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SMOKING COMPOSITION AND METHOD OF IMPARTING FLAVOR THERETO

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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 tri-o-thymotide and a guest 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 containing channel-like spaces. Typical among these compounds are such well known substances as urea, thiourea, and desoxycholic acid. There are also polymolecular host compounds having cage-like spaces. These compounds form inclusion complexes known as "clathrates." Compounds such as the 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.

Flavoring materials are known to be 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 material 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 material 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 suitable terpene compounds include menthone, citronelal, myrcene and cineol.

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

In general, with tri-o-thymotide, the preferred host compound of this invention, the guest compound may be any organic tobacco flavoring compound capable of forming a complex with a tri-o-thymotide host compound which complex decomposes upon heating to the pyrolysis temperature of tobacco.

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

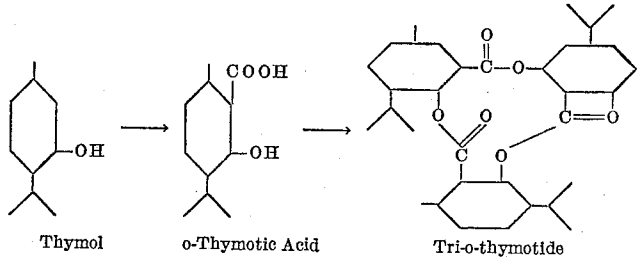
The aliphatic and aromatic aldehydes are likewise applicable to this invention. A typical example is 2,4-hexadienal.

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 in the complex.

The preferred host compound of this invention is tri-o-thymotide. This compound is of a cyclic structure containing three benzene rings and is ordinarily manufactured from thymol by a two-stage synthesis. The reaction proceeds as follows:



Thymol o-Thymotic Acid Tri-o-thymotide

The exact spatial configuration of the tri-o-thymotide molecule is not known. The literature indicates that the molecule is not planar but instead, is folded so that there is no significant empty space in the middle of the ring. There is some theory in the literature to the effect that this molecule has roughly the form of a discus with protuberances similar to a three-bladed propeller. Apparently, when tri-o-thymotide molecules act as hosts to form inclusion complexes, either channel type or cage type voids can be filled by the prospective guest molecules. In the channel type inclusion complex, several molecules of tri-o-thymotide form a spiral about the channel containing the guest molecule.

Whatever the structure and mechanism of the complex formation, it has been found that inclusion complexes of tri-o-thymotide tobacco flavoring substances are particularly and unusually advantageous for use in tobacco compositions. Thus, tri-o-thymotide has no odor and therefore contributes no undesirable odors to tobacco. The inclusion complexes are likewise unaffected by moisture and accordingly are stable under the usual tobacco storage conditions. Further, it has been found that tri-o-thymotide inclusion complexes transfer flavoring substances efficiently into the aerosol phase of tobacco upon

pyrolysis of the tobacco. The decomposition products of tri-o-thymotide which result from pyrolysis of the tobacco product to which an inclusion complex has been added are not only nontoxic but in addition, impart pleasant and desirable thymolic notes to the tobacco smoke. On heating at higher temperatures, tri-o-thymotide decomposes to thymol and o-thymotic acid, plus trace amounts of other volatile substances. All of these decomposition products are physiologically harmless and pleasantly fragrant when present in tobacco smoke.

The tri-o-thymotide inclusion complex generally contains from about 0.16 to about 1.0 mole of included guest compounds per mole of tri-o-thymotide. Thus, the inclusion complexes will contain from about 3% to about 15% by weight of included flavor compounds. 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 about 10 to 1,000 micrograms per cigarette delivered in the smoke and for most flavors is less than about 100 micrograms per cigarette. The most advantageous amount of inclusion complex to be added will therefore usually be in the range of about 1 to 10 milligrams per gram of tobacco.

The preferred inclusion complex of this invention is the inclusion complex of tri-o-thymotide with menthol. This complex is particularly useful and advantageous.

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 tri-o-thymotide inclusion complexes is to dissolve the host compound in either the guest compound or in a neutral solvent in which the guest compound is also dissolved. The inclusion complex will thereafter precipitate out of solution.

Further details of the method of utilizing this invention may be had from the following working examples:

Example 1

A mixture of 5.3 grams of dl-menthol, 0.31 gram of tri-o-thymotide and 7.0 ml. of 2,2,4-trimethylpentane (a solvent which does not form an inclusion complex with tri-o-thymotide) was heated until complete solution occurred. The mixture was then cooled to 30° C. and the crystals of inclusion complex were filtered and washed with cold 2,2,4-trimethylpentane to remove any menthol adhering thereto. The crystal yield was 0.29 gram and contained 4.6% by weight of menthol. These crystals were found to be large, transparent and dendritic and had a melting point of 160° C. They were odorless, insoluble in water and in other cold solvents and were found to be stable indefinitely at room temperature. They decomposed upon heating to yield menthol and tri-o-thymotide, thereby indicating that an inclusion complex had been formed. Complete decomposition of the complex required about 3½ hours when performed at 165° C. and only about 5 minutes when performed in 195° C. The decomposition reaction took only a few seconds when carried out at 220° C.

On prolonged heating at higher temperatures, the tri-o-thymotide decomposed to thymol and o-thymotic acid with traces of other volatile substances. When a sample of the inclusion complex prepared above was heated at 400 to 450° C., it slowly decomposed. After 20 minutes,

the product had completely volatilized, leaving no non-volatile residue.

Example 2

Five parts by weight of a menthol-tri-o-thymotide inclusion complex prepared in accordance with the method of Example 1 were added to 500 parts by weight of bright tobacco by spraying the tobacco with a fine aqueous suspension of the inclusion complex. The treated tobacco was then made into cigarettes which were subsequently smoked on a constant volume smoking machine. In accordance with standard procedure, the puffs were of two second duration (about 8 puffs per cigarette) and had a volume of 35 ml. The cigarettes were smoked to a 25 mm. butt length and the smoke was collected on a Cambridge filter pad which pad is capable of trapping particles larger than 0.3 micron. The smoke was found to contain from 150 to 200 micrograms of menthol per cigarette as determined from vapor phase chromatography. Subjective smoking tests indicated that these cigarettes not only transmitted the menthol flavor into the smoke phase but also transmitted additional, desirable thymolic notes. The smoke was found to have a mild, pleasing taste as compared to cigarettes made from bright tobacco that had not been treated with the inclusion complexes of this invention.

Example 3

0.52 gram of tri-o-thymotide was placed in a paper thimble in a Soxhlet apparatus. The reactor was charged with 50 ml. of a solution of 2-2-4-trimethylpentane containing 8.1 grams of menthol. Continuous extraction was carried on for 48 hours. The solution in the reactor was then allowed to cool to room temperature. The crystals which formed were isolated by filtration and were washed with cold trimethylpentane until they were free of menthol. A yield of 0.41 gram of complex was obtained. The crystals had a melting point of 163° C. Other properties of the crystals were the same as those obtained by the method of Example 1. The decomposition products produced by heating were menthol and tri-o-thymotide. Analytical tests and subjective smoking tests of tobacco treated with the inclusion complexes of this invention showed excellent transmission of the menthol flavor into the smoke phase.

Example 4

In accordance with the procedure of Example 1, inclusion complexes of tri-o-thymotide with d-limonene, anethole, p-cymene, pyridine, o-cresol, m-cresol and p-cresol were prepared. These inclusion complexes were then added to smoking tobacco in accordance with the procedure in Example 2. Pyrolysis of the tobacco-inclusion complex combination released the flavorants into the smoke phase to impart pleasant aromatic notes to the smoke. No flavorants were released during storage of the tobacco and hence these complexes did not add undesirable notes to the pack aroma and were transferred efficiently into the aerosol phase of the smoke.

Example 5

This example illustrates another method of preparing the tri-o-thymotide-menthol inclusion complex useful in this invention. 0.47 gram of tri-o-thymotide was added to 6.4 grams of dl-menthol, and the mixture was heated at 120° C. until complete solution occurred. The solution was cooled at the rate of 5° C. per hour. Crystallization began at 85° C. When the temperature reached 60° C., the excess menthol was poured off and the crystals were washed repeatedly with cold 2,2,4-trimethylpentane. The yield of clathrate was 0.44 gram. The crystals had the same properties as those described in Example 1. They decomposed upon heating to 165° C. to yield menthol and tri-o-thymotide. Analysis for menthol, using the procedure given in Example 1, gave a menthol content of 5.0%.

The tri-o-thymotide-menthol clathrate when added to tobacco, made into cigarettes, and smoked as in Example 2, transmitted the menthol flavor and thymolic notes into the smoke in desirable amounts and improved the aroma and taste of the cigarettes.

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. Having thus described the invention, that which is desired to be claimed and protected by Letters Patent is as follows:

1. A composition of matter comprising smoking tobacco and a tri-o-thymotide inclusion complex.

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

3. A composition as in claim 2 wherein the flavoring material is comprised of an organic tobacco flavoring compound having a molecular diameter of less than about 12 Angstrom units.

4. A composition as in claim 2 wherein the said 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 tobacco.

5. A composition as in claim 3 wherein the said flavoring compound is selected from the group consisting of n-octane, 2,4-hexadienal, pyridine, cresol, cyclohexanone, acetophenone, ethyl-n-caprylate, methyl salicylate and vanillin.

6. A composition as in claim 3 wherein the said flavoring material comprises a terpene compound.

7. A composition as in claim 6 wherein the terpene compound is selected from the group consisting of d-limonene, menthol, pinene, p-cymene, thymol, linalool, geraniol, menthone, citronellal, myrcene and cineol.

8. A method of imparting a flavor to smoking tobacco comprising forming an inclusion complex between tri-o-thymotide and a guest tobacco flavoring material 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.

9. A method as in claim 8 wherein the said flavoring material comprises a compound selected from the group consisting of n-octane, 2,4-hexadienal, pyridine, cresol, cyclohexanone, acetophenone, ethyl-n-caprylate, methyl salicylate and vanillin.

10. A method as in claim 8 wherein the said flavoring material comprises a terpene compound.

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

12. A composition comprising smoking tobacco and an inclusion complex of tri-o-thymotide with menthol.

13. A composition of matter comprising smoking tobacco and an inclusion complex of tri-o-thymotide with menthone.

14. A composition comprising smoking tobacco and an inclusion complex of tri-o-thymotide with d-limonene.

15. A composition comprising smoking tobacco and an inclusion complex of tri-o-thymotide with anethole.

16. A composition comprising smoking tobacco and an inclusion complex of tri-o-thymotide with p-cymene.

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