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# SMOKING TOBACCO ADDITIVES IN THE FORM OF MENTHYL ETHERS

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This invention relates to an improved smoking tobacco product and the method of making the same and, more particularly, to an improved smoking tobacco product having incorporated therein aroma- and flavor-producing additives which improve the smoking characteristics thereof.

The use of flavoring additives in tobacco products are of increasing importance in the tobacco industry. Menthol, either natural or synthetic, is used in many forms. It is desirable because of the characteristic taste, flavor and aroma it imparts to the smoke stream; also for the distinctive cooling sensation that it produces. However, if only the cooling sensation is desired but not its other characteristics, menthol can not be used as the flavoring additive.

It is therefore a primary object of our invention to provide flavoring additives for tobacco products which impart a cooling sensation to the smoker when the tobacco product is smoked. Moreover, each flavoring additive that we have found has a distinctive taste, flavor and aroma which they impart to the smoke stream of a tobacco product.

Our invention contemplates incorporating in smoking tobacco or in smoking tobacco products an ether of menthol which is volatile below the pyrolysis temperature of smoking tobacco and which may be derived from aliphatic, aromatic, or heterocyclic organic radicals. The menthol portion of the ether may be derived from either natural or synthetic menthol or a mixture of natural and synthetic menthol.

Menthyl ethers have been found to improve the flavor and aroma characteristics of smoking tobacco products when incorporated therein have the following general formula:

R—O—R′

in which R is menthyl and R′ is an organic radical selected from the group consisting of aliphatic, aromatic or heterocyclic radicals.

It should be understood that R′ includes menthyl and comes within the class of aliphatic compounds in its broadest concept.

Specific examples of aliphatic organic radicals which may be employed in our improved flavoring ethers are those having up to 16 carbon atoms in the main chain, as for example: methyl, ethyl, propyl, butyl, amyl, hexyl, heptyl, octyl, decyl, dodecyl and hexadecyl. The corresponding branched chain aliphatic radicals, the corresponding unsaturated aliphatic radicals and the corresponding unsaturated branched chain aliphatic radicals may also be employed, such as 3-hexenyl, 5-hexenyl.

As previously indicated, menthyl ethers of various aromatic materials may be employed, as for example: benzyl, phenyl, and p-methoxyphenyl.

Specific examples of ethers of menthol that may be incorporated in a smoking tobacco or in a smoking tobacco product which are organoleptically pleasing to the smoker and which have the desired cooling effect when the smoke is inhaled are as follows: menthyl methyl ether, menthyl ethyl ether, menthyl propyl ether, menthyl butyl ether, menthyl amyl ether, menthyl hexyl ether, menthyl heptyl ether, menthyl octyl ether, menthyl decyl ether, menthyl dodecyl ether, menthyl hexadexyl ether,



menthyl 3-hexenyl ether, menthyl 5-hexenyl ether, benzyl menthyl ether, phenyl menthyl ether and p-methoxyphenyl menthyl ether.

The release of a flavor-producing additive incorporated in a smoking tobacco product is accomplished when the tobacco product is smoked. The mechanism of release employed herein according to our invention is a thermal release without decomposition of the additive. The menthyl either vaporizes into the smoke stream when the tobacco product is smoked. Thus, a pleasing cooling sensation associated with a mentholated tobacco product results without the characteritsic flavor and aroma of menthol.

The menthyl ethers that have been found to improve the cooling and flavor characteristics in a smoking tobacco product according to our invention may be prepared by the following general procedure: menthol, either natural or synthetic or a mixture of both, is reacted with elemental sodium to form sodium menthoxide in the presence of dry toluene. To this mixture is added an organic halide with sufficient heat to start the reaction. When the reaction is completed, the by-product sodium halide is removed by filtration and the menthyl ether is obtained by distillation of the filtrate under reduced pressure.

Specific examples of the preparation of menthyl ethers that may be used as flavoring additives for tobacco products are as follows:

*Example 1*

Menthyl methyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting 7.95 gms. (0.3459 mole) of metallic sodium with 56.30 gms. (0.3605 mole) of menthol in the presence of dry toluene. To the sodium menthoxide is added dropwise 42.65 gms. (0.3005 mole) of methyl iodide with constant stirring. During the first five minutes of addition there is no evidence of reaction. Heat is applied for 15 minutes until sodium iodide begins to form. During the next 25 minutes of addition, the temperature of the reaction mixture increases from 75° to 100° C. without application of heat. The reaction mixture is maintained at a temperature of from 75° to 85° C. for 4 hours with constant stirring. After cooling to room temperature, the sodium iodide is filtered off by suction and washed thoroughly with ethyl ether. The filtrate and washings are combined, and the solvents distilled from the mixture. The remaining liquid is fractionated under reduced pressure using a heated column packed with glass helices to give 41.16 gms. (67%) of menthyl methyl ether, B.P. 79.5–54° C. (12 mm.).

Two steps are required to purify the product: (1) it is passed through a chromatographic column packed with neutral alumina using petroleum ether as the solvent; and (2) vacuum distilled over sodium, B.P. 83° C. (12 mm), $n_D^{20°}$ 1.442, $d^{24°\,C.}$ 0.865 $[\alpha]_D$—94.71°.

*Analysis.*—Calculated for $C_{11}H_{22}O$: C, 77.56; H, 13.03. Found: C, 77.83; H, 12.91.

*Example 2*

Menthyl ethyl ether is prepared in the following manner:

Sodium methoxide is prepared by reacting from 8.46 gms. (0.368 mole) of sodium with 50.00 gms. (0.320 mole) of menthol in the presence of dry toluene. The sodium menthoxide is heated to 75° C., and 59.90 gms. (0.384 mole) of ethyl iodide is added dropwise with constant stirring. Formation of sodium iodide occurs approximately one hour after the beginning of the ethyl iodide addition. The reaction mixture is refluxed for 3½ hours at 115° C. After cooling to room temperature, the mixture is filtered and the sodium iodide is washed thoroughly with ethyl ether. The ethyl ether containing the

reaction product is distilled from the combined filtrate and washings, and the remaining liquid is fractionated over sodium under reduced pressure to yield 40.99 gms. (69.9%) of menthyl ethyl ether B.P. 105–110° C. (24 mm.).

The method of purification is the same as that described for menthyl methyl ether in Example 1. The pure menthyl ethyl ether has the following physical properties: B.P. 104.0–104.2° C. (24 mm.), $n_D^{17.1}$ 1.4439, $d^{22.5°\ C.}$ 0.847, $[\alpha]_D$ −100.0°.

*Analysis.*—Calculated for $C_{12}H_{24}O$: C, 78.19; H, 13.13. Found: C, 78.23; H, 12. 94.

*Example 3*

Menthyl propyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting 7.36 gms. (0.320 mole) of sodium with 50.00 gms. (0.320 mole) of menthol in the presence of dry toluene. The sodium menthoxide is heated to 75° C., and 72.00 gms. (0.480 mole) of n-propyl iodide is added dropwise with constant stirring until the temperature of the reaction mixture gradually rises to 115° C. No reaction is evident until the temperature of the reaction mixture is about 98° C. (about 40% of the iodide has been added). After completion of addition, the reaction mixture is refluxed for 3½ hours at 115° C. The reaction product is isolated (yield: 48.88 gms. 76.9%) and purified in the same manner as for menthyl methyl ether described in Example 1. The menthyl propyl ether was found to have the following physical properties: B.P., 104.2° C. (12 mm.), $n_D^{20}$ 1.4453, $d^{22.5°\ C.}$ 0.860, $[\alpha]_D$ −89.59.

*Analysis.*—Calculated for $C_{12}H_{26}O$: C, 78.72; H, 13.21. Found: C, 78.85; H, 13.36.

*Example 4*

Menthyl butyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting from 7.36 gms. (0.320 mole) of sodium with 50.00 gms. (0.320 mole) of menthol in the presence of dry toluene. The sodium menthoxide is heated to 95° C. and 131.50 gms. (0.960 mole) of 1-bromobutane is added dropwise with constant stirring as the temperature gradually rises to 115° C. No sodium bromide forms until 15 minutes after the beginning of addition of 1-bromobutane. Upon completion of addition, the reaction mixture is refluxed for 5½ hours at 117° C. and then cooled to room temperature. The reaction mixture is filtered and the sodium bromide washed thoroughly with ethyl ether. The ethyl ether is distilled from the combined filtrate and washings. The remaining material is heated for 5½ hours at from 160° to 180° C. in the presence of sodium, cooled to room temperature and filtered. The filtrate is vacuum distilled to give 51.5 gms. (75.7%) of menthyl butyl ether, B.P. 94–120° C. (12 mm.).

The menthyl butyl ether is purified by fractionation over sodium, B.P. 119.5–120° C. (12 mm.), $n_D^{20}$ 1.4466, $d^{22°\ C.}$ 0.834, $[\alpha]_D$ 87.73°.

*Analysis.*—Calculated for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.19; H, 13.23.

*Example 5*

Menthyl amyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting 4.42 gms. (0.192 mole) of sodium with 30.00 gms. (0.192 mole) of menthol in the presence of dry toluene. To the sodium menthoxide is added dropwise 87.00 gms. (0.576 mole) of 1-bromopentane with constant stirring at 110 to 125° C. over a period of 1½ hours. Sodium bromide forms after the first ten minutes of the addition of 1-bromopentane. The reaction mixture is refluxed for 3½ hours at 125° C. and is thereafter cooled in an ice bath. The reaction product is extracted with ethyl ether and



is washed with water to remove the sodium bromide. The ethyl ether is removed by distillation and the remaining material is refluxed over sodium for 6½ hours in the presence of toluene. The reaction mixture is cooled, filtered, and vacuum distilled to yield 33.20 gms. (76.3%) of menthyl amyl ether, B.P. 105–133° C. (12 mm.).

The compound was purified by fractionation over sodium, B.P. 132° C. (12 mm.), $n_D^{20}$ 1.4484, $d^{22.5°\ C.}$ 0.846, $[\alpha]_D$ −81.83°.

*Analysis.*—Calculated for $C_{15}H_{30}O$: C, 79.57; H, 13.36. Found: C, 79.59; H, 13.30.

*Example 6*

Menthyl hexyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting 5.9 gms. (0.256 mole) of sodium with 40.0 gms. (0.256 mole) of menthol in the presence of dry toluene. The sodium menthoxide is reacted with 84.5 gms. (0.512 mole) 1-bromohexane by the same method as described for the preparation of menthyl propyl ether in Example 3. The addition temperature of 1-bromohexane is approximately from 115 to 135° C. The refluxing time is 6 hours at 145° C. The isolation of menthyl hexyl ether yielded 41.62 gms. (66.6%) and is purified by fractionation over sodium B.P. 142.5–143° C. (12 mm.), $n_D^{20}$ 1.4499, $d^{23°\ C.}$ 0.816, $[\alpha]_D$ −80.51°.

*Analysis.*—Calculated for $C_{16}H_{32}O$: C, 79.93; H, 13.42. Found: C, 79.81; H, 13.23.

*Example 7*

Menthyl heptyl ether is prepared in the following manner:

Using 91.7 gms. (0.512 mole) of 1-bromoheptane, the same procedure is followed as that described for the preparation of menthyl hexyl ether in Example 6. The isolation of menthyl heptyl ether yielded 34.4 gms. (52.9%) and the menthyl heptyl ether is purified by fractionation over sodium, B.P. 157.5–158° C. (12 mm.), $n_D^{20}$ 1.4508, $d^{22.5\ °C.}$ 0.845, $[\alpha]_D$ −62.60.

*Analysis.*—Calculated for $C_{17}H_{34}O$: C, 80.24; H, 13.47. Found C, 80.18; H, 13.51.

*Example 8*

Menthyl octyl ether is prepared in the following manner:

Using 99.0 gms. (0.512 mole) 1-bromooctane, the same procedure was followed as that described for the preparation of menthyl hexyl ether in Example 5. The refluxing temperature is approximately 155° C. The yield obtained is 44.1 gms. (64.1%) and the menthyl octyl ether is purified by fractionation over sodium, B.P. 167–168° C. (12 mm.) $n_D^{20}$ 1.4522, $d^{23.5°\ C.}$ 0.806, $[\alpha]_D$ −65.4°.

*Analysis.*—Calculated for $C_{18}H_{36}O$: C, 80.52; H, 13.52 Found: C, 80.02; H, 13.30.

*Example 9*

Menthyl decyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting 4.42 gms. (0.192 mole) of sodium with 30.00 gms. (0.192 mole) of menthol in the presence of dry toluene. The sodium menthoxide is reacted with 84.8 gms. (0.384 mole) of 1-bromodecane by the same method as described for the preparation of menthyl propyl ether. The reaction mixture is refluxed for four hours. The isolation of the product yielded 28.27 gms. (50.6%).

The menthyl decyl ether is purified by fractionation over sodium, B.P. 193° C. (12 mm.), $n_D^{20}$ 1.4541, $d^{21.5°\ C.}$ 0.843, $[\alpha]_D$ −60.14°.

*Analysis.*—Calculated for $C_{20}H_{40}O$: C, 81.00; 13.60. Found: C, 80.82; H, 13.41.

*Example 10*

Menthyl dodecyl ether is prepared in the following manner:

Using 95.6 gms. (0.384 mole) 1-bromododecane, the same procedure was followed as that described for the preparation of menthyl decyl ether. The reaction mixture is refluxed for 12 hours at 185° C. The isolation of the product yielded 33.51 gms. (53.8%).

The menthyl dodecyl ether is purified by fractionation over sodium, B.P. 102° C. (0.06 mm.), $n_D^{20}$ 1.4564, $d^{22°\,C.}$ 0.848, $[\alpha]_D$ −55.27°.

The menthyl dodecyl ether after being refrigerated for several days, the compound crystallizes to form white crystals which melts at room temperature (about 22° C.).

*Analysis.*—Calculated for $C_{22}H_{44}O$: C, 81.41; H, 13.66. Found: C, 81.49; H, 13.56.

*Example 11*

Menthyl hexadexyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting 3.68 gms. (0.160 mole) of sodium with 25.00 gms. (0.160 mole) of menthol in the presence of dry toluene. The sodium menthoxide is reacted with 97.6 gms. (0.320 mole), 1-bromohexadecane by the same method as described for the preparation of menthyl propyl ether. The reaction mixture is refluxed for 6½ hours at 150° C. The isolation of menthyl hexadexyl ether yielded 25.1 gms. (41.3%).

The menthyl hexadexyl ether is purified by recrystallization from hexane to give a white solid, M.P. 25° C., $\alpha_{obs}$ −38.31° (0.1065 gms./ml. in $CHCl_3$).

*Analysis.*—Calculated for $C_{26}H_{52}O$: C, 82.03; H, 13.77. Found: C, 81.92; H, 13.80.

*Example 12*

Menthyl phenyl ether is prepared in the following manner:

Sodium menthoxide is prepared by reacting 7.36 gms. (0.32 mole) of sodium with 100 gms. (0.64 mole) of menthol in the presence of dry toluene. To this mixture is added 75.4 gms. (0.48 mole) of bromobenzene and 1.5 gms. of copper powder. The mixture is refluxed for 7 hours. After the reaction is complete the mixture is cooled, filtered and the filtrate distilled under pressure to yield 76.6 gm. (45.0% of theoretical) of menthyl phenyl ether, B.P. 155°–157° C. at 12 mm. Hg A, M.P. 49°–50° C.

*Elemental analysis.*—Calculated for $C_{16}H_{24}O$: C, 82.70; H, 10.41. Found: C, 82.89; H, 10.27.

The examples set forth above are for illustrative purposes only and do not limit our invention to the compounds listed. Any ether of menthol that imparts a cooling sensation to tobacco products when smoked as previously described may be used.

The proportion of menthyl ether that may be incorporated in a tobacco product may be widely varied in accordance with taste.

However, we have found that desirable results which impart the desired cooling sensation are obtained when the menthyl ether content is between 0.01 and 1.0% by weight of the smoking tobacco product.

In practicing our invention, we have found that any convenient method may be used to incorporate the menthyl ethers in smoking tobacco products. Thus, the menthyl ether may be disssolved in a suitable solvent and may be applied to the cured, cased and blended tobacco by spraying or dipping. Also, the menthyl ether may be applied to the paper or leaf wrapper by spraying, dipping or brushing or any other method in general use in the industry.

Specific examples of incorporating menthyl ethers in a tobacco product are as follows:

*Example 13*

Approximately 2.0 gms. of menthyl butyl ether is dissolved in 100 cc. of absolute ethanol. The solution is sprayed on approximatey 500 gms. cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes.



*Example 14*

Approximately 2.0 gms. of menthyl amyl ether is dissolved in 100 cc. of absolute ethanol. The solution is sprayed on approximately 500 gms. cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes.

*Example 15*

Approximately 2.0 gms. of menthyl hexyl ether is dissolved in 100 cc. of absolute ethanol. The solution is sprayed on approximately 500 gms. cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes.

We have found that the menthyl ethers of butyl, amyl and hexyl give the most desirable organoleptic results in which the tobacco product tested imparted a desirable and pleasing cooling sensation when smoked. It is understood that taste varies widely and other menthyl ethers or combinations thereof may give preferred desirable results. The tobacco products described herein were tested organoleptically and were found to impart a desirable cooling sensation associated with menthol of the tobacco product without the characteristic taste, flavor or aroma when smoked.

Modifications may be made in the illustrated examples which have been described in detail, and it will be understood that variations can be effected within the spirit and scope of the invention as described herein and as defined in the appended claims.

We claim:

1. The method of imparting cooling characteristics of menthol to a smoking tobacco product without the characteristic flavor, taste and aroma of menthol which comprises incorporating therein a menthyl ether which volatilizes below the pyrolysis temperature of a smoking tobacco product.

2. The method of imparting cooling characteristics of menthol to a smoking tobacco product without the characteristic flavor, taste and aroma of menthol as set forth in claim 1 wherein the menthyl ether constitutes between 0.01 and 1.0% by weight of the tobacco product.

3. The method of imparting cooling characteristics of menthol to a smoking tobacco product without the characteristic flavor, taste and aroma of menthol which comprises incorporating therein a menthyl ether which volatilizes below the pyrolysis temperature of a smoking tobacco product and which has the formula:

R—O—R′

in which R is menthyl and R′ is an organic radical selected from the group consisting of aliphatic, aromatic and heterocyclic radicals.

4. The method of imparting cooling characteristics of menthol to a smoking tobacco product without the characteristic flavor, taste and aroma of menthol which comprises incorporating therein a material selected from the group consisting of menthyl methyl ether, menthyl ethyl ether, menthyl propyl ether, menthyl butyl ether, menthyl amyl ether, menthyl hexyl ether, menthyl heptyl ether, menthyl octyl ether, menthyl decyl ether, menthyl dodecyl ether, menthyl hexadexyl ether, benzyl menthyl ether, phenyl menthyl ether, p-tolyl menthyl ether, p-methoxyphenyl menthyl ether, menthyl-3-hexenyl ether and menthyl-5-hexenyl ether.

5. The method of imparting cooling characteristics of menthol to a smoking tobacco product without the characteristic flavor, taste and aroma of menthol which comprises incorporating therein menthyl butyl ether.

6. The method of imparting cooling characteristics of menthol to a smoking tobacco product without the char-

acteristic flavor, taste and aroma of menthol which comprises incorporating therein menthyl amyl ether.

7. The method of imparting cooling characteristics of menthol to a smoking tobacco product without the characteristic flavor, taste and aroma of menthol which comprises incorporating therein menthyl hexyl ether.

8. A smoking tobacco product which has the cooling characterstics of menthol without the distinctive taste, flavor and aroma of menthol which comprises a smoking tobacco material and menthyl ether which volatilizes below the pyrolysis temperature of a smoking tobacco product.

9. A smoking tobacco product which has the cooling characteristics of menthol without the distinctive taste, flavor and aroma of menthol as set forth in claim 8 wherein the menthyl ether constitutes between 0.01 and 1.0% by weight of the tobacco product.

10. A smoking tobacco product which has the cooling characteristics of menthol without the distinctive taste, flavor and aroma of menthol which comprises a smoking tobacco material and a menthyl ether which volatilizes below the pyrolysis temperature of a smoking tobacco product and which has the following formula:

$$R—O—R'$$

in which R is menthyl and R' is an organic radical selected from the group consisting of aliphatic, aromatic and heterocyclic radicals.

11. A smoking tobacco product which has the cooling characteristics of menthol without the distinctive taste, flavor and aroma of menthol which comprises a smoking tobacco material and a material selected from the group consisting of menthyl methyl ether, menthyl ethyl ether, menthyl propyl ether, menthyl butyl ether, menthyl amyl ether, menthyl hexyl ether, menthyl heptyl ether, menthyl octyl ether, menthyl decyl ether, menthyl dodecyl ether, menthyl hexadexyl ether, benzyl menthyl ether, phenyl menthyl ether, 2-phenylethyl menthyl ether, p-tolyl menthyl ether and p-methoxyphenyl menthyl ether.



12. A smoking tobacco product which has the cooling characteristics of menthol without the distinctive taste, flavor and aroma of menthol which comprises a smoking tobacco material and menthyl butyl ether.

13. A smoking tobacco product which has the cooling characteristics of menthol without the distinctive taste, flavor and aroma of menthol which comprises a smoking tobacco material and menthyl amyl ether.

14. A smoking tobacco product which has the cooling characteristics of menthol without the distinctive taste, flavor and aroma of menthol which comprises a smoking tobacco material and menthyl hexyl ether.

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