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SMOKING TOBACCO ADDITIVES IN THE FORM OF MENTHYL ACETALS

Charles H. Jarboe and John G. Esterle, Louisville, Ky., assignors to Brown & Williamson Tobacco Corporation, Louisville, Ky., a corporation of Delaware

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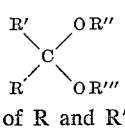
This invention relates to an improved smoking tobacco product and the method of making the same, and more particularly to an improved smoking tobacco product having incorporated therein aroma- and flavor-producing additives which improve the smoking characteristics thereof.

Smoking tobacco products, particularly cigarettes having menthol therein, are of increasing significance in the tobacco products industry. Unfortunately, however, there are a number of difficulties and disadvantages in connection therewith. This is due to the volatility of natural and synthetic menthol. The manufacturing rooms and equipment of tobacco products factories are frequently contaminated by menthol with the result that unmentholated tobacco products are affected thereby. In addition, menthol-containing tobacco products have a relatively short shelf life. A further difficulty arises from the smoker's response to menthol when smoking a mentholated tobacco product. Menthol is released at an increasing rate during the smoking period but has the opposite effect on the smoker, namely, one of a decreasing menthol response. Thus, the release of menthol in a tobacco product does not impart a pleasing and improved organoleptic effect to the smoker throughout the smoking period.

It is an object of this invention to overcome the difficulties and disadvantages heretofore encountered in connection with mentholated smoking tobacco products and to provide an improved smoking tobacco product and method of making the same having a menthol-derived additive incorporated therein; in which the danger of contamination of the manufacturing rooms and equipment is eliminated or minimized; which has a protracted shelf life; and in which a pleasing and improved organoleptic effect is imparted to the smoker throughout the smoking of the product.

Our invention contemplates incorporating in a smoking tobacco or in a smoking tobacco product a menthyl acetal derived from an aldehyde or ketone and from one or more alcohols and in which one of the alcohol-derived groups is derived from menthol. The menthol portion of the acetal may be derived from natural or synthetic or a mixture of synthetic and natural menthol.

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



in which at least one of R and R' is an organic radical and the other is a radical selected from the group consisting of hydrogen and an organic radical and at least one of R'' and R''' is menthyl and the other of R'' and R''' is a radical selected from the group consisting of menthyl and an organic radical.

The organic radicals may be monofunctional or polyfunctional, saturated or unsaturated, aliphatic or aromatic, or heterocyclic.

Similarly, the aldehyde or ketone (carbonyl) derived portion of the menthyl-containing derivatives may be monofunctional or polyfunctional, saturated or unsaturated, aliphatic or aromatic, or heterocyclic. However, the aldehyde or ketone should be one which is not harmful to human beings when ingested with smoke from the smoking tobacco product and which is organoleptically pleasing and beneficial or at least is organoleptically neutral. In addition, the carbonyl-derived portion may be either a monoaldehyde or a ketone or a dialdehyde or a diketone.

Specific examples of aldehydes from which the acetals may be derived are as follows: piperonal, anisaldehyde, cumaldehyde, cinnamaldehyde, benzaldehyde, veratraldehyde, p-tolualdehyde, heptaldehyde, malonaldehyde, acetaldehyde and 5-hydroxyvaleraldehyde.

As previously indicated, at least one of the alcohol derived groups of the acetal is derived from menthol and the acetal may be simple menthyl acetals or mixed acetals.

Specific examples of acetals which may be incorporated in tobacco products to impart improved organoleptic characteristics thereto in accordance with our invention are as follows: benzaldehyde dimenthyl acetal, p-tolualdehyde dimenthyl acetal, veratraldehyde dimenthyl acetal, veratraldehyde menthyl ethyl acetal, piperonal dimenthyl acetal, cumaldehyde dimenthyl acetal, cinnamaldehyde dimenthyl acetal, anisaldehyde dimenthyl acetal, heptaldehyde dimenthyl acetal, 1-menthoxy-1-ethoxymethane, 1,1,3,3-tetramenthoxypropane and 2-menthoxytetrahydropyran.

Upon smoking of tobacco products having menthyl acetals incorporated therein in accordance with our invention, a pleasing and improved release of menthol occurs. The menthyl acetals hydrolyze in the presence of water and acid contained in the smoke stream. Upon hydrolysis, the menthol is released into the smoke stream at a rate which results in a pleasing and improved organoleptic effect throughout the smoking period.

The menthyl acetals may be prepared by the following general procedure: The diethyl acetal of the appropriate aldehyde is mixed with menthol, either synthetic or natural, and the resulting mixture is agitated and heated at from 60° to 80° C. for several hours. After completion of the reaction, the co-product ethyl alcohol is removed in vacuo. The crude menthyl acetal is purified by distillation under reduced pressure, and recrystallization is effected from petroleum ether when applicable.

Specific examples of the preparation of menthyl acetals which may be used as tobacco product additives in accordance with our invention are as follows:

Example 1

1-ethoxy-1-menthoxyethane is prepared in the following manner: A mixture of 43.3 gms. ethyl vinyl ether and 31.2 gms. of l-menthol is cooled to 13° C. and is agitated while 0.08 gm. of p-toluenesulfonic acid is added. After an additional hour at 15° to 20° C. 70 ml. of a solution of 10% by weight sodium hydroxide in water is added and the mixture is stirred for 10 minutes. The organic layer is separated, washed with 50 ml. of a solution of 10% by weight sodium hydroxide in water and dried over anhydrous sodium sulfate. The mixed acetal is isolated by fractional distillation under reduced pressure in the presence of anhydrous potassium carbonate. There was obtained 9.6 gms., 47.6% of theoretical, of 1-ethoxy-1-menthoxyethane, B.P. 100–103° C./4 mm. Hg A, $D^{20}1.4455$, $d_4^{22.5}$ 0.887 g./ml. Elemental analysis: Calculated for $C_{14}H_{28}O_2$: C, 73.63; H, 12.36. Found: C, 73.42; H, 11.95.

Example 2

1,1,3,3-tetramenthoxypropane is prepared in the following manner: A mixture of 4.6 gms. 1,1,3,3-tetramethoxypropane, 25 gms. l-menthol and 3 drops concen-

trated hydrochloric acid is heated under reflux at 50 mm. Hg A pressure for 1.5 hours. The crude product is purified by distillation under reduced pressure to remove low boiling materials following by recrystallization of the stripped residue from dioxane to yield crystals, M.P. 130–131° C. Elemental analysis: Calculated for $C_{43}H_{80}O_4$: C, 78.12; H, 12.19. Found: C, 77.93; H, 11.90.

Example 3

Benzaldehyde dimethyl acetal is prepared in the following manner: A mixture of 48.0 gms. of diethyl acetal of benzaldehyde and 106.0 gms. of 1-menthol is heated on a water bath at from 60° to 80° C. for 3 hours. After completion of the reaction, the co-product, ethyl alcohol is removed in vacuo. The crude benzaldehyde dimethyl acetal is purified by distillation under reduced pressure to remove the excess of 1-menthol. The residue is recrystallized from ethanol to yield 25.0 gms., 23% of theoretical of benzaldehyde dimethyl acetal, M.P. 50°–51° C. Elemental analysis: Calculated for $C_{27}H_{44}O_2$: C, 80.94; H, 11.07. Found: C, 80.66; H, 11.11.

Example 4

Piperonal dimenthyl acetal is prepared in the following manner: A mixture of 82.3 gms. of piperonal diethyl acetal and 125.0 gms. of 1-menthol is agitated and heated at from 60° to 80° C. for two hours. After completion of the reaction, the co-product ethyl alcohol is removed in vacuo. The crude product, piperonal dimenthyl acetal, is purified by distillation under reduced pressure and the distillate recrystallized from petroleum ether to yield 51.0 gms., 31.9% of theoretical of piperonal dimenthyl acetal, boiling point 72°–73° C. Elemental analysis is: Calculated for $C_{28}H_{44}O_4$: C, 75.63; H, 9.97. Found: C, 75.67; H, 9.99.

Example 5

Veratraldehyde menthyl ethyl acetal is prepared in the following manner: A mixture of 120.0 gms. of the diethyl acetal of veratraldehyde and 156.0 gms. of 1-menthol is heated at from 60° to 80° C. for two hours. After completion of the reaction the co-product ethyl alcohol, is removed by distillation in vacuo. The crude product, veratraldehyde menthyl ethyl acetal, is recrystallized 70.5 gms., 40% of theoretical of veratraldehyde menthyl ethyl acetal, M.P. 87°–88° C. Elemental analysis: Calculated for $C_{21}H_{34}O_4$: C, 71.96; H, 9.77. Found: C, 71.45; H, 9.72.

It should be understood that Examples 1 to 5 set forth above are for illustrative purposes only and do not limit our invention to the compounds listed. Any menthyl acetal may be used that improves flavor and aroma in a smoking tobacco product. The menthyl acetals used are derived from aldehydes or ketones which are not harmful to human beings when ingested with the smoke from a smoking tobacco product and which are organoleptically pleasing and beneficial or are at least organoleptically neutral. The proportions of menthol and acetal used may be adjusted in accordance with the molecular weights thereof. The proportion of menthyl acetal to be incorporated in a smoking tobacco product may be widely varied in accordance with taste, but we have found that desirable results which improve flavor and aroma are obtained when the menthol content of the acetal is between 0.01 and 1.0% by weight to the smoking tobacco.

We have found in practicing our invention that any convenient method may be used to incorporate the menthyl acetals in smoking tobacco products. Thus, the menthyl acetal may be dissolved in a suitable solvent and either sprayed on the cured, cased and blended tobacco or the tobacco may be dipped therein. In addition, the menthyl acetal may be applied to the leaf or paper wrapper or to tobacco filter material by a suitable applicator, such as could be applied by brushing, spraying, dipping or any other method in general use in the industry.

Specific examples of incorporating the menthyl acetals into the tobacco product are as follows:

Example 6

Approximately 1.0 gm. of veratraldehyde menthyl ethyl acetal is dissolved on 50 ml. of absolute ethanol and the solution is sprayed on approximately 100.0 gms. of cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes.

Example 7

Approximately 1 gm. of piperonal dimenthyl acetal is dissolved in 50 ml. of absolute ethanol and the solution is sprayed on approximately 100.0 gms. of cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes.

Example 8

Approximately 1.0 gm. of benzaldehyde dimenthyl acetal is dissolved in '50 ml. of absolute ethanol and the solution is sprayed on approximately 100 gms. of cured, cased and blended commercial tobacco. The tobacco so treated is manufactured into cigarettes.

We have found that of the tobacco products incorporating the menthyl acetals which have been tested, the most desirable results were obtained when the dimenthyl acetals of benzaldehyde and piperonal and veratraldehyde menthyl ethyl acetal were used as the additive. It should be understood that taste varies widely and that other menthyl acetals may give preferred desirable results. The tobacco products described herein when tested organoleptically, were found to have increased flavor and aroma characteristics and a pleasing, cooling, improved taste of menthol was experienced by the smoker.

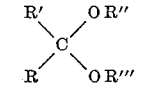
Modifications may be made in the illustrated examples of our invention without departing from the scope thereof set forth in the accompanying claims.

We claim:

1. A smoking tobacco product with improved flavor and aroma characteristics having added thereto a menthyl acetal.

2. A smoking tobacco product with improved flavor and aroma characteristics as set forth in claim 1 wherein the menthol content of the acetal constitutes between 0.01 and 1.0% by weight of the tobacco.

3. A smoking tobacco product with improved flavor and aroma characteristics having added thereto a menthyl acetal with the following formula



in which at least one of R and R′ is an organic radical and the other is a radical selected from the group consisting of hydrogen and an organic radical, and at least one of R″ and R‴ is menthyl and the other of R″ and R‴ is a radical selected from the group consisting of menthyl and an organic radical.

4. A smoking tobacco product with improved flavor and aroma characteristics having added thereto a material selected from the group consisting of benzaldehyde dimenthyl acetal, p-tolualdehyde dimenthyl acetal, veratraldehyde dimenthyl acetal, veratraldehyde menthyl ethyl acetal, piperonal dimenthyl acetal, cumaldehyde dimenthyl acetal, anisaldehyde dimenthyl acetal heptaldehyde dimenthyl acetal, 1-menthoxy-1-ethoxymethane, 1,1,3,3-tetramenthoxypropane and 2-menthoxytetrahydropyran.

5. A smoking tobacco product with improved flavor and aroma characteristics having added thereto benzaldehyde dimenthyl acetal.

6. A smoking tobacco product with improved flavor and aroma characteristics having added thereto veratraldehyde menthyl ethyl acetal.

7. A smoking tobacco product with improved flavor and aroma characteristics having added thereto piperonal dimenthyl acetal.

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