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TOBACCO

Claude Edward Teague, Jr., Winston-Salem, N. C., assignor to R. J. Reynolds Tobacco Company, Winston-Salem, N. C., a corporation of New Jersey

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This invention relates to tobacco and has for an object the provision of a smoking tobacco product having improved aroma and flavor characteristics which become apparent during smoking.

Smoking tobacco as now prepared for use in cigarettes comprises essentially a blended mixture of various types of tobaccos which are desired to produce a characteristic flavor and aroma when the tobacco is smoked. Present day cigarette tobaccos normally comprise blends of (1) heat-cured tobaccos, which are sometimes known as flue-cured, bright leaf or Virginia tobaccos, (2) air-cured tobaccos, which are sometimes known as burley or Kentucky and Maryland tobaccos, and (3) sun-cured tobaccos, which are known as Turkish or Oriental tobaccos. The relative proportions of these various types blended to produce a desired cigarette tobacco mixture depend in a large measure upon the characteristic flavor or aroma that is desired to be achieved when the tobacco is smoked. Also it is common practice to add various substances, such as flavoring materials and humectants, in order to provide other desired properties.

A further object of this invention is to provide a smoking tobacco which when smoked will have improved or enhanced flavor and odor characteristics which will be pleasing to the smoker.

A further object of this invention is the provision of a smoking tobacco having added thereto a compound or compounds which, when the tobacco is smoked, will liberate one or more organic acids imparting a selected and desired flavor and aroma to the smoke.

A still further object of this invention is the provision of a tobacco product having added thereto a substantially nonvolatile substance which in itself does not substantially change the flavor or aroma of the tobacco but which when burned on the tobacco releases to the smoke certain desired flavor- or aroma-producing acids.

A still further object of this invention is the provision of a tobacco having added thereto an organic compound which, when the tobacco is smoked or burned, will liberate several types of flavoring acids whereby the desired improvement in the flavor and aroma of the smoke may be achieved.

A still further object of this invention is the provision of additives for tobacco which may be easily and simply prepared and which may be incorporated into the tobacco at any stage during the processing thereof.

Further and additional objects will appear from the following description and the appended claims.

In the copending application of Samuel O'Brien Jones, Serial No. 445,891, filed July 26, 1954, it is disclosed that certain esters of flavor-producing acids when added to tobacco will, when smoked or burned with the tobacco, release the acid or acids which latter impart a desired characteristic odor and/or flavor to the smoke, thereby contributing to the enjoyment of the smoker.

In accordance with the broad aspects of this invention, a smoking tobacco composition is provided which contains as an additive a small amount of an esterified polymer such as a polyvinyl alcohol condensation product having in the molecule a plurality of esterified hydroxyl groups. It has been found that these esters, when smoked or burned with the tobacco, will release one or more of the esterifying acids which, to provide the desired flavor and aroma, are preferably those having from 3 to 8 carbon atoms. These acids, when present in the smoke in suitable concentrations, will impart characteristic and desirable flavor and aroma to the tobacco smoke, thus contributing to the enjoyment of the smoker. The additives of this invention are substantially nonvolatile under ordinary tobacco storage conditions and will remain dispersed throughout the tobacco until such time as it is smoked and as smoking takes place they will remain in the burning area of the tobacco to permit the acid release to occur. Obviously the additive should not volatilize much ahead of the burning zone or the desired acid release may not occur. The additives herein disclosed are quite stable under the usual tobacco storage conditions; consequently the principal release of flavoring acid or acids does not occur until the tobacco is smoked.

The hydroxyl compounds that are esterified to produce the additives of this invention are synthetic polymers or condensation products normally having free hydroxyl groups in the molecule and are preferably those related to polyvinyl alcohol and vinyl alcohol type condensation products. They may be readily prepared by the polymerization of vinyl esters or by condensing a vinyl ester with other unsaturated type compounds that are known to condense with vinyl alcohol or the esters thereof, suitable other unsaturated compounds being the vinyl ethers, crotonic acid, styrene, butadiene, aldehydes, and ketones. Also the ester additives may, under certain conditions, be prepared by the direct esterification of a polyvinyl alcohol or polyvinyl alcohol condensation product which as in its molecular structure free esterifiable hydroxyl groups. It will be understood that other types of ester polymers may be employed for use in tobacco in accordance with the broader aspects of this invention. For example, the flavoring acid esters of polymers, such as substituted vinyl or allyl alcohol polymers or condensation products, glyptal or alkyd type condensation products, phenol-formaldehyde type condensation products, butyral condensation products, or in general any type of polymer or condensation product having esterified or esterifiable hydroxyl groups, may be utilized. Thus the ester additive is a polymer or condensation product having chemically combined therewith, in ester form, an organic flavoring acid which is released or liberated when the tobacco containing the additive is smoked.

The flavor-producing acids which are released by the esters in accordance with this invention are preferably those flavoring acids which will volatilize and will be carried by the smoke, such acids usually being the organic carboxylic acids having 3, 4, 5, 6, 7 or 8 carbon atoms, herein collectively referred to as those having from 3 to 8 carbon atoms. Representative acids are the saturated aliphatic fatty acids, such as propionic, n-butyric, isobutyric, n-valeric, isovaleric, 2-methylbutyric, n-caproic, 4-methylvaleric, 3-methylvaleric, 2,2-dimethylbutyric, 2-methylisovaleric, straight or branched chain heptoic, or straight or branched chain caprylic acids; the unsaturated aliphatic fatty acids, such as acrylic, crotonic, vinylacetic, 4-methyl-4-hexenoic and 5-methylsorbic acids; the cycloalkane or cycloalkene aliphatic acids, such as cyclopentanecarboxylic, cyclohexanecarboxylic, cyclopentaneacetic or cyclohexaneacetic acids or the corresponding unsaturated cycloalkenes; the aromatic carboxylic acids, such as benzoic or toluic acids; and phenylacetic acid. Also the volatile derivatives of such acids, such as hydroxy acids or keto acids, may be the acid com-

pound released to impart the desired odor or flavor to the smoke. It is preferred that the flavoring acid be an aliphatic or alicyclic saturated monocarboxylic acid of the fatty acid series having 4, 5 or 6 carbon atoms, herein collectively referred to as those having from 4 to 6 carbon atoms.

It will be apparent that the ester additive may be selected or prepared in such a manner that any one of the foregoing acids will be released during smoking. Also a single additive or mixture of additives may be selected and added to the tobacco so that a plurality of desired flavoring acids may be simultaneously liberated if desired, thus effecing a blend of the various types of aromas which has the characteristics of the several flavoring acids. Also, if desired, the several hydroxyl groups in the polymer compound may be esterified with one or more different flavoring acids or less than all of the hydroxyl groups may be esterified to produce the additive used in accordance with this invention. The specific flavor-producing acid or acids that are combined with the hydroxy compound to form the ester will depend upon the flavor and aroma desired in the tobacco smoke. As indicated above, the particular flavoring acid selected for the preparation of the ester is of consequence only insofar as the particular flavor contributed by that particular acid is important. Any of the flavor-producing acids may be utilized and, as previously indicated, they generally comprise the saturated or unsaturated organic carboxylic acids containing from 3 to 8 carbon atoms, preferably the saturated aliphatic monocarboxylic acids having from 4 to 6 carbon atoms.

The additives contemplated by this invention may be incorporated into the tobacco in any desired manner. For example, solutions of the additive in a suitable solvent, such as alcohol, ethyl ether, acetone or the like, may be applied to the tobacco as by spraying or otherwise, whereafter the solvent is driven off as a vapor leaving the additive thoroughly incorporated with the tobacco. The additive may also be uniformly dispersed in water and applied in a like manner if desired. The incorporation of the additive may take place at any time prior to the final packaging of the tobacco product. In the case of cigarette tobacco, it may be incorporated before or after blending of the various tobaccos if, in fact, blended tobacco is employed, and the additives may be applied to one or all of the blend constituents. Under certain circumstances the additive may be incorporated into the tobacco before aging and curing; however, this would not ordinarily be done if the additive has a tendency to decompose during the aging and curing process. In the case of cigarettes the additive in some instances might be applied to the paper instead of to the tobacco.

The amount of additive in the final product contemplated by this invention is quite small but will vary widely with the particular additive employed and the amount of acid released upon burning or the flavor or aroma desired in the smoke. Thus an additive that releases only a comparatively small fraction of its total available flavoring acid on burning will be required in higher concentrations than those additives which are more efficient with respect to the amount of flavoring acid released. Also it is well known that some of the aliphatic fatty acids having 4 to 6 carbon atoms have a disagreeable odor per se when vapors of these acids are smelled in certain concentrations. However, in very low concentrations they provide in the tobacco smoke a desirable flavor and aroma, and the amount of additive in the tobacco should be such as not to exceed the amount which, when the tobacco is smoked, will release desirable quantities of the acid. This amount in many cases will be determined by actual experimentation. Generally speaking, however, desirable flavor and aroma are produced if the additives are incorporated into the final tobacco product in amounts between about 0.01 and 1.0 percent by weight (dry basis).

As pointed out in the copending Jones application hereinbefore referred to, a number of methods have been employed for incorporating acid-releasing compounds into cigarette tobacco and evaluating them for acid release. Certain of such methods are further suggestive of procedures that may be used in actual commerical practice and include the following:

METHOD 1

One gram of shredded flue-cured tobacco was spread out on a watch glass of 10 cm. diameter. One milliliter of a solution of the additive in a suitable solvent such as ethyl ether was added uniformly to the tobacco from a pipette. The amounts of the additives vary but in general 10 milligrams of additive were applied to the one gram sample. After the ether had evaporated the tobacco was rolled into a cigarette which was stored at 75° F. and about 60% relative humidity.

METHOD 2

A small quantity of liquid additive in the amount of 1 to 5 milligrams was streaked longitudinally along the paper of a cigarette by means of a stirring rod.

METHOD 3

The additive was dissolved in a volatile solvent, such as acetone, alcohol or ether, using 2 to 40 milligrams of additive per milliliter of solvent. One-fourth milliliter of the resulting solution was then distributed through a one-inch portion (which was to be burned) of a cigarette by means of a ¼ milliliter hypodermic syringe. The volatile solvent was then blown out of the cigarette with a stream of compressed air, leaving the additive dispersed in the cigarette.

METHOD 4

The additive was dissolved in ethyl alcohol or other suitable solvent and sprayed onto shredded flue-cured tobacco spread out on a table. Two hundred milliliters of solution containing 1 to 20 grams of additive were used for each 3 kilograms of tobacco. The tobacco was exposed to the air until substantially all of the solvent had evaporated and then was manufactured into cigarettes in the usual manner having an average weight of one gram each. These were stored for a period of 1 to 12 months at 75° F. and 60% relative humidity in order to ascertain the stability of the additive when stored on tobacco.

METHOD 5

The additive was dissolved in alcohol or other suitable solvent and sprayed onto one of the types of leaf tobacco that is used in a blended cigarette. This leaf tobacco was allowed to dry and was cut on a shredding machine. The shredded tobacco was blended with other types of shredded tobaccos that had not been treated with additive and the blend was made into cigarettes.

The compound or additive under test when applied to a low flavor tobacco or a cigarette made therefrom as indicated in one of the foregoing methods was evaluated by organoleptic testing. This was carried out by smoking the cigarette and examining the smoke by sensory methods. In each of these tests special efforts were made to determine whether any acid odor was present in the smoke. This included a careful sensory study of both the main stream and the side stream. If the acid odor was detected in either the side stream or the main stream, it was concluded that the additive released the acid during the smoking or burning of the treated tobacco or cigarette.

An example will be presented in the following disclosing a two-step method of preparing a compound that is useful as an additive in accordance with this invention and which releases isovaleric acid upon smoking. How-

ever, it will be apparent to one skilled in the art how other esters releasing other particular flavoring acids may be prepared. Furthermore, it will be understood that essentially the same or similar means known to chemists could be employed for preparing related vinyl type esters or vinyl ester type condensation products and that all such esters are contemplated as additives within the scope of this invention.

Vinyl isovalerate

A mixture of 102 grams (1 mole) of isovaleric acid, 516 grams (6 moles) of freshly distilled vinyl acetate, 3 grams of mercuric acetate, and 0.3 milliliter of sulfuric acid (sp. gr. 1.84) was refluxed under an atmosphere of nitrogen for 3 hours. Then 3 grams of sodium acetate trihydrate and 3 grams of hydroquinone were added, and the mixture was distilled until the vapor temperature reached 80° C. The pot residue was then distilled rapidly in vacuo (30 mm. of mercury) until the vapor temperature reached 130° C. The vacuum-distilled fraction was diluted with 500 milliliters of ethyl ether and washed with 10 per cent aqueous sodium carbonate until free of acid. The ether solution was dried over anhydrous sodium sulfate, filtered, treated with 1 gram of hydroquinone, and then distilled at atmospheric pressure until free of ether. Fractional distillation of the residual liquid gave 76.1 grams of vinyl isovalerate, boiling point, 126°–128° C.

Polyvinyl isovalerate

A mixture of 600 milliliters of water and 0.06 gram of an emulsifying agent (Alconox) was heated to boiling and treated with 30 grams of vinyl isovalerate and a solution of 0.3 gram of potassium persulfate in 10 milliliters of water. The mixture was stirred and refluxed for 6 hours, adding 0.1 gram of potassium persulfate in 10 milliliters of water at the end of the first hour, and again at the end of the second hour. Then the condenser was set downward and the milky polymer emulsion was steam-distilled, maintaining its volume essentially constant throughout, for removal of unreacted monomer or other steam volatiles. No organic layer separated from the steam distillate, showing essentially quantitative conversion of monomer to polymer. The emulsion of polyvinyl isovalerate was cooled and filtered with suction through Whatman's No. 1 filter paper. The filtered aqueous emulsion was stable to dilution with water or 90 per cent ethyl alcohol, and was unchanged after standing 3 months in a stoppered bottle.

Treatment of the polymer emulsion with aqueous sodium chloride caused the emulsion to break, coagulating the polyvinyl isovalerate to form a tacky, amorphous polymer mass.

The emulsion formed as above may be applied directly to the tobacco by spraying or the tacky mass may be dissolved in a suitable solvent and then applied to the tobacco in any suitable manner as previously indicated.

A specific example of a method of incorporating the additive into tobacco is as follows: Three hundred grams of flue-cured tobacco strips were sprayed uniformly with a mixture of 18 milliliters of an emulsion of polyvinyl isovalerate (this volume of polymer emulsion contained 0.9 gram of polyvinyl isovalerate) and 72 milliliters of 95% ethyl alcohol. The treated strips were then blended with 900 grams of burley strips and 1800 grams of flue-cured strips. The entire blend was shredded, and the shredded mixture was made into cigarettes which were then packaged in the usual manner. The packaged cigarettes were stored in a room maintained at 75° F. and 60% relative humidity. A test shortly after manufacture by a panel of smokers and subsequent tests at the end of 60, 150 and 220 days showed that isovaleric acid was present in the smoke from the cigarettes in pleasing amount.

It will be understood that the foregoing is only representative of the large number of esters of the vinyl condensation products that may be used in accordance with this invention to release acid on smoking. For example, polyvinyl 2-methylbutyrate, polyvinyl 3-methylvalerate and polyvinyl cyclopentanecarboxylate have been prepared by essentially the same method indicated above and incorporated into tobacco. It will also be understood that these compounds may be prepared by other methods that are well known to the art generally. Also, as previously suggested, the polymeric esters of other types may be employed. While the vinyl ester type polymers are preferred, any other synthetic polymers or condensation products having hydroxyl groups esterified with the flavoring acid may be used.

A feature of this invention is that the additive may be readily constituted in such a manner that a plurality of flavoring acids will be released upon smoking to provide a desired blend thereof. To accomplish the result a mixed ester is prepared and this may be done in a number of ways. For example, the specific procedure given in the foregoing could be modified to treat the vinyl acetate with a mixture of flavoring acids to produce a mixture of vinyl flavoring acid esters which mixture is thereafter subjected to polymerization treatment. Also a number of individual vinyl esters of different flavoring acids may be separately prepared, mixed in any desired proportion, and then polymerized to produce the desired additive. A further characteristic of the additives of this invention is that they are quite stable under the usual tobacco storage conditions and that they have a sufficiently high molecular weight so that they are substantially non-volatile. Thus, these esters of the polymers or condensation products do not volatilize ahead of the burning area of the tobacco and thus are present in the burning area wherein the pyrolytic, oxidative and/or hydrolytic action occurs, insuring maximum acid release to the tobacco smoke.

Studies have been made in order to determine the extent to which various compounds will actually release acid when smoked with tobacco. As pointed out in the above mentioned copending Jones application, an arbitrary scale has been set up for comparing or evaluating various additives that may be incorporated into tobacco. The additives which liberate the largest amount of acid on an organoleptic test basis during smoking with tobacco have been arbitrarily assigned a rating of 10. The additives at the bottom of the scale liberating detectable but small quantities of acid on an organoleptic test basis have been assigned a rating of 1. Using this arbitrary scale and evaluating the various additives by a test panel of a number of smokers, it has been found that the polyvinyl esters have a rating of 6.

Also in accordance with this invention, it may in certain instances be desirable to employ an ester in which less than all of the hydroxyl groups in the compound are esterified with one or more of the flavoring acids. However, at least theoretically, such compounds on a mole for mole basis are capable of releasing fewer molecules of flavoring acids. Generally, however, the degree of acid release in each instance should be tested by actual trial since the degree of acid release does not always appear to be directly proportional to the number of esterified groups in the hydroxy compound.

It will be understood that compositions have been prepared in accordance with this invention which have improved or enhanced aroma and flavor to give increased pleasure during smoking. Infinite variations with respect to the kinds and amounts of flavor-producing acids are possible and may be readily controlled. The additives may be particularly useful with tobaccos which are ordinarily low in the type of flavor imparted by the flavoring acids. While the invention has been specifically described with reference to cigarettes, it will be apparent that it has application in the manufacture of other smoking tobaccos such as used for hand-rolled cigarettes, pipes and cigars.

While several particular embodiments of this invention are suggested above, it will be understood, of course, that the invention is not to be limited thereto, since many modifications may be made, and it is contemplated, therefore, by the appended claims, to cover any such modifications as fall within the true spirit and scope of this invention.

I claim:

1. An article of manufacture comprising a tobacco product having added thereto a polymeric derivative of a volatile organic flavoring acid having more than 3 carbon atoms.

2. An article of manufacture comprising tobacco and a high molecular weight polymer having hydroxyl groups esterified with a volatile organic flavoring acid having more than three carbon atoms.

3. An article of manufacture comprising tobacco and a polyhydroxy polymeric compound esterified with at least one organic monocarboxylic volatile, flavoring acid having more than 3 carbon atoms.

4. A smoking tobacco having added thereto a small amount of a polyhydroxy polymeric compound esterified with an organic flavoring acid having from 3 to 8 carbon atoms.

5. An article of manufacture comprising tobacco and a polyhydroxy condensation product of a vinyl compound esterified with a volatile organic flavoring acid having from 3 to 8 carbon atoms.

6. An article of manufacture comprising tobacco and a condensation product of vinyl alcohol having hydroxyl groups esterified with an organic flavoring acid having from 3 to 8 carbon atoms.

7. An article of manufacture comprising tobacco and a polyvinyl alcohol esterified with an organic flavoring acid having from 3 to 8 carbon atoms.

8. An article of manufacture comprising tobacco and a polymerized vinyl alcohol esterified with an organic acid having from 3 to 8 carbon atoms.

9. An article of manufacture comprising tobacco and a vinyl alcohol condensation product esterified with a volatile monocarboxylic organic acid having from 3 to 8 carbon atoms.

10. An article of manufacture comprising tobacco and polyvinyl alcohol esterified with a volatile monocarboxylic acid having from 3 to 8 carbon atoms.

11. A body of smoking tobacco having dispersed throughout a small amount of an esterified vinyl alcohol condensation product.

12. A smoking tobacco having added thereto a small amount of polyvinyl alcohol esterified with an organic acid having from 3 to 8 carbon atoms.

13. A smoking tobacco having added thereto a small amount of polyvinyl alcohol esterified with a volatile organic monocarboxylic flavoring acid having from 3 to 8 carbon atoms.

14. The tobacco recited in claim 13 wherein said acid is isovaleric acid.

15. The tobacco recited in claim 13 wherein said acid is 2-methylbutyric acid.

16. The tobacco recited in claim 13 wherein said acid is 3-methylvaleric acid.

17. The tobacco recited in claim 13 wherein said acid is cyclopentanecarboxylic acid.

18. The smoking tobacco recited in claim 13 wherein the amount of said esterified polyvinyl alcohol is between about 0.01 and about 1.0 percent (by weight) and wherein said acid is an aliphatic acid having from 4 to 6 carbon atoms.

19. A body of smoking tobacco having dispersed throughout between about 0.01 and about 1.0 percent by weight (dry basis) of a polymeric derivative of a volatile organic flavoring acid.

20. A smoking tobacco having admixed therewith between about 0.01 and about 1.0 percent by weight (dry basis) of a polyhydroxy polymeric compound esterified with a volatile organic monocarboxylic flavoring acid having from 3 to 8 carbon atoms.

21. A smoking tobacco having admixed therewith between about 0.01 and about 1.0 percent by weight (dry basis) of a condensation product of vinyl alcohol having hydroxyl groups esterified with a volatile organic monocarboxylic flavoring acid having from 3 to 8 carbon atoms.

22. An article of manufacture comprising tobacco and a polymeric type compound which, upon smoking with tobacco, is capable of releasing a volatile organic flavoring acid having more than 3 carbon atoms.

23. A body of smoking tobacco having dispersed throughout a polyhydroxy polymeric compound at least partially esterified with a volatile organic flavoring acid.

24. The body recited in claim 23 wherein said acid is a monocarboxylic acid having from 3 to 8 carbon atoms.

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