fresh air. This may be done either by ventilating the system or by removing the tobacco from the chamber and blowing air over it. If desired the vapor phase operation may be conducted as a continuous or semicontinuous process, the tobacco entering the chamber and slowly traversing a path therein for a sufficient time to permit production of organoleptic material, and finally leaving the room and being exposed to the atmosphere or a current of air which serves to remove residual vapors.

The reacted tobacco may be directly fabricated into a greatly enhanced smoking tobacco, either singly, or blended with other tobaccos.

Another method useful in the practice of this invention is the production of organoleptic product by the reaction between tobacco and a lower alkyl alcohol in liquid form, in the presence of a dissolved mineral acid catalyst. This process is particularly advantageous in making possible a very broad range of pleasing and novel smoking products and generally requires less time than for reaction in vapor phase. By selection and blending of organoleptic materials and by controlling the amount of such material used, flavors and aromas of desirable

and decidedly differing character may be obtained. The organoleptic product may be isolated and embodied in the smoking tobacco as a flavoring or odor enhancing attribute or constituent by spraying or other means of application.

In order to form significant amounts of organoleptic material in the liquid phase mode of this invention, we have found it essential that the pH be maintained below a certain point which is lower than that of a mixture of tobacco and lower alkyl alcohol. Thus, no significant amount of fragrant material is formed in a bright stem-ethyl alcohol mixture at its normal pH of about 5. Correspondingly, burley stems do not react with ethyl alcohol while the pH remains at its normal level of approximately 6. When the pH is lowered to about 3.5 by addition of a mineral acid, however, reaction between the lower alkyl alcohol and organic tobacco substances occurs to a significant extent and organoleptic material is formed. A pH below about 3 is preferred to derive economic yields and a pH below about 1.5 is considered optimum.

Alternatively, the amount of acid used may be calculated as at least equivalent to the alkalinity of the stem ash. This value is determined by reducing a small representative sample of the ground tobacco to ash in a muffle furnace. An excess of 0.2 N HCl is added to the ash and after warming to 60° C., the mixture is back-titrated with 0.2 N and NaOH to a phenolphthalein end point. Alkalinity of bright stems is commonly in the range of 0.17 to 0.21 equivalent per 100 grams. The preferred range of acid is from 10 to 30% in excess of this value. In runs where a 20% excess of HCl has been used, the pH of the alcoholic reaction liquor has ranged from 0.1 to 0.9.

The mineral acid selected as the catalyst should be capable of bringing the reaction mixture to the desired pH, and salts of such acids having the requisite acidity may also be used. Hydrochloric acid, sulfuric acid, phosphoric acid, sulfonic acids, and acidic salts such as those of aluminum, iron or magnesium, for example the chlorides, sodium and potassium acid sulfates, and sodium and potassium acid phosphates are exemplary of suitable catalysts.

The rate of reaction will be increased by elevating the temperature and, subject to the volatility of the reactants, a temperature in the range of 40 to 78° C. is preferred. The time required for the reaction will of course vary with the reactants and conditions. It has been found that the variety of tobacco also influences the rate, due in part, it is believed, to differences in mineral content.

Upon completion of the reaction, the pH of the mixture is adjusted to a point on the acid side of neutral. Sodium hydroxide or other common base may suitably be used for this purpose. We have found that the flavor and fragrance of the organoleptic materials and of the tobacco product in which they may be incorporated is affected by the pH to which the reaction mix is brought. Useful material will be derived if the pH is brought within the range of about 6 to 7, with the sweetest flavors obtained in the preferred range of about 6.3 to about 6.8.

After adjustment of the pH the mix may be filtered to remove the exhausted tobacco and the organoleptic material may be recovered, as by distillation or other conventional methods.

Through choice of alcohol or mixture of alcohols, products have been obtained whose odors encompass a broad range, including sour-bitter, sweet-bitter, meaty and sweet. The particular tobaccos treated will of course influence of the characteristics of the organoleptic materials formed, due to variation in the organic and mineral constituents of varieties of plants and the soil conditions under which they are grown. Further, the variation in flavor and aroma of different types of to-

baccos, when combined with the esterification and alcoholysis products of similar and different plants, makes possible a very broad range of useful, novel and pleasing characteristics not heretofore available.

Another mode of practicing this invention comprises extraction of tobacco with an organic solvent or water, and the reaction of this extract with a lower alkyl alcohol in the presence of mineral acid catalyst.

Among the solvents which may be used in preparing the tobacco extract are water, methyl, ethyl, propyl, and isopropyl alcohols, acetone, methyl ethyl ketone, ethyl ether, tetrahydrofuran, dioxane, "Freons," methylene chloride, chloroform, other halocarbons, liquid hydrocarbons from C₃ to C₈, benzene, etc. Organic solvents generally are useful for extraction of the tobacco.

We have found that mineral acid, such as that used in catalyzing the esterification reaction, when added to the above solvents, will markedly increase their solvating power. The acid need not be present in the amounts appropriate in esterification, and the extracting medium may have a pH in the range of 2.0 to 4.0. Thus the tobacco may be extracted with solvent containing a small amount of acid to provide a liquor containing substance esterifiable to the organoleptic products of this invention. If lower alkyl alcohol or mixture of lower alkyl alcohols has been used to prepare the extract the esterification reaction can be conducted following extraction merely by the addition, if necessary, of sufficient mineral acid catalyst to attain the desired pH below 3.5, and preferably below about 1.5, as previously described in connection with the liquid phase reaction. Alternatively, the extract may be concentrated, if desired, and blended with a suitable lower alkyl alcohol or alcohols, as described above, and a suitable mineral acid catalyst. At completion of the reaction the pH of the reaction mix is adjusted to a slightly acid level as described above and the organoleptic material may be recovered by conventional methods.

A significant advantage of liquid phase and extract modes of producing organoleptic material by this invention is that stems and other portions of the plant which are waste or are generally considered inferior or suitable for use only after re-processing in manners known to the art may now be processed to provide a useful product. The organoleptic material may be isolated and embodied in the tobacco product as a flavoring or odor-enhancing attribute or constituent by spraying or other suitable means of application. It is possible to isolate organoleptic material formed in the vapor phase by washing or extraction, but for reasons of convenience we prefer to employ this mode principally for reaction of leaf. The amount of recovered organoleptic material employed in cigarette filler, for example, will vary depending upon the effect desired, but between about 0.01% and about 5% by weight of the tobacco has been found suitable. We have found the preferred amount to be between about 0.05% and about 2.0%.

Cigarettes and smoking tobacco have been prepared incorporating organoleptic material obtained by the processes described herein. The products were subjected to customary sensory evaluation tests and their smoke was found to have enhanced fragrance and was pleasingly savory. The organoleptic condiments were found to complement the characteristics of the tobacco and the ordinary flavoring ingredients commonly included in the preparation of smoking tobacco.

The flavors and aromas produced by this invention are subtle and intriguing and complement the smoke; they are not dominant like flavors such as menthol or spearmint. The smoker is aware of the enhancement of the flavor and aroma, but is not conscious of any radical change such as that associated with cigarettes flavored with menthol or similarly strong artificial additives known in the art.

The following examples of modes of practicing this

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invention are for illustrative purposes and are not to be taken in a limiting sense.

Example I

Anhydrous hydrogen chloride gas was introduced into absolute ethyl alcohol until a concentration of about 25% (weight/volume) was attained. 25 ml. of this reagent were placed in the bottom of a vacuum desiccator and 320 grams of dry, crushed stems were placed on the desiccator shelf. A vacuum of 100 mm. Hg (absolute) was applied, the desiccator sealed, and placed in an air oven and heated slowly to 75° C. The absolute pressure at 75° C. was in the range of 350–450 mm. Hg. This temperature was maintained for 11½ hours, at the end of which time air was admitted to the system and the reacted stems transferred to a clean, dry desiccator where they were held at an aspirator vacuum of approximately 35 mm. Hg (absolute) for one hour, removing much of the excess HCl and ethanol. The product was spread out in a hood and allowed to come to equilibrium with air at 75° F. and 60% relative humidity. The stems were slightly acidic (a 2% dispersion in distilled water gave a pH of 4.2) and had a pleasant fruity odor.

Example II

Example I was repeated using 50 ml. of alcohol-acid reagent and reaction for 18 hours. The product was more acidic (the pH of a 2% dispersion of product in distilled water was 3.5) and more strongly flavored. It was shredded, blended in equal parts with cut bright tobacco, and used to make cigarettes. On smoking, a sweet, fruity flavor was imparted to the smoke.

Example III

227 grams of regular tobacco leaf cigarette filler but additive-free were placed in a 4-liter flask which was deeply immersed in a Dry Ice-acetone bath. After the contents of the flask had been brought to the temperature of the bath, a low vacuum was drawn on the flask. Use of the low-temperature bath avoided loss of volatile tobacco constituents upon application of the vacuum.

Fifteen ml. of dry methanol and vapors from 3 ml. of fuming sulfuric acid were then separately admitted to the flask. By reason of the low pressure within the flask both reagents were converted to vapors and were dispersed uniformly throughout the tobacco leaf filler. The sealed flask was removed from the cold bath and permitted to reach room temperature, where it was held for 8 hours.

The flask was opened and the contents removed. The tobacco had a very fruity, raisin-apple aroma which was discernible also in the smoke of cigarettes made from it as noted hereinafter.

Example IV

Eight hundred grams of dried bright stems were placed in a 3-liter trident flask and covered with 1750 ml. of absolute ethyl alcohol containing 50 grams of dry hydrogen chloride. 200 ml. of benzene were then added, and the mixture was heated to reflux in a water bath and distilled slowly at a high reflux ratio into a jacketed glass fractionating column filed to a depth of 18 inches with ¼-inch Burl saddles. As azeotropic mixtures of benzene, ethyl alcohol and water were removed, absolute ethyl alcohol was added to the reaction vessel periodically to maintain a constant level of liquid. This process was carried out on two consecutive working days, and 600 ml. of azeotropic mixtures which boiled below 78° C. were removed from the system. By this time, all benzene had been removed as distillate, along with a substantial amount of water of reaction.

At this point, the reaction liquor was separated from the stems, and the latter were washed carefully with 500 ml. of absolute ethyl alcohol. Washings and liquor were combined and reduced to a volume of about 600

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ml. by distillation at atmospheric pressure. The material was adjusted to a pH of 5.5, using 285 ml. of water containing about 13 grams of sodium bicarbonate, as the flask was cooled in an ice bath.

The mixture was made up with water to about 3½ liters and transferred to a 4-liter continuous extractor and extracted with ether for 24 hours. The ether extract was dried with anhydrous sodium sulfate. After removing excess ether and ethyl alcohol, the residue was vacuum distilled at 2 to 3 mm. to yield 33.2 grams of organoleptic material which boiled over the range 76° to 123° C.

To obtain a sweet, pleasant flavor it is important that the pH of the distilled product be made slightly acid. The material should be also checked carefully for excessive acidity or alkalinity before proceeding with the final high vacuum distillation.

Example V

The esterification of bright stem extract solids with higher boiling alcohols was carried out in the apparatus and following the procedure described in Example IV, heating the reactor in a glycerine bath.

For the extract 2000 grams of bright stems having a 15% moisture content were extracted three times with tepid water. The liquor was separated from the stems in a press and evaporated to a solids content of about 70% in an open pan in a circulating air oven at 100° C., yielding approximately 1170 grams. 364 grams of this extract were refluxed with one liter of isobutanol containing 39 grams of 95% sulfuric acid. An azeotropic mixture of water and isobutanol (B.P. 88.5° C.) was collected for approximately 8 hours, and the isobutanol was redried over K₂CO₃ and returned to the reactor at intervals. The head temperature increased slowly and when it had reached 103° C. the reaction was considered complete.

The reaction mixture was neutralized to pH 6.3 with about 150 ml. of 10% NaOH and the stems removed and washed with four 100 ml. portions of water. The isobutanol was removed under vacuum, and the residue was taken up in 300 ml. of ether and centrifuged to remove solids. After removing ether, 184 grams of material remained. This was distilled in a Claisen flask at 2.5 mm. Hg and 49 grams of products was obtained (B.P. 60–110° C.). The odor was described as "woody," "like pine oil" and "distinctly camphoraceous." The saponification equivalent weight was about 141, and the theoretical amount of isobutanol was recovered from a saponified sample.

Example VI

The esterification reaction of Example V was carried out using n-hexanol in place of isobutanol. The method used was essentially the same, except that 114 ml. of 37½% hydrochloric acid was used in place of sulfuric acid, and benzene was used to reduce temperatures in the later stages of cooking, permitting removal of most of the water at temperatures well below the boiling point of hexanol. At 2 to 4 mm. Hg, the n-hexyl esters distilled up to about 137° C. About 40 g. of organoleptic material was obtained. It had an odor of low intensity which was distinctly pleasant and "nutty," at lower dilutions.

Organoleptic material prepared in accordance with the foregoing examples was incorporated into cigarettes. The smoke from these cigarettes was compared with that from cigarettes containing filler from the same batch but not containing organoleptic material. It was found that the smoke of those containing the organoleptic material was noticeably enhanced, having interesting and pleasing qualities of taste and aroma. The alteration of these characteristics of the smoke was not dramatic, but rather pleasing and definitely discernible. By combining the products of the examples differing flavors and aromas

were obtained. It was further found that a substantially linear relationship existed between the amount of organoleptic material incorporated in the cigarette and the apparentness of its presence.

It will be understood that the foregoing examples are to be considered only as illustrative and that we do not intend to limit ourselves to the particular materials, proportions or procedures stated therein.

We claim:

1. A method of preparing organoleptic material from tobacco which comprises reacting said tobacco with lower alkyl alcohol in the presence of mineral acid catalyst.

2. A method of forming organoleptic material in tobacco which comprises reacting said tobacco with vaporous lower alkyl alcohol in the presence of vaporous mineral acid catalyst.

3. The method of claim 2 in which the ratio between the vaporous mineral acid catalyst and the tobacco is between about 0.03 to about 0.20 gram equivalents of acid per 100 grams of tobacco.

4. The method of claim 2 in which the lower alkyl alcohol is ethanol and the mineral acid catalyst is hydrogen chloride.

5. A method of preparing organoleptic material from tobacco which comprises reacting said tobacco with liquid lower alkyl alcohol in the presence of sufficient mineral acid catalyst to reduce the pH of said tobacco, liquid lower alkyl alcohol and mineral acid catalyst below about 3.5, adjusting the pH after reaction to between about 6 to 7, and recovering the reaction product.

6. The method of claim 5 wherein the pH of the tobacco, alcohol and catalyst during reaction is maintained below about 1.5.

7. The method of claim 5 wherein the lower alkyl alcohol is ethanol and the mineral acid catalyst is hydrochloric acid.

8. The method of claim 5 wherein the lower alkyl alcohol is isobutanol and the mineral acid catalyst is sulfuric acid.

9. The method of claim 5 wherein the lower alkyl alcohol is n-hexanol and the mineral acid catalyst is hydrochloric acid.

10. A method of preparing organoleptic material from tobacco which comprises reacting said tobacco with lower alkyl alcohol in the presence of mineral acid catalyst, the amount of said catalyst being from 10% to 30% in excess of the stoichiometric equivalent required to neutralize the combustion ash of said tobacco, adjusting the pH after reaction to between about 6 to 7, and recovering the reaction product.

11. A method of preparing organoleptic material from tobacco which comprises extracting said tobacco with organic solvent extracting medium, reacting the resultant extract with lower alkyl alcohol in the presence of sufficient mineral acid catalyst to reduce the pH of the mixture of said extract, said lower alkyl alcohol and said mineral acid catalyst below about 3.5, adjusting the pH of the mixture after reaction to between about 6 to 7, and recovering the reaction product.

12. The method of claim 11 wherein the organic solvent extracting medium contains sufficient mineral acid to bring the pH thereof between about 2 to 4.

13. The method of claim 12 in which the pH of the extract, lower alkyl alcohol, and mineral acid catalyst is below about 1.5.

14. A method of preparing organoleptic material from tobacco which comprises extracting said tobacco with water, reacting the resultant extract with lower alkyl alcohol in the presence of sufficient mineral acid catalyst to reduce the pH of the mixture of said extract, said lower alkyl alcohol and said mineral acid catalyst below about 3.5, adjusting the pH of the mixture after reaction to between about 6 to 7, and recovering the reaction product.

15. The method of claim 14 in which the water contains sufficient mineral acid to bring the pH thereof between about 2 to 4.

16. A method of preparing organoleptic material from tobacco which comprises extracting said tobacco with a lower alkyl alcohol extracting medium, acidifying the resultant extract with mineral acid catalyst in an amount sufficient to reduce the pH below about 3.5, whereby reaction takes place between the alcohol and tobacco, adjusting the pH after reaction to between about 6 to 7, and recovering the product.

17. The method of claim 16 in which the lower alkyl alcohol extracting medium contains mineral acid in an amount that will bring the pH of said medium between about 2 to 4.

18. As a composition of matter, tobacco which has been reacted with lower alkyl alcohol in the presence of mineral acid catalyst.

19. As a composition of matter, tobacco in which organoleptic material has been formed by reaction of said tobacco with vaporous lower alkyl alcohol in the presence of vaporous mineral acid catalyst.

20. A composition of matter which comprises (a) tobacco, and (b) organoleptic material which is the reaction product prepared by reacting tobacco with lower alkyl alcohol in the presence of mineral acid catalyst.

21. A tobacco product which has incorporated therein organoleptic material prepared by reacting tobacco with lower alkyl alcohol in the presence of mineral acid catalyst, said organoleptic material being present in an amount corresponding to between about 0.01% and about 5% by weight of the tobacco.

22. A composition of matter which comprises (a) tobacco, and (b) organoleptic material which is the reaction product prepared by reacting a solvent extract of tobacco with lower alkyl alcohol in the presence of a mineral acid catalyst.

References Cited in the file of this patent

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

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John D. Hind et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 28, for "0.2 N and NaOH" read -- 0.2 N NaOH --; column 3, line 71, strike out "of", first occurrence.

Signed and sealed this 26th day of December 1961.

(SEAL)

Attest:

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