

1

3,288,146

COMPOSITION FOR INCORPORATING FLAVOR
INTO TOBACCO SMOKE

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This invention relates to a method and composition for incorporating flavor into tobacco smoke. More particularly, the present invention relates to a composition for embodying predetermined flavorants into tobacco smoke, which flavorants can be maintained and preserved during storage of the tobacco products containing them.

Conventional methods now in use for incorporating flavors into tobacco smoke have many disadvantages. Organic flavorings have been directly incorporated in tobacco filler. 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 lost during storage. In addition, 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 of the flavorant into the smoke 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 smoke 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 accordance with U.S. Patents 3,047,431 and 3,047,432, flavorants can be incorporated into tobacco smoke by incorporating in the tobacco an inclusion complex which comprises a host compound and a guest flavoring material which has been rendered inert under normal temperature conditions but which flavoring material is released under the conditions of elevated temperature which exist when the tobacco is burned.

We have unexpectedly discovered that inclusion complexes comprising a host compound and a guest flavoring material can be incorporated in a filter for tobacco smoke, said filter being incorporated in a cigarette, cigar, pipe or the like, and that the flavorant contained in the host compound will be released into the smoke as the smoke passes through the filter. This method of incorporating flavorants in tobacco smoke has a number of advantages over the above-described method. One advantage of this method is that the flavorants are incorporated in the smoke without any undesirable break-down products of the host materials. Another advantage is that the filter containing the inclusion complex serves the dual purpose of releasing one or more desired flavorants into the smoke while simultaneously removing undesired particulate matter from the smoke, the particulate matter replacing the flavors in the complex. This also results in a more effective removal of particulate matter from the smoke than would be the case with a conventional filter.

It is an object of the present invention to incorporate a desired flavor into a filter for tobacco smoke in such a

2

manner that the flavor will not be released prior to the time that the tobacco smoke passes through the filter.

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

A still further object of this invention is to incorporate a flavorant into a cigarette in such a manner that it is not subjected to the temperature of pyrolysis, thus preventing the formation of undesired pyrolytic products.

While we do not wish to be bound by any particular mechanism of reaction, it is believed that the flavorants are released from the complexes substantially completely through the mechanism of displacement or exchange with no component of the complex being decomposed. Thus, the present process and compositions which utilize this mechanism represent an unexpected improvement over the use of complexes in tobacco, where the flavorants are released by heat.

The present invention comprises the formation of an inclusion complex between a host compound and a flavoring material, wherein the flavoring material is rendered inert until it is displaced from the host compound by the displacement action of certain constituents in tobacco smoke, and the incorporation in a filter for tobacco smoke of said inclusion complex.

The inclusion complexes which can be employed in the present invention are solid materials comprised of two distinct components: a host compound and a guest molecule. The guest molecule is enclosed within the host substance which generally forms a channel or cage-like structure and the guest is thereby rendered inert to external forces. 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 which can be employed 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 those polymolecular host compounds having cage-like spaces. These compounds form inclusion complexes known as "clathrates." Compounds such as hydroquinone and phenol, for example, will form clathrates. There are some host compounds with cage-like spaces that form clathrates with guest compounds that act on a monomolecular basis. There are also some host compounds with flat spaces between planes of atoms. Typical among these compounds are the zeolites, the bentonites and the montmorillonites.

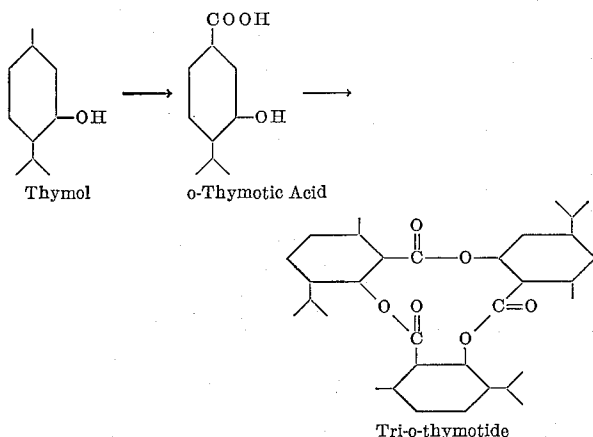
One preferred group of host compounds of the present invention is the cyclodextrins, preferably the alpha, beta and gamma cyclodextrins. These compounds are also referred to in the literature as Schardinger dextrins and the alpha, beta and gamma compounds are often referred to as cyclohexaamylose, cycloheptaamylose, and cyclooctaamylose, respectively. Further details on these

3

compounds may be found in "Advances in Carbohydrate Chemistry," volume 12 (Academic Press, 1957), pages 190-257. The cyclodextrin inclusion complex will generally contain from about 0.5 to about 2.0 moles of included guest compounds per mole of cyclodextrin.

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 50 milligrams per gram of tobacco in the tobacco product to which the filter is attached.

Another 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:



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 for incorporation in filters for tobacco compositions. Thus, tri-o-thymotide has no odor and therefore contributes no undesirable odors to the tobacco or filter. The inclusion complexes are likewise unaffected by moisture and accordingly are stable under the usual storage conditions for tobacco products. Further, it has been found that tri-o-thymotide inclusion complexes transfer flavoring substance efficiently into the aerosol phase when contacted with 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

4

most flavors is less than about 100 micrograms per cigarette. The most advantageous amount of inclusion complex to be added to a filter will therefore usually be in the range of about 1 to 50 milligrams per gram of tobacco in the tobacco product to which the filter is attached.

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

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 rapidly upon contact with tobacco smoke. A further requirement of the host compound is that it not be physiologically toxic. 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.

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. 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 filter 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 the manufacturing steps and during the course of storage. Only when the final product is ultimately used 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 by the action of the smoke passing through the filter in which the complex is present.

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 filter. A typical method of performing this incorporation would be to uniformly disperse the inclusion complex in water and then spray the resultant dispersion onto the filter material. Equally good results are obtained by grinding the inclusion complexes and dusting them onto the inner filter plug. The inclusion complex may also be formed in situ in the filter. Any incorporation means may be employed provided the ultimate product contains a uniform dispersion of the inclusion complex in the filter.

It will be understood that by this method a plurality of different inclusion complexes may be used as additives to the filter so that a plurality of desired flavors may be liberated simultaneously in the smoke.

Typical flavoring compounds desirable as smoke flavorants 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 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 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 smoke. 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.

In general with tri-o-thymotide, 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.

Particularly preferred guest compounds are anethole, menthol, cinnamaldehyde, vanillin, benzaldehyde, eugenone, piperonal, methyl heptenone, hexadienal, phenyl ethyl alcohol, and benzyl alcohol.

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.

This invention is not limited to use in cigarette filters. The clathrated flavors may be incorporated into any filtering medium which is capable of holding them or they may be pelletized for use in cigarette holders or in pipe stems.

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 or the cyclodextrin 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.

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

Mixed cyclodextrins (5.0 grams) were dissolved in 200 ml. of water. Six milliliters of anethole were added and the mixture was stirred for 2 hours. The inclusion compound was filtered off, washed successively with ethanol and ether, and dried in air. The yield of inclusion compound, a white odorless solid was 4.2 g. Analysis of the inclusion compound by a gas chromatographic method showed that it contained 6.2% anethole by weight.

This inclusion compound was added to cellulose acetate filter tow by sprinkling it on as a fine dust. The dusted tow was then made into cigarette filters in the conventional manner. Each 17 mm. filter contained 42 mg. of the inclusion compound. These filters were attached to 57 mm. Marlboro brand cigarette fillers.

The flavor of anethole in the smoke from these cigarettes was detected organoleptically by a panel of smokers. The cigarettes were also machine smoked to a 30 mm. butt length in a constant volume smoking device which took a 35 cc. puff of 2 seconds duration

once a minute. The total particulate matter in the smoke was analyzed for anethole by differential ultraviolet spectroscopy. It was found that the smoke contained 18 μ g./cigt. of anethole.

Example 2

An inclusion compound from β -cyclodextrin and menthol was prepared by the method given in Example 1. The inclusion compound was analyzed by a gas-chromatographic procedure and was found to contain 10.0% menthol by weight.

Cigarette filters containing this material were prepared by dusting it onto cellulose acetate tow, as described in Example 1. The level was 42 mg. of inclusion compound per 17 mm. filter rod.

Cigarettes prepared from these filters were smoked mechanically as in Example 1. The amount of menthol in the smoke was determined to be 110 μ g./cigt. as determined by gas chromatographic analysis. The presence of menthol in the smoke was also detected organoleptically by a panel of judges who smoked the cigarettes.

Example 3

Cellulose acetate tow filter rods (standard Marlboro brand filter rods) were moistened with a 13% solution of α -cyclodextrin in water. Anethole vapors in air were then passed over these filter rods for 48 hours until the cyclodextrin inclusion compound had formed in situ on the filters, after which the filter rods were dried until they were odorless, were cut into 15 mm. lengths, and were attached to PM regular cigarettes. The filters were analyzed for cyclodextrin by extracting them with boiling water and measuring the optical rotation of the filtered extract, and were analyzed for anethole by continuously extracting them with ether for 48 hours and determining anethole in the ethereal extract by ultraviolet absorption spectroscopy. It was found that each 15 mm. filter contained 5.2 mg. of inclusion compound, of which 1.5 mg. was anethole.

Example 4

Absorbent paper (Kimberley-Clark Type 900-S, 5 by 8 $\frac{3}{4}$ inch) was dipped in a 10% solution of α -cyclodextrin in water, then was sprayed while still moist with a 10% alcoholic solution of anethole in order to form the inclusion compound on the paper and in the interstices of the paper. After drying, the paper, which had no odor of anethole, was made into cigarette filter rods. The rods were cut into 15 mm. lengths and attached to 70 mm. cigarette tobacco fillers. The filters were analyzed by the procedures detailed in Example 3. Each 15 mm. filter plug was found to contain 25 mg. of inclusion compound, of which 1.7 mg. was anethole.

These cigarettes were mechanically smoked as described in Example 1, and the total particulate material collected. Differential ultraviolet spectroscopic analysis showed the presence of 125 μ g./cigt. of anethole. The flavor of anethole could also be detected subjectively when these cigarettes were smoked by smoking panel members.

Example 5

Filter cigarettes were prepared from filters containing 30 mg. per cigarette of the cinnamaldehyde α -cyclodextrin inclusion compound. The inclusion compound was added as in Example 1 by dusting it onto the cellulose acetate fibers before filter manufacture. Upon smoking, the cinnamaldehyde was released into the smoke stream and its characteristic flavor was detected in the smoke when evaluated by smoking panel members.

Example 6

Filter cigarettes were prepared, as in Example 5, containing 30 mg. of the ethyl vanillin β -cyclodextrin inclusion compound on the filter. The cigarettes were mechanically smoked and the smoke analyzed as in Exam-

ple 4. 138 mg./cigt. of ethyl vanillin was found to be in the smoke.

Example 7

Filter cigarettes were prepared with the filters containing inclusion compounds from various flavors. Inclusion compounds from α , β , or γ cyclodextrins and benzaldehyde, eugenol, cinnamaldehyde, piperonal, vanillin, methyl heptenone, hexadienal, phenyl ethyl alcohol, and benzyl alcohol were applied as in Example 5 at various levels in various combinations. The cigarettes so prepared were smoked by an expert panel. The flavors added to the smoke by displacement from the inclusion compounds on the filters were detected by the panel members.

Example 8

The inclusion compound from cinnamaldehyde and α -cyclodextrin was ground with ethanol until a fine suspension was obtained. This suspension was sprayed from an atomizer onto cellulose acetate filter tow, and the tow was then manufactured into filter tips. Analysis as in Example 3 showed that each 15 mm. filter plug contained 50 mg. of the clathrate. The filters were attached to 57 mm. Marlboro brand cigarette fillers and the resulting cigarettes were smoked. The flavor of cinnamaldehyde was subjectively detected in the smoke.

Example 9

The inclusion compound from cinnamaldehyde and β -cyclodextrin was ground to a fine powder and placed in the space between the carbon filter and the cellulose acetate filter in a dual filter type cigarette. When these cigarettes were smoked, cinnamaldehyde was displaced from the inclusion compound and could be detected in the smoke.

Example 11

A mixture of 0.31 g. of tri-o-thymotide and 5.3 g. of dl-menthol was dissolved in 7.0 ml. of 2,2,4-trimethylpentane by heating at 90°. The solution was maintained at 70° until crystallization of the clathrate began, then was cooled at a rate of 15° per hour. After crystallization was complete, the crystals were filtered off and washed with 2,2,4-trimethylpentane until free from unclathrated menthol, thus yielding 0.29 g. of tri-o-thymotide menthol clathrate, slender dendritic crystals, M.P. 165°. This material, analyzed for menthol by a colorimetric procedure, contained 5.45% menthol. The clathrate was decomposed to menthol and tri-o-thymotide rapidly upon heating above its melting point and slowly upon dissolution in boiling water.

Example 12

Tri-o-thymotide, 3.01 g., was placed in the thimble of

a Soxhlet extraction apparatus and a solution of 10 g. racemic menthol in 50 ml. of 2,2,4-trimethylpentane was placed in the pot. Continuous extraction was carried out for 24 hours, at which time 1.64 g. of tri-o-thymotide menthol clathrate had crystallized out in the pot. After filtration and thorough washing with 2,2,4-trimethylpentane, the product had M.P. 164° and contained 5.84% menthol.

This material was powdered and mixed with twice its weight of a diatomaceous earth (chromosorb W). 0.15 g. of the resulting powder was placed between two plugs of glass wool in the cavity of a cigarette holder. When cigarettes were smoked through this holder, the flavor and cooling sensation of menthol was detectable in the smoke. The amount of clathrate used sufficed to give menthol flavor to four or five cigarettes smoked through the holder.

We claim:

1. A tobacco product comprising a tobacco section and a filter section, said filter section including, prior to ignition of said tobacco section, an inclusion complex formed between a host compound and an organic flavoring material, said host compound being selected from the group consisting of cyclodextrin host compounds and tri-o-thymotide host compounds, said tobacco section being substantially free of said inclusion complex, said inclusion complex being adapted to release said organic flavoring material upon contact with tobacco smoke resulting from the burning of said tobacco section.
2. The tobacco product of claim 1, wherein the organic flavoring material is selected from the class consisting of anethole, menthole, cinnamaldehyde, vanillin, benzaldehyde, eugenone, piperonal, methyl heptenone, hexadienal, phenyl ethyl alcohol and benzyl alcohol.

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