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**SMOKING TOBACCO PRODUCT AND METHOD
OF MAKING THE SAME**

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This invention relates to an improved smoking tobacco product having improved smoking flavor characteristics and to the method of making the improved smoking tobacco product.

The use of natural and synthetic menthol in smoking tobacco, particularly in cigarettes, to impart its characteristic cooling flavor and aroma thereto is of increasing significance to the tobacco products industry. Unfortunately, there are several difficulties and disadvantages associated with the use of menthol. Thus, due to its volatility, the manufacturing rooms of a tobacco products factory and also the unmentholated tobacco products are frequently contaminated by menthol and also considerable quantities of menthol are lost during the manufacturing process and the resulting menthol containing tobacco products also have a relatively short shelf life. Also, in the smoking of a menthylated tobacco product the menthol is frequently released unevenly into the smoke stream.

It is a primary object of the present invention to overcome the difficulties and disadvantages heretofore encountered and to provide an improved tobacco product and method of making the product wherein the tobacco product incorporates a menthol-containing additive imparting a desirable and pleasant cooling flavor and aroma which substantially eliminates the problem of contamination of the manufacturing rooms and unmentholated products in which the tobacco product has a protracted shelf life and in which the additive or its desirable menthol component is released into the smoke stream on smoking of the tobacco product in a satisfactory regulated manner.

My invention contemplates incorporating in smoking tobacco or in a smoking tobacco product a mono ester of synthetic or natural menthol and a saturated or unsaturated aliphatic or aromatic or heteroaromatic polycarboxylic acid or a substituted analogue of such an acid. In the case of saturated or unsaturated aliphatic mono menthyl esters I prefer employing as acid components compounds with two carboxyl groups in the cis arrangement on adjacent carbon atoms or substituted 1, 3 in relation to one another. In the case of aromatic or heteroaromatic dicarboxylic acids, the 1, 3 substitution includes only the homo dicarboxylates such as homophthalic acid and homoquinolinic acid.

Specific examples of the polycarboxylic acids which may be used as the acid components of the ester are butanedioic (succinic) acid; cis-butenedioic (maleic) acid; pentanedioic (glutaric) acid; cis-pentanedioic (glutaconic) acid; phthalic acid; camphoric acid; cis-cyclohexene-1,2-dicarboxylic acid; cis-4-cyclohexene-1,2-dicarboxylic acid; homophthalic acid; homoquinolinic acid; 2,3-dimethylsuccinic acid; 2,2-dimethylsuccinic acid; 1,2,3-benzenetricarboxylic acid (hemimellitic acid); methylsuccinic acid; itaconic acid; aconitic acid; cis-cyclopropane-1,2-dicarboxylate; malic acid.

As the menthol component I may employ 1-menthol, d-menthol and racemic menthol. Specific examples of

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the mono menthyl esters of polycarboxylic acids which may be used as tobacco products additives in accordance with my invention are mono menthylmaleate, mono menthylsuccinate; mono menthylphthalate; mono menthyl-2-methylmaleate; mono menthyl-3-methylmaleate; α -menthylcamphorate; cis-mono-menthylcyclohexene-1,2-dicarboxylate; cis-1-menthyl-4-cyclohexene-1,2-dicarboxylate; monomenthylhomophthalate; mono menthylhomooquinolate; mono menthyl-meso-dimethylsuccinate; mono menthyl- α , α -dimethylsuccinate; 2-menthylhemimellitate; mono menthyl-methylsuccinate; mono menthylaconitate; mono menthylitaconate; mono menthyl-cis-cyclopropane-dicarboxylate; mono menthylmalate; cis-mono menthylglutaconate.

15 The mono menthyl esters that have been found to improve the flavoring characteristics when incorporated in a tobacco product may be characterized by the formula:



in which R is the menthyl radical and R' is a material selected from the group consisting of saturated and unsaturated aliphatic and aromatic and heteroaromatic polycarboxylic acid radicals and substituted analogues thereof and n is the total number of carboxyl groups in the acid from which the ester is derived.

25 The mono menthyl esters may be prepared in any desired fashion. Thus, the dicarboxylic acid anhydride may be reacted directly with menthol and the mono menthyl ester can then be recrystallized from a suitable solvent. If preferred, menthol may be added as a suspension to an aqueous solution of the polycarboxylic acid and after heating and thereafter cooling the resultant crystals are filtered from the suspension and washed and dried.

30 Specific examples of the preparation of a suitable mono menthyl ester of a polycarboxylic acid which may be used as a tobacco product additive in accordance with my invention are as follows:

Example I

35 Twenty grams of maleic anhydride are melted in a 50 cc. three-neck flask kept at 80° C. with a water bath. To the continuously stirred maleic anhydride, 31.2 grams of menthol are slowly added and the mixture is allowed to react at 80° C. for eight hours. At this stage, the reaction mixture has a melting point of approximately 70° C. The mono menthylmaleate can be separated from the 40 mixture by cooling it and recrystallizing it from a suitable solvent such as the mixture commercially known as Skellysolve B, which is essentially n-hexane. Approximately 44 grams (approximately 87% of the reaction materials) of mono menthylmaleate is obtained having a melting point between 83-85° C.

Example II

45 Approximately 16 grams of menthol are dissolved in 20 milliliters of anhydrous toluene. This mixture is added dropwise, over a period of 1 hour, to a stirred and refluxing solution of approximately 10 grams maleic anhydride in 25 milliliters of anhydrous toluene containing 0.01 gram of p-toluenesulfonic acid. After 12 hours at reflux the mixture is cooled to room temperature and extracted with 100 milliliters of distilled water to remove

the p-toluene sulfonic acid and any unreacted maleic anhydride. The toluene is removed by flash evaporation at room temperature and the product recrystallized as above, yielding 16.1 g. (67.8%) of mono menthylmaleate, M.P. 83-85° C.

Example III

Approximately 392 g. of di-menthylmaleate are dissolved in 500 milliliters of p-dioxane and brought to 100° C. on a steam bath. To this stirred solution is added, over a three-hour period, approximately 40 grams of sodium hydroxide dissolved in 200 milliliters of water. After an additional six hours the reaction mixture is diluted with 1 liter of water, cooled to 10° C. and filtered to remove the menthol formed on hydrolysis. The supernatant liquid is acidified to a pH of 2 with 12 Normal sulfuric acid, cooled to 5° C. and filtered. The semi-crystalline precipitate of mono menthylmaleate is recrystallized as above, yielding approximately 200 grams (78.9%) of mono menthylmaleate, M.P. 84-85° C.

Example IV

Approximately 15.6 grams of menthol were dissolved in 25 milliliters of anhydrous chloroform and added dropwise, over a three-hour period, to a stirred refluxing solution of 10 grams of freshly prepared succinic anhydride in 35 milliliters of anhydrous chloroform. On cooling mono menthylsuccinate precipitates, M.P. 58-59° C. in 50% yield (11.9 grams).

Example V

Approximately 7.8 grams of menthol are dissolved in 20 milliliters of anhydrous toluene and added dropwise, over a thirty-minute period to a refluxing solution of 5 grams of succinic anhydride in 25 milliliters of toluene containing 0.1 gram of p-toluenesulfonic acid. The mixture was refluxed an additional 4 hours. After cooling to room temperature the mixture was extracted with three 25 milliliter fractions of water to remove the p-toluenesulfonic acid catalyst. The toluene was evaporated from the crude product at room temperature by flash evaporation. The mono menthylsuccinate is recrystallized from n-hexane at -20° C. producing approximately 23.6 g. or substantially quantitative yields of mono menthylsuccinate, M.P. 58-59° C.

Example VI

Approximately 15.6 grams of menthol are dissolved in 20 milliliters of anhydrous xylene. This mixture is added dropwise, over a period of 1 hour to a stirred and refluxing solution of approximately 24.6 grams of 1,2,3-benzene-tricarboxylic acid (hemimellitic acid) in 25 milliliters of anhydrous commercial xylene mixture containing 0.01 gram of p-toluenesulfonic acid. After 12 hours at reflux the mixture is cooled to room temperature and extracted with 100 milliliters of distilled water to remove the p-toluenesulfonic acid catalyst. The xylene is removed by flash evaporation at 80° C. and the product mono menthylhemimellitate obtained as above.

It should be understood that in the Examples I to VI set forth above any of the other indicated polycarboxylic organic acids may be substituted for the acids indicated in the examples and the proportions adjusted in accordance with the molecular weight thereof. The mono menthyl esters may be incorporated in the tobacco product either alone or in mixture with each other or mixed with menthol. The proportion of the mono menthyl ester incorporated in the tobacco product may be widely varied in accordance with taste, but I have found that satisfactory results are obtained if the proportion by weight on a dry basis is between 0.01 and 1.0% of the mono ester to the smoking tobacco. Where menthol is mixed with the ester, the proportion by weight on a dry basis may be reduced to as little as 0.005% of the combined ester and menthol to the smoking tobacco.

Any convenient method for incorporating the mono

menthyl ester in the tobacco product may be employed. Thus, the ester may be dissolved in a suitable solvent and either sprayed on the cured, cased and blended tobacco or the tobacco dipped therein. Alternatively, an aqueous suspension of the mono ester may be prepared which, in turn, may be sprayed on the cured, blended and cased tobacco or the tobacco dipped therein. Under certain circumstances, a solution or aqueous suspension of the mono menthyl ester may be applied by a suitable applicator to the paper or leaf wrapper for the smoking product.

Specific examples of methods of incorporating the mono menthyl ester in a tobacco product are as follows:

Example VII

Approximately 100.5 grams of mono menthylmaleate is dissolved in 500 cc. of an absolute ethanol and the solution is sprayed on approximately 30 pounds of cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes using normal factory procedures and equipment.

Example VIII

Approximately 100.5 grams of mono menthylmaleate is mixed with 500 cc. of water and the resultant suspension is homogenized and sprayed on approximately 30 pounds of cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes using normal factory procedures and equipment.

Example IX

Approximately 227 grams of mono menthylmaleate is dissolved in 1520 cc. of 95% ethanol and the solution sprayed, in conjunction with other flavoring matter, onto 200 pounds of cured, cased, blended and shredded commercial tobacco. The tobacco mixture so treated is manufactured into cigarettes using the procedures and equipment normal to conventional manufacture.

Example X

Approximately 276 grams of mono menthylmaleate and 57 grams of either natural or synthetic menthol is dissolved in 1520 cc. of 95% ethanol and the solution sprayed, in conjunction with other flavoring matter, onto 200 pounds of cured, cased, blended and shredded commercial tobacco. The tobacco mixture so treated is manufactured into cigarettes using the procedures and equipment normal to conventional manufacture.

Example XI

Approximately 475 grams of mono menthylmaleate and 97 grams of either natural or synthetic menthol is dissolved in 1520 cc. of 95% ethanol and the solution sprayed, in conjunction with other flavoring matter, onto 200 pounds of cured, cased, blended and shredded commercial tobacco. The tobacco mixture so treated is manufactured into cigarettes using the procedures and equipment normal to conventional manufacture.

Example XII

Approximately 100.6 grams of mono menthylsuccinate are dissolved in 500 cc. of absolute ethanol and the solution sprayed on approximately 30 pounds of cured, cased and blended commercial tobacco. The tobacco treated in this fashion is manufactured into cigarettes using normal factory procedures and equipment.

Example XIII

Approximately 119.5 grams of mono menthylphthalate are dissolved in 500 cc. of absolute ethanol and the solution sprayed on approximately 30 pounds of cured, cased and blended commercial tobacco. The tobacco treated in this fashion is manufactured into cigarettes using normal factory procedures and equipment.

Example XIV

Approximately 136.8 grams of mono menthylhemimellitate are dissolved in 500 cc. of absolute ethanol and the solution sprayed on approximately 30 pounds of cured, cased and blended commercial tobacco. The tobacco treated in this fashion is manufactured into cigarettes using normal factory procedures and equipment.

Example XV

Approximately 105.3 grams of mono methyl-3-methylmaleate are dissolved in 500 cc. of absolute ethanol and the solution sprayed on approximately 30 pounds of cured, cased and blended commercial tobacco. The tobacco treated in this fashion is manufactured into cigarettes using normal factory procedures and equipment

Example XVI

Approximately 133.6 grams of mono methylcamphorate are dissolved in 500 cc. of absolute ethanol and the solution sprayed on approximately 30 pounds of cured, cased and blended commercial tobacco. The tobacco treated in this fashion is manufactured into cigarettes using normal factory procedures and equipment.

Tobacco products made in accordance with the specific examples given herein have been evaluated and the products were observed to burn slower at smolder than a comparable control, to have increased firmness and to require more puffs under a controlled smoking regime and, when tested organoleptically, the smoking products were found to deliver smoke having a pleasing and cooling taste and aroma characteristic of menthol at an apparently increasing rate when the ester alone was used and at an apparently constant rate when menthol was mixed with the ester.

Modifications may be made in the described embodiments of my invention and in the illustrated examples without departing from the scope of the invention set forth in the accompanying claims.

I claim:

1. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein a material selected from the group consisting of mono menthylmaleate, mono menthylsuccinate; mono methylphthalate; mono methyl-2-methylmaleate; mono methyl-3-methylmaleate; mono methylcamphorate; cis-mono methylcyclohexene - 1,2 - dicarboxylate; cis-1-methyl-4-cyclohexene-1,2-dicarboxylate; mono methylhomophthalate; mono methylhomooquinolate; mono methyl - meso - dimethylsuccinate; mono methyl- α , α -dimethylsuccinate; mono menthylhemimellitate; mono menthylmethylsuccinate; mono menthylaconitate; mono menthylitaconate; mono methyl-cis-cyclopropanedicarboxylate and mono menthylmalate; cis-mono menthylglutaconate.

2. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein mono menthylmaleate.

3. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein mono menthylsuccinate.

4. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein mono methylphthalate.

5. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein mono methyl-2-methylmaleate.

6. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein mono methyl-3-methylmaleate.

7. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein mono menthylhemimellitate.

8. The method of imparting improved smoking flavor

characteristics to a tobacco product which comprises incorporating in smoking tobacco a material selected from the group consisting of mono menthylmaleate, mono menthylsuccinate; mono methylphthalate; mono methyl-2-methylmaleate; mono methyl-3-methylmaleate; mono methylcamphorate; cis-mono methylcyclohexene-1,2-dicarboxylate; cis-1-methyl-4-cyclohexene-1,2-dicarboxylate; mono methylhomophthalate; mono methylhomooquinolate; mono methyl-meso-dimethylsuccinate; mono methyl- α , α -dimethylsuccinate; mono menthylhemimellitate; mono menthylmethylsuccinate; mono menthylaconitate; mono menthylitaconate; mono methyl-cis-cyclopropanedicarboxylate; mono menthylmalate and cis-mono menthylglutaconate.

9. The method of imparting improved smoking flavor characteristics to a tobacco product which comprises incorporating in smoking tobacco mono menthylmaleate.

10. The method of imparting improved smoking flavor characteristics to a tobacco product which comprises incorporating in smoking tobacco mono menthylsuccinate.

11. The method of imparting improved smoking flavor characteristics to a tobacco product which comprises incorporating in smoking tobacco mono methylphthalate.

12. The method of imparting improved smoking flavor characteristics to a tobacco product which comprises incorporating in smoking tobacco mono-menthyl-2-methylmaleate.

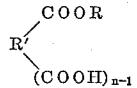
13. The method of imparting improved smoking flavor characteristics to a tobacco product which comprises incorporating in smoking tobacco mono methyl-3-methylmaleate.

14. The method of imparting improved smoking flavor characteristics to a tobacco product which comprises incorporating in smoking tobacco mono-menthylcamphorate.

15. The method of imparting improved smoking flavor characteristics to a tobacco product which comprises incorporating in smoking tobacco mono menthylhemimellitate.

16. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein between 0.01 and 1% by weight of a mono methyl ester of a polycarboxylic acid.

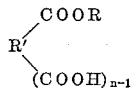
17. A smoking tobacco product having improved smoking flavor characteristics comprising a smoking tobacco having incorporated therein between 0.01 and 1% by weight of a mono methyl ester of a polycarboxylic acid having the formula:



in which R is the methyl radical and R' is a material selected from the group consisting of saturated and unsaturated aliphatic and aromatic and heteroaromatic polycarboxylic acid radicals and n is the total number of carboxyl groups in the acid from which the ester is derived.

18. The method of imparting improved smoking flavor characteristics to a smoking tobacco product which comprises incorporating in smoking tobacco between 0.01 and 1% by weight of a mono methyl ester of a polycarboxylic acid.

19. The method of imparting improved smoking flavor characteristics to a smoking tobacco product which comprises incorporating in smoking tobacco between 0.01 and 1% by weight of a mono methyl ester of a polycarboxylic acid having the formula:



in which R is the methyl radical and R' is a material selected from the group consisting of saturated and unsaturated aliphatic and aromatic and heteroaromatic poly-

carboxylic acid radicals and n is the total number of carboxyl groups in the acid from which the ester is derived.

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