

PATENT SPECIFICATION

939,576

NO DRAWINGS.

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939,576

Index at Acceptance :—Classes 180, C(12:20); and 2(3), C3A10E1.

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COMPLETE SPECIFICATION.

Improvements in or relating to Smoking Tobacco Product and Method of Making the Same.

We, BRITISH-AMERICAN TOBACCO COMPANY, LIMITED, a company organized under the laws of Great Britain, of 7 Millbank, Westminster House, London, S.W.1., England, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

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

15 The use of natural and synthetic menthol in smoking tobacco, particularly in cigarettes, to impart its characteristic cooling flavour 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.

35 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 flavour 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.

The invention, briefly, relates to a smoking tobacco product in which there is incorporated a mono ester of menthol and a polycarboxylic acid or acid anhydride. In the case of saturated or unsaturated aliphatic mono menthyl esters it is preferred to employ 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 butenedioic (succinic) acid; cis-butenedioic (maleic) acid; pentanedioic (glutaric) acid; cis-pentenedioic (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 there may be employed *l*-menthol, *d*-menthol and racemic menthol natural or synthetic. Specific examples of the mono menthyl esters of polycarboxylic acids which may be used as

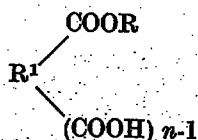


butenedioic

[Price 4s. 6d.]

tobacco products additives in accordance with the 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-methyl-4-cyclohexene-1,2-dicarboxylate; monomethylhomophthalate; mono mentylhomoguinolate; mono menthyl-dimethylsuccinate; mono menthyl- α , α -dimethylsuccinate; 2-methylhemimellitate; mono menthylmethylsuccinate; mono menthylaconitate; mono menthylitaconate; mono menthyl-cis-cyclopropanedicarboxylate; mono menthylmalate; cis-mono menthylglutaconate.

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



in which R is the menthyl radical and R' is a saturated or unsaturated aliphatic or aromatic or heteroaromatic polycarboxylic acid residue or a substituted analogue thereof and n is the total number of carboxyl groups in the acid from which the ester is derived.

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.

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 the invention are as follows:—

EXAMPLE I.

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 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.

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 grams 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 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. (87.8%) 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. $58-59^{\circ}\text{C}$.

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-benzenetricarboxylic acid (hemimellitic acid) in 25 milliliters of anhydrous commercial xylene mixture containing 0.01 grams 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 and 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 methyl 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 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 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 flavouring 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 flavouring matter, onto 200 pounds of cured, cased, blended and shredded commercial tobacco. The tobacco mixture so treated is manufactured into cigarettes using the procedure 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 flavouring 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

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80

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120

procedures

- 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 menthyl-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 menthylcamphorate 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.

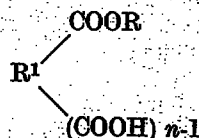
- Tobacco products made in accordance with the specific examples given herein have been evaluated and the products were observed to burn slower at smoulder than a comparable control, to have increased firmness and to require more puffs under a controlled smoking regime and, when tested organoleptically, 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.

- We are aware of the Customs and Excise Act, 1952 (15 and 16 Geo. 6 and 1. Eliz. 2, Ch. 44) and we make no claim to use the invention in contravention of any of the provisions of that Act.

WHAT WE CLAIM IS:—

1. A smoking tobacco product having improved properties, in particular having improved flavour-release properties, comprising a smoking tobacco having incorporated therein a mono-ester of menthol and a polycarboxylic acid or anhydride thereof.

2. The smoking tobacco product of Claim 1, wherein the ester is a mono-ester of the general formula:—



in which R is the menthyl radical and R¹ is a saturated or unsaturated aliphatic or aromatic or heteroaromatic polycarboxylic acid residue thereof and n is the total number of carboxyl groups present on the molecule.

3. The smoking tobacco product of Claims 1 or 2, wherein the polycarboxylic acid or anhydride is a dicarboxylic acid or acid anhydride.

4. The smoking tobacco product of Claim 3, wherein the ester is a maleate or a methyl substituted maleate.

5. The smoking tobacco product of Claim 3, wherein the ester is a succinate or methyl substituted succinate.

6. The smoking tobacco product of Claim 3, wherein the ester is phthalate or homophthalate.

7. The smoking tobacco product of Claim 3, wherein the ester is a camphorate.

8. The smoking tobacco product of Claim 3, wherein the ester is a cyclohexane dicarboxylate.

9. The smoking tobacco product of Claim 3, wherein the ester is cyclopropane dicarboxylate.

10. The smoking tobacco product of Claim 3, wherein the ester is an itaconate.

11. The smoking tobacco product of Claim 3, wherein the ester is a glutaconate.

12. The smoking tobacco product of Claim 3, wherein the ester is maleate.

13. The smoking tobacco product of Claims 1 or 2, wherein the acid or anhydride is a tricarboxylic acid or acid anhydride.

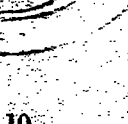
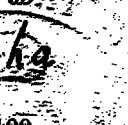
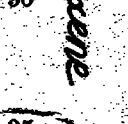
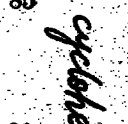
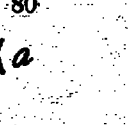
14. The smoking tobacco product of Claim 13, wherein the ester is a hemimellitate or an aconitate.

15. The smoking tobacco product of any one of Claims 1 to 14, wherein there is incorporated menthol in addition to the ester thereof.

16. The smoking tobacco product of any one of Claims 1 to 14, wherein the ester is incorporated in amounts between 0.01% and 1.0% relative to the weight of the smoking tobacco on a dry basis.

17. The smoking tobacco product of Claim 15, wherein there is incorporated a total minimum amount of 0.005% of ester and menthol relative to the weight of the smoking tobacco on a dry basis.

18. The method of making a smoking tobacco product having improved properties,



cigarettes

cyclohexane



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 menthyl-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.

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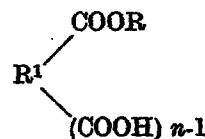
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2. The smoking tobacco product of Claim 1, wherein the ester is a mono-ester of the general formula:—



in which R is the menthyl radical and R¹ is a saturated or unsaturated aliphatic or aromatic or heteroaromatic polycarboxylic acid residue thereof and n is the total number of carboxyl groups present on the molecule.

3. The smoking tobacco product of Claims 1 or 2, wherein the polycarboxylic acid or anhydride is a dicarboxylic acid or acid anhydride.

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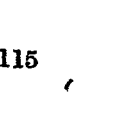
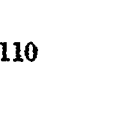
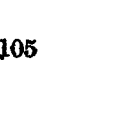
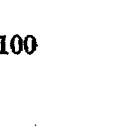
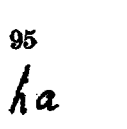
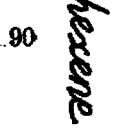
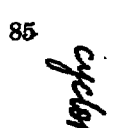
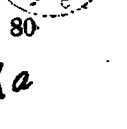
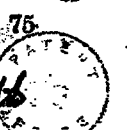
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16. The smoking tobacco product of any one of Claims 1 to 14, wherein the ester is incorporated in amounts between 0.01% and 1.0% relative to the weight of the smoking tobacco on a dry basis.

17. The smoking tobacco product of Claim 15, wherein there is incorporated a total minimum amount of 0.005% of ester and menthol relative to the weight of the smoking tobacco on a dry basis.

18. The method of making a smoking tobacco product having improved properties,



cyclohexane

ha

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cigarettes

5 particularly improved flavour-release properties, comprising spraying a solution or suspension of a mono-ester of menthol and a polycarboxylic acid or anhydride onto the tobacco.

10 19. The method of making a smoking tobacco product having improved properties, particularly improved flavour-release properties, wherein the tobacco is dipped into a solution or suspension of a mono-ester of menthol and a polycarboxylic acid or anhydride.

15 20. The method of making a smoking tobacco product having improved properties, particularly improved flavour-release properties, wherein a solution or suspension of a mono-ester of menthol and a poly-

carboxylic acid is applied to the paper or leaf wrapper of the smoking tobacco product.

21. A smoking tobacco product having improved properties, particularly improved flavour-release properties, substantially as described herein. 20

22. The method of making a smoking tobacco product having improved properties, particularly improved flavour-release properties, substantially as described herein, with reference to Examples VII to XVI. 25

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