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3,047,431

SMOKING COMPOSITION

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No Drawing. Filed May 8, 1961, Ser. No. 108,300
20 Claims. (Cl. 131-17)

This invention relates to tobacco and more particularly relates to a method and compositions for embodying predetermined flavors in tobacco which flavors can be maintained and preserved during subsequent processing and storage of the tobacco.

It is an object of this invention to permit the incorporation of a flavor into a tobacco product which flavor will not be lost or altered during subsequent manufacturing steps or during storage. The incorporation is by way of an inclusion complex and the products with which the present invention is particularly concerned comprise smoking compositions.

In accordance with the invention the desired flavor is incorporated in a smoking tobacco composition in a manner such that it will not be released prior to the time the tobacco product is smoked. By the term "tobacco" as used throughout the discussion is meant any composition intended for human consumption by smoking whether composed of tobacco plant parts or substitute materials or both.

It is a further object of this invention to control the amount of flavor released during the smoking of a tobacco product to insure uniformity of tobacco flavor during the entire smoking process.

It is a still further object of this invention to obtain a flavoring composition uniquely suited for use in tobacco products.

Further details of the objects and procedures of this invention may be found from the following description.

Essentially, this invention involves the formation of an inclusion complex between a host compound and a flavoring material wherein the flavoring material is rendered inert under normal temperature conditions but which flavoring material is released under conditions of elevated temperature.

The use of inclusion complexes has heretofore been known to the chemical arts in general. In essence, an inclusion complex can be described as a single solid made up of two distinct components, the host and the guest. The guest molecule or compound is enclosed within the host molecule or compound which host molecule or compound often forms a channel or cage-like structure and the guest is thereby rendered inert to external forces. Generally, upon the application of higher temperatures, the complex breaks down and the guest molecule is released, its chemical composition being substantially unchanged.

More particularly, inclusion complexes are binary complexes of the general formula AB_n where n need not be integral. A, the host substance, is characterized by the presence in its crystal lattice of voids or cavities, which may be open ended and roughly cylindrical or completely enclosed and roughly spherical. The guest molecule, B, must have molecular dimensions that will allow it to fit snugly into one of these cavities. In the complex, a varying number of cavities in the host are filled with guest molecules. No chemical bonding between the guest and host molecules is believed to occur, but instead their enforced proximity is believed to give rise to forces of the van der Waals type which suffice to give considerable stability to the complex.

Host compounds are divided into a number of different types. There are the polymolecular host compounds con-

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taining channel-like spaces. Typical among these compounds are such well known substances as urea, thiourea, and desoxycholic acid. There are also those polymolecular host compounds having cage-like spaces. These compounds form inclusion complexes known as "clathrates." Compounds such as hydroquinone and phenol have been known to form clathrates. There are some host compounds with cage-like spaces that form clathrates with guest compounds that act on a monomolecular basis. That is, there is just one host molecule for each guest molecule. The cyclodextrins and particularly the alpha, beta, and gamma cyclodextrins are believed to act in this manner with certain guest compounds but not with others.

Flavoring materials are commonly very volatile and very readily contaminated by other materials present in the product to be flavored so that much of the original flavor is often lost by volatilization, adulteration, etc. during the manufacturing operation when flavor is added at some advantageous intermediate stage. Also, several flavorants may combine to yield an unsatisfactory composite flavor. When, in accordance with the method of this invention, the flavoring compound is added to the product in the form of an inclusion complex, the presence of the host compound will prevent the flavoring compound from being affected during the course of remaining manufacturing steps and during the course of storage. Only when the final product is ready for use will the flavor be released. Thus, in the case of smoking tobacco, only when it is being smoked, as in a cigarette for example, will the flavor be released.

Conventional methods now in use for incorporating flavors into tobacco materials have many disadvantages. Organic flavorings are usually introduced into tobacco directly. Menthol and other natural flavoring extracts are now added to tobacco in this manner. This method is not satisfactory in that many of the desirable organic flavor compounds are lost during the manufacturing operation because of combination with other flavors present in the tobacco. A further disadvantage is that many of the flavoring compounds are dissipated during storage, or a large percentage of the flavor is lost by volatilization ahead of the burning area of the tobacco and upon the initial puffs and thus the delivery is not uniform or gradual as is desired. Additionally, these flavoring methods may contribute undesirable odors to the pack aroma of cigarettes.

The flavor is sometimes produced in tobacco by adding a polymer emulsion containing esters of certain organic acids which will, as a result of pyrolysis of the esters, form olefins and acids that improve the flavor and aroma of smoke. This method of introducing flavors provides only a limited means of producing flavors, however, since it is necessarily limited to a specific class of compounds.

In the case of products made from smoking tobacco, the typical practice of this invention involves the formation of an inclusion complex in a manner to be described below, between a guest flavoring compound and a suitable host compound. This inclusion complex is then incorporated into the smoking tobacco. A typical method of performing this incorporation would be to uniformly disperse the inclusion complex in water and then spray the resultant dispersion onto finely divided tobacco. Equally good results are obtained by grinding up the inclusion complexes and dusting them onto the tobacco. It will be readily understood that the methods of combining the tobacco with the inclusion complexes are not critical to this invention. Any incorporation means may be employed provided the ultimate product contains a uniform dispersion of the inclusion complex.

It will be understood that by this method a plurality of different inclusion complexes may be used as additives

to tobacco so that a plurality of desired flavors may be liberated simultaneously in the smoked tobacco.

Typical flavoring compounds for use in smoking tobaccos include menthol, d-limonene, pinene, paracymene, thymol, linalool and geraniol. The foregoing are representative of terpene compounds suitable for the purpose. Additional terpene compounds include menthone, citronellal, myrcene and cineol. The essential oils are also suitable for use in this connection.

Although the terpene compounds are particularly preferred as flavorants, other organic compounds give satisfactory flavoring characteristics when present as guest compounds.

In general, with the cyclodextrins, the preferred host compounds of this invention, the guest compound may be any tobacco-flavoring organic compound having a molecular diameter of less than about 12 Angstrom units and capable of forming a complex with a cyclodextrin host compound which complex decomposes upon heating to the pyrolysis temperature of tobacco. The 12 Angstrom unit maximum limitation is necessary in order to preclude the use of compounds with molecules too large for complexing with a cyclodextrin host compound. No complex will be formed if larger potential guest molecules are employed.

Aromatic hydrocarbons meeting the above requirements may be used as guest compounds to flavor tobacco. Aliphatic hydrocarbons are also applicable, for example, n-octane.

The aliphatic and aromatic aldehydes are likewise applicable to this invention. A typical example is 2,4-hexadienal.

Suitable heterocyclic hydrocarbons include pyridine. The o-, m- and p-cresols are also suitable guest compounds.

The aliphatic and aromatic ketones such as cyclohexanone and acetophenone may also be used. Organic esters are also applicable, as for example, ethyl-n-caprylate and methyl salicylate. A representative lactone is coumarin. Vanillin is a suitable ether.

It is to be understood that mixtures of more than one flavoring compound may be used to make up the tobacco flavoring material to be used to form an inclusion complex. Alternately, several different inclusion complexes may be added to the same tobacco product.

The preferred host compounds are the cyclodextrins, preferably the alpha, beta and gamma cyclodextrins. These compounds are also referred to in the literature as Schardinger dextrins and the alpha, beta and gamma compounds are often referred to as cyclohexaamylose, cycloheptaamylose and cyclooctaamylose, respectively. Further details on these compounds may be found in "Advances in Carbohydrate Chemistry," volume 12 (Academic Press, 1957), pages 190-257.

Other host compounds are likewise suitable for use to form inclusion complexes with tobacco flavorants. In general, the host compound must be a compound capable of forming an inclusion complex with a tobacco flavoring material as above described, which inclusion complex will break down quickly upon heating at the pyrolysis temperature of tobacco. A further requirement of the host compound is that it not be physiologically toxic and that it not decompose into physiologically toxic products at temperatures below about 1000° C. Additional details on some typical host compounds may be found in an article by Mandelcorn, "Clathrates" in Chemical Reviews, volume 59, No. 5, October 1959, pages 827-839. A list of references on the general subject matter of inclusion complexes is appended thereto.

The alpha, beta and gamma cyclodextrins are particularly preferred host compounds for use in connection with tobacco flavoring since there is no possibility of their adding any undesirable products to the gas phase of smoke. These cyclodextrins, chemically, are made up of six, seven or eight glucose units linked in a cyclic manner.

The pyrolysis and combustion products from cyclodextrins do not differ materially from the pyrolysis and combustion products from glucose or from other carbohydrates containing glucose units such as sucrose, maltose or cellulose. All of these carbohydrates occur naturally in tobacco or are commonly added to it during the manufacturing process. Therefore, in cigarettes made from tobacco mixed with cyclodextrin inclusion complexes, pyrolysis of the cyclodextrin yields only those products which are normally found in cigarette smoke. Thus, the tobacco flavor is greatly improved by the use of cyclodextrin inclusion complexes without in any way changing the flavor or physiological effects otherwise to be expected from tobacco smoke. The cyclodextrin inclusion complex generally contains from about 0.5 to about 2.0 moles of included guest compounds per mole of cyclodextrin. Thus, the inclusion complexes will contain from about 3% to about 15% by weight of included flavoring material. The amount of flavor compound desired in cigarette smoke naturally varies with the nature of the particular flavor used but is usually within the range of 10 to 1000 micrograms per cigarette delivered in the smoke and, for most flavors, is less than 100 micrograms per cigarette. The most advantageous amount of cyclodextrin inclusion complex to be added will therefore usually be in the range of about 1 to about 10 milligrams per gram of tobacco.

The method of forming the inclusion complex is not critical to this invention. Any known method of complex formation is satisfactory. The preferred method with respect to cyclodextrin inclusion complexes is to dissolve the host compound in a suitable inert solvent which does not act as a guest compound for the particular host and thereafter the guest compound may be added to the solution. The complex will thereafter precipitate out of solution.

The method of forming inclusion complexes will necessarily vary with other host compounds. Additional details on methods of forming complexes with various host compounds may be found in the above-mentioned article by Mandelcorn. Further details on the method of utilizing this invention may be had from the following working examples:

Example 1

Ten parts by weight of alpha-cyclodextrin were dissolved in a hundred parts by weight of water. Ten parts by weight of menthol was added to this solution which was then allowed to stand with occasional agitation for four hours. A menthol-alpha-dextrin inclusion complex was then filtered from the solution and was washed with ethanol and ether and dried under vacuum at 110° for twenty-four hours. Seven parts by weight of inclusion complex were obtained. This inclusion complex was a white, odorless, crystal in substance, soluble in water to the extent of 13.6 grams per liter and insoluble in many other solvents. It was found to be stable indefinitely at room temperature either as a dry solid or in a clear solution or suspension in water. The inclusion complex was found to decompose on heating at about 300° C. with liberation of the included menthol. Likewise, menthol was found to be liberated when the aqueous suspension of the inclusion complex in water was heated to boiling. Analysis of the inclusion complex by means of colorimetry showed a menthol content of 3.60%. Collection and determination of the menthol liberated from a boiling aqueous suspension gave a value of 3.64% menthol present in the inclusion complex.

Three parts by weight of the menthol-alpha-cyclodextrin inclusion complex thus prepared were added to five hundred parts of bright smoking tobacco by spraying the tobacco with a fine aqueous suspension and the tobacco so treated was made into cigarettes. The cigarettes were smoked on a constant volume smoking machine. The puffs were of two second duration (about 8 puffs per

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cigarette) and had a volume of 35 ml. The cigarettes were smoked to a 25 mm. butt length and the smoke collected on a Cambridge filter pad which trapped particles greater than a 0.3 micron size. The smoke contained 35 to 50 micrograms of menthol per cigarette, as determined by vapor phase chromatography and subjective tests indicated a pleasing menthol flavor.

Example 2

5 parts by weight of beta-cyclodextrin were dissolved in 250 parts by weight of water. 5 parts by weight of menthol were added and the mixture was allowed to stand for 24 hours. The menthol-beta-cyclodextrin inclusion complex was isolated by filtration, washed well with ethanol and ether and dried in air. 4 parts by weight of inclusion complex were obtained and appear to be a colorless, odorless, crystalline material, insoluble in water and in many other solvents. It was stable at room temperature both as a solvent and in aqueous suspension. Analysis by colorimetric procedure showed a menthol content of 6.42%. It was found that the menthol could be liberated from the complex either by boiling an aqueous suspension of the inclusion complex or by heating the dry complex to a temperature above 310° C.

Cigarettes were made from bright tobacco containing 3.0 grams of the menthol-beta-cyclodextrin inclusion complex per 120 grams of tobacco and were smoked in accordance with the procedure in Example 1. The menthol present in the smoke from these cigarettes was detected by gas chromatography and by other analytical methods. The yield of menthol was found to be from 130 to 160 micrograms per cigarette. In subjective smoking tests, these cigarettes had a mild, pleasing taste and pleasant menthol flavor.

Example 3

An inclusion complex from alpha-cyclodextrin and d-limonene was prepared in accordance with the method of Example 1 and was obtained as a stable, odorless, white solid containing 3.1% limonene. Cigarettes made from 100 parts by weight of tobacco filler to which 4 parts by weight of the inclusion complex was added were found by subjective smoking tests to have a pleasant, fragrant flavor. Limonene was detected in the smoke.

Example 4

An inclusion complex from alpha-cyclodextrin and anethole was prepared by the method of Example 1 and was found to be a stable, odorless, white solid containing 5.2% anethole. Cigarettes made from tobacco to which the inclusion complex has been added were found by subjective smoking tests to have a pleasing, anise flavor.

Example 5

The method given in Example 1 was utilized to prepare alpha-cyclodextrin inclusion complexes with organic flavorant compounds including cyclohexanone, ethyl n-caprylate, coumarin, pyridine, o-, m-, and p-cresols and 2,4-hexadienal.

All the inclusion complexes were stable, odorless, white, crystalline solids, whose composition could be determined by standard analytical procedures. In each case, the flavorant could be released by boiling an aqueous suspension of the inclusion complex or by heating it to a temperature above 300°, and the released flavorant was detected or determined by standard physical or chemical methods. When added to tobacco, the inclusion complexes decomposed to yield the flavoring material to the tobacco smoke.

Example 6

The method given in Example 2 was used to prepare inclusion complexes from beta-cyclodextrin and the following compounds: n-octane, cyclohexanone, d-limonene, linalool, geraniol, methyl salicylate, coumarin, vanillin,

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2-4-hexadienal, acetophenone, menthone, citronellal, myrcene, cineol, thymol, pinene and paracymene.

These inclusion complexes were stable, odorless, crystalline solids whose composition could be determined by standard analytical procedures. They were decomposed, with release of the organic flavorant, by heating to a temperature above 310° or by boiling in an aqueous suspension. The flavorant released was detected by mass spectrography or by vapor chromatography. When added to tobacco, the inclusion complexes decomposed to yield the flavoring material to the tobacco smoke.

Example 7

Utilizing the method given in Example 1, inclusion complexes were made from gamma-cyclodextrin and the following compounds: thymol, menthol, methyl salicylate, linalool and toluene.

These inclusion complexes were white, odorless, crystalline solids, stable to water at room temperature. They decomposed with liberation of the organic flavorant in boiling water or on heating to a temperature above 300° and were found suitable for use in flavoring tobacco.

Example 8

The method given in Example 2 was used to prepare inclusion complexes from beta-cyclodextrin and the following essential oils: Oil of Lemon (USP California Coldpressed), Oil of Sweet Orange (USP California Coldpressed) and True Peach Fruit Concentrate.

These inclusion complexes were colorless, odorless, stable, crystalline substances. They were decomposed, with release of the flavorants, by heating to a temperature above 300° or by boiling in an aqueous suspension. The flavors thus liberated were judged by subjective evaluation to be identical with those of the natural oils.

When these inclusion complexes were added to smoking tobacco, subjective tests indicated that the natural oils were liberated upon pyrolysis of the tobacco.

Since various changes in carrying out the method, and certain modifications in the product which embody the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. A method of imparting a flavor to smoking tobacco comprising forming an inclusion complex between a host compound and a guest flavoring material, and thereafter combining the said smoking tobacco in a major proportion with the said inclusion complex in a minor proportion, whereby the said flavoring material is rendered inert within said smoking tobacco until such time as the tobacco is subjected to elevated temperatures, said flavoring material being capable of release upon combustion of the tobacco.

2. A composition comprising a major proportion of smoking tobacco and a minor proportion of an inclusion complex of a host compound and a guest tobacco flavoring material said flavoring material being capable of release upon combustion of the tobacco.

3. A composition as in claim 2 wherein the flavoring material comprises a terpene.

4. A composition as in claim 2 wherein the flavoring material is selected from among the group consisting of n-octane, 2,4-hexadienal, pyridine, cresol, cyclohexanone, acetophenone, ethyl-n-caprylate, methyl salicylate and vanillin.

5. A composition as in claim 2 wherein the flavoring material is an essential oil.

6. A composition comprising a major proportion of smoking tobacco and a minor proportion of an inclusion complex of a cyclodextrin host compound and a guest tobacco flavoring material, said flavoring material being capable of release upon combustion of the tobacco.

7. A composition as in claim 6 wherein the said cyclo-

dextrin inclusion complex contains from about 3 to about 15 percent by weight of guest flavoring material and is present in amount from about 1 to about 10 milligrams per gram of smoking tobacco.

8. A composition as in claim 6 wherein the flavoring material is comprised of an organic compound having a molecular diameter less than about 12 Angstrom units.

9. A composition as in claim 6 wherein the flavoring material is comprised of a terpene compound.

10. A composition as in claim 9 wherein the terpene compound is selected from the group consisting of d-limonene, menthol, pinene, thymol, linalool, geraniol, menthone, citronellal, myrcene and cineol.

11. A composition as in claim 6 wherein the flavoring material is an essential oil.

12. A composition as in claim 6 wherein the flavoring material is comprised of a compound of the class consisting of n-octane, 2,4-hexadienal, pyridine, cresol, cyclohexanone, acetophenone, ethyl-n-caprylate, methyl salicylate and vanillin.

13. A method of imparting a flavor to smoking tobacco comprising forming an inclusion complex between a cyclodextrin host compound and an organic tobacco-flavoring material and thereafter combining the said smoking tobacco with the said inclusion complex, whereby the said flavoring compound is rendered inert within said smoking tobacco until such time as the tobacco is subjected to elevated temperatures.

14. A method of imparting a flavor to smoking tobacco comprising forming an inclusion complex between a cyclodextrin host compound and a terpene flavoring material, and thereafter combining the said smoking tobacco with the said inclusion complex, whereby the said terpene flavoring material is rendered inert within said smoking

tobacco until such time as the tobacco is subjected to elevated temperatures.

15. A method of imparting a flavor to smoking tobacco comprising forming an inclusion complex between a cyclodextrin host compound and a tobacco flavoring material selected from among the compounds consisting of n-octane, 2,4-hexadienal, pyridine, cresol, cyclohexanone, acetophenone, ethyl-n-caprylate, methyl salicylate and vanillin, and thereafter combining the said smoking tobacco with the said inclusion complex, whereby the said flavoring material is rendered inert within said smoking tobacco until such time as the tobacco is subjected to elevated temperatures.

16. A composition comprising smoking tobacco and an inclusion complex of a cyclodextrin host compound with menthol.

17. A composition comprising smoking tobacco with an inclusion complex of a cyclodextrin host compound with d-limonene.

18. A composition comprising smoking tobacco with an inclusion complex of a cyclodextrin host compound with anethole.

19. A composition comprising smoking tobacco with an inclusion complex of a cyclodextrin host compound with thymol.

20. A composition comprising smoking tobacco with an inclusion complex of a cyclodextrin host compound with menthone.

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