United States Patent Office 3,082,125 Patented Mar. 19, 1963

3,082,125

PROCESS FOR IMPROVING THE FLAVOR AND AROMA OF TOBACCO AND PRODUCT

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No Drawing. Filed May 23, 1961, Ser. No. 111,935
19 Claims. (Cl. 131—17)

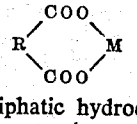
This invention relates to a process for improving the flavor and aroma of tobacco and more particularly, to a process for improving the flavor and aroma of tobacco smoke by incorporating therein cyclic ketones at the time the tobacco is burned, and to tobacco compositions comprising cyclic ketones or salts of aliphatic dicarboxylic acids which form in situ cyclic ketones during pyrolysis of the tobacco.

Fragrant organic flavoring materials are conventionally incorporated into tobacco in order to improve the flavor and aroma of tobacco smoke. These materials are often difficult, however, to apply directly to tobacco. Many of these have a high vapor pressure at room temperature and have a tendency to vaporize before the tobacco is burned. Many liquids are hard to handle during tobacco processing because of their volatility. In addition, in many cases, while the flavoring compounds used impart satisfactory flavors to tobacco smoke, they often contribute undesirable aromas to the tobacco product prior to smoking.

These problems are resolved in accordance with the invention by incorporating with the tobacco not the flavoring material itself but a solid compound which forms the flavoring and aroma-producing material in situ during pyrolysis of the tobacco. In this way, it is possible to employ a solid compound in lieu of a volatile liquid and thus avoid any possibility of loss of the flavoring material before burning.

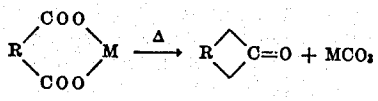
The preferred flavor and aroma-producing additives in accordance with the invention are polyvalent metal salts of aliphatic dicarboxylic acids which form cyclic ketones under the conditions of pyrolysis of tobacco. Since these salts are nonvolatile and odorless, they do not contribute undesirably to pack odor, they are not affected by moisture, are stable under usual tobacco storage conditions, and do not release the flavor and aroma-producing cyclic ketones before pyrolysis. During pyrolysis they transfer the cyclic ketone efficiently into the smoke aerosol phase to impart the desired odor or flavor to the smoke.

The salts of the invention form cyclic ketones having a saturated ring structure during pyrolysis of tobacco and can be defined by the following general formula:



in which R is an aliphatic hydrocarbon group having from four to about twenty-nine carbon atoms. M is a polyvalent metal having a valence of two or more. R includes a saturated alkane chain connecting the two carboxylic acid groups, which chain may contain saturated or unsaturated aliphatic hydrocarbon groups as substituents.

The basic reaction by which the salts are converted into the corresponding cyclic ketones may be represented as follows, M being in this case a bivalent metal:



Small amounts of additional by-products may also be formed.

Salts in which R is a saturated aliphatic hydrocarbon radical having four, five or six carbon atoms form cyclic ketones having five, six and seven membered rings. These cyclic ketones are most readily formed, are the most stable, and the most flavorful, and accordingly such salts are preferred.

The main aliphatic hydrocarbon chain linking the carboxylic acid groups can be straight or branched, and the branched portion can be one or a plurality of saturated or unsaturated aliphatic hydrocarbon groups including, among other groups, methyl, ethyl, propyl, isopropyl, butyl, pentyl, hexyl, methylene, ethylene, propylene, butylene and pentylene. In general, the polyvalent metal salts of any acid of the formula HOOCRCOOH, wherein R is as above defined can be employed. Acids having substituent groups on the carbon atoms alpha or beta to the carboxylic groups tend to form cyclic ketones in better yield because of the effect of the substituent group in forcing the carboxyl groups nearer in space, thus favoring ring closure.

The salts are preferably nontoxic salts of bivalent metals. Calcium and thorium salts are preferred. However, nontoxic salts of other bivalent metals such as magnesium, strontium, cerium, yttrium and zirconium can also be employed.

The pyrolysis of certain salts of some dicarboxylic acids may result in the formation of small amounts of volatile decomposition products such as carbon dioxide and light hydrocarbons. However, these are also found in ordinary tobacco smoke untreated by the addition of these salts and thus do not impart an adverse flavor or physiological effect.

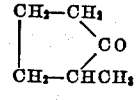
Where processing conditions so permit and it is so desired, cyclic ketones can be added directly to smoking tobacco. Depending upon their molecular weights, these ketones may be either liquids or solids.

The cyclic ketones and their salts of the invention are readily incorporated with tobacco by any of several conventional methods. When solids, they can, for example, be finely ground, and then dusted on the tobacco. Both liquids and solids can be dispersed in water and applied by spraying, dipping or immersing. A single compound may be employed or a mixture of a plurality of compounds may be used so as to produce simultaneously a mixture of cyclic ketones to obtain any desired assortment of flavors and aromas.

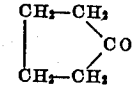
The cyclic ketones are quite variable in flavor and aroma and produce flavor notes resembling peppermint (cyclopentanone and cyclohexanone), menthol (menthone), camphor (2-camphanone), musk (muscone and exaltone) and other flavors conventionally used as additives in tobacco. They also supplement and improve the flavor characteristics of menthol in tobacco smoke.

Examples of some cyclic ketones that are effective flavorants include the following.

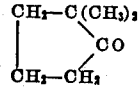
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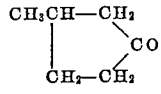
(*b*) Cyclopentanone:



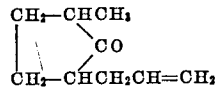
(*c*) 2,2-dimethyl cyclopentanone:



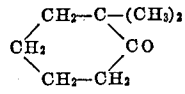
(*d*) 3-methyl cyclopentanone:



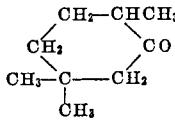
(*e*) 2-methyl-5-allyl cyclopentanone:



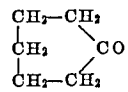
(*f*) 2,2-dimethyl cyclohexanone:



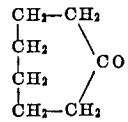
(*g*) 2,5,5-trimethyl cyclohexanone:



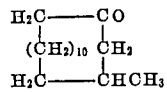
(*h*) Cyclohexanone:



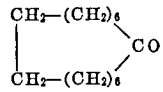
(*i*) Cycloheptanone:



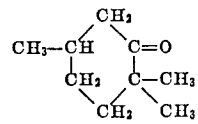
(*j*) Muscone:



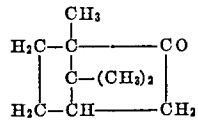
(*k*) Exaltone (cyclopentadecanone):



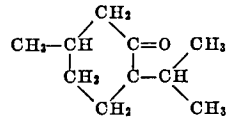
(*l*) 2,2-dimethyl-5-methylcyclohexanone:



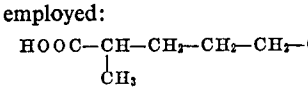
m) Camphonone:

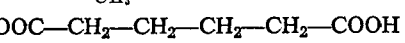


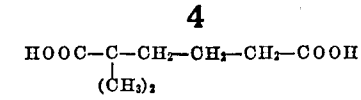
(*n*) Menthone:

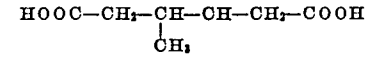


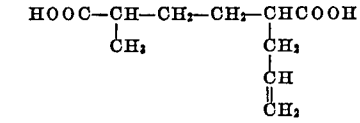
It will be readily understood from the foregoing that these compounds may be added to tobacco smoke by the incorporation in smoking tobacco either directly, as the ketone or preferably, as the salt, preferably the calcium or thorium salt, of the corresponding acid. In the case of the foregoing cyclic ketones, salts of the following acids would be employed:

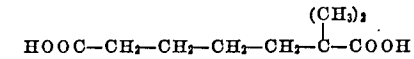
(*a*) 

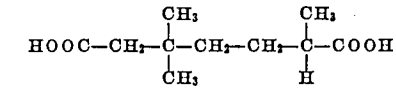
(*b*) 

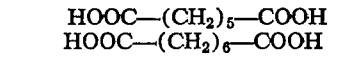
(*c*) 

(*d*) 

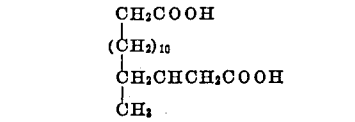
(*e*) 

(*f*) 

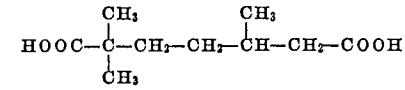
(*g*) 

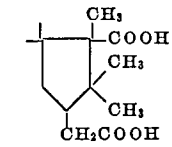
(*h*) 

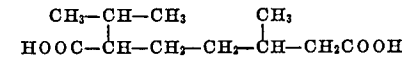
(*i*)

(*j*) 

(*k*) 

(*l*) 

(*m*) 

(*n*) 

The bivalent metal salts of adipic acid, alpha methyl adipic acid, pimelic and suberic acids are preferred. Additional examples include dodecanedioic, sebacic, azelaic, brassylic and thapsic acids, as well as the corresponding methyl and ethyl substituted acids.

While several compounds have been specifically mentioned above, it is to be understood that different and additional hydrocarbon substituents can be present on the ring and different rings can be employed. For example, the cyclohexanones, cycloheptanones, cyclooctanones, cyclononanones, cyclodecanones, cyclohendecanones, cyclododecanones, cyclotridecanones, cyclotetradecanones, cyclopentadecanones, cyclohexadecanones, cycloheptadecanones and cyclooctadecanones, either substituted or unsubstituted can be employed as long as the total number of carbon atoms, in addition to the carbonyl carbon atom does not exceed twenty-nine.

The cyclic ketones and salts of the invention can be employed in connection with tobacco products of all kinds, including for example, cigarette filler, cigar filler, pipe tobacco and the like.

The amount of salt that is added to the tobacco will depend upon the desired flavor and aroma and upon the yield of cyclic ketone in the pyrolysis of the particular salt added. The latter varies considerably with the metal cation and the acid anion, but can readily be determined experimentally by heating the salt in the presence of tobacco. In general, the amount of salt or the amount of ketone added directly should be sufficient to produce from one to about two thousand micrograms of ketone per cigarette, i.e., from about one to about two thousand micrograms of ketone per gram of tobacco burned, taking into account the fact that the yield of cyclic ketone upon pyrolysis of the salt will vary to from about 15 to

about 90%. The amount of salt by weight of the tobacco will be within the range from about 0.05 to about 10 parts by weight per 100 parts by weight of tobacco.

Subjective tests by smoking panels and analytical tests by gas chromatography and mass spectrometry have shown that the cyclic ketones formed in the pyrolysis of tobacco from the salts of the invention are transferred efficiently into tobacco smoke to give pleasant and desirable flavors thereto. Details of such tests are given in the working examples which follow and which in the opinion of the inventors represent typical embodiments of their invention.

Example 1

One mole of adipic acid was dissolved in water and the resulting acidic solution brought to a pH of approximately 10.5 by addition of sodium hydroxide. The pH should not be increased beyond about 10.5 so as to avoid formation of a precipitate. The resulting clear basic solution was mixed with a solution of one mole of calcium chloride dissolved in water and this heated at a temperature just below the boiling point, under which conditions a precipitate formed. The precipitate, calcium adipate, was filtered and dried in an oven for several hours at 120° C. The expected presence of calcium adipate was confirmed by infra-red analysis.

Conversion of the calcium adipate to the corresponding cyclic ketone was carried out as follows: A 38 milligram sample of calcium adipate was placed in a pyrolysis tube. The tube was heated to 800° C. (the temperature attained by a burning cigarette) for three minutes. The pyrolysis products formed in the tube were collected in a trap maintained at liquid nitrogen temperature. The volatile sample collected in the trap was analyzed mass spectrometrically. The residual material in the pyrolysis tube weighed 33 milligrams and this was analyzed by infra-red spectroscopy. The residual material was composed of unpyrolyzed calcium adipate, calcium carbonate and calcium oxide. The volatile material collected in the nitrogen trap was a mixture of carbon dioxide and cyclopentanone. 309 micrograms of cyclopentanone was obtained. Other hydrocarbons also were detected in this fraction, but in minor concentrations.

The conversion of calcium adipate to cyclopentanone in the pyrolysis of tobacco was then confirmed by the following procedure. A commercial cigarette filler was first sprayed with a 4% aqueous solution of corn syrup. The sprayed filler was then divided in half. One half was set aside to be used as a control. The other half while still sticky with the corn syrup solution was mixed with calcium adipate in a blender. Cigarettes were then prepared from both the control batch and the batch containing the added calcium adipate. These cigarettes were made on a standard hand-making machine. Both the test and the control cigarettes weighed 1.2 grams per cigarette, and each test cigarette contained 100 milligrams of calcium adipate. These cigarettes, both the test and control cigarettes, were smoked under identical conditions, alternating test and control. A standard gas phase collection smoking machine was used. The cigarettes were 70 mm. in length and were smoked to a 20 mm. butt length. The smoking conditions were those conventionally employed, that is, a 35 cc. volume puff of two seconds' duration at intervals of one puff every minute.

The smoke from these cigarettes was collected at liquid nitrogen temperature and analyzed mass spectrometrically. The mass spectrometric results on five separate analyses showed that the cyclopentanone content of the smoke from the test cigarette had increased by about 1.7 milligrams per cigarette. The results were as follows.

Test cigarette:	Cyclopentanone, mg./cigt.
Sample No. 1	1.46
Sample No. 2	1.69
Sample No. 3	1.64
Sample No. 4	1.83
Sample No. 5	1.74
Average	1.67

The smoke from the test cigarettes contained significant amounts of cyclopentanone. All of the other smoke components were approximately the same in both the test and the control cigarettes. Additional cigarettes were prepared by this method and subjective tests by a smoking panel gave improved responses to flavor particularly in the case of metholated cigarettes. It was found that the amount of menthol needed could be substantially decreased by the use of these cyclic ketones.

Example 2

The calcium salt of pimelic acid, calcium pimelate, was prepared according to the procedure given in Example 1, identified by infra-red spectroscopy and pyrolyzed. The pyrolysis products were analyzed as in Example 1 establishing the identity of the cyclic ketone as cyclohexanone, which gives an odor similar to peppermint when present as a constituent of tobacco smoke.

The calcium pimelate thus prepared was incorporated with tobacco filler used in the preparation of cigarettes in accordance with the method described in Example 1. Cigarettes prepared from the filler were smoked by the same smoking procedure described in that example. Cyclohexanone was found to be present in the cigarette smoke in significant amounts according to analytical tests. Subjective smoking panel tests showed that the cyclohexanone contributed significantly to the pleasing flavor and aroma of the smoke.

Example 3

The calcium salt of suberic acid, calcium suberate, was prepared in accordance with the procedure in Example 1, identified by infra-red spectroscopy and pyrolyzed by the same procedure. Cycloheptanone was identified by mass spectrometry as one of the pyrolysis products.

The calcium suberate thus prepared was incorporated in tobacco filler used in the preparation of cigarettes by the spraying and tumbling method described in Example 1. Cigarettes were prepared from the treated filler and smoked by the smoking procedure of Example 1. The smoke was trapped and analyzed mass spectrometrically. Cycloheptanone was found to be present as a smoke constituent in significant amounts. Subjective smoking tests carried out by a smoking panel showed that the cycloheptanone contributed significantly to the pleasing flavor and aroma of the smoke.

Example 4

The thorium salt of adipic acid, thorium adipate, is added to smoking tobacco in accordance with the procedure of Example 1. Cigarettes may then be made from this treated tobacco, each cigarette containing 100 milligrams of thorium adipate. Upon smoking of these cigarettes, the peppermint-like flavor and aroma of cyclopentanone is observed in the cigarette smoke.

Example 5

The magnesium salt of adipic acid, magnesium adipate, is added to smoking tobacco in accordance with the procedure of Example 1. Cigarettes may then be made from this treated tobacco, each cigarette containing 100 milligrams of magnesium adipate. Upon smoking of these cigarettes, the peppermint-like flavor and aroma of cyclopentanone is observed in the cigarette smoke.

Example 6

The strontium salt of adipic acid, strontium adipate, is added to smoking tobacco in accordance with the proce-

dure of Example 1. Cigarettes may then be made from this treated tobacco, each cigarette containing 100 milligrams of strontium adipate. Upon smoking of these cigarettes, the peppermint-like flavor and aroma of cyclopentanone is observed in the cigarette smoke.

Example 7

The cerium salt of adipic acid, cerium adipate, is added to smoking tobacco in accordance with the procedure of Example 1. Cigarettes may then be made from this treated tobacco, each cigarette containing 100 milligrams of cerium adipate. Upon smoking of these cigarettes, the peppermint-like flavor and aroma of cyclopentanone is observed in the cigarette smoke.

Example 8

The yttrium salt of adipic acid, yttrium adipate, is added to smoking tobacco in accordance with the procedure of Example 1. Cigarettes may then be made from this treated tobacco, each cigarette containing 100 milligrams of yttrium adipate. Upon smoking of these cigarettes, the peppermint-like flavor and aroma of cyclopentanone is observed in the cigarette smoke.

Example 9

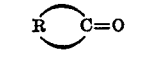
The zirconium salt of adipic acid, zirconium adipate, is added to smoking tobacco in accordance with the procedure of Example 1. Cigarettes may then be made from this treated tobacco, each cigarette containing 100 milligrams of zirconium adipate. Upon smoking of these cigarettes, the peppermint-like flavor and aroma of cyclopentanone is observed in the cigarette smoke.

As aforesaid, the method of this invention is not limited to use in cigarettes. Any tobacco product may be improved in flavor and aroma by means of this invention, including cigars, pipe tobacco and other forms of smoking tobacco. By the term "tobacco" as used throughout the discussion is meant any composition intended for human consumption by smoking whether composed of tobacco plant parts or substitute materials or both.

Since various changes in carrying out the method and certain modifications in the product which embodied the invention may be made without departing from its scope, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

We claim:

1. A tobacco composition having improved flavor and aroma comprising smoking tobacco and an amount sufficient to improve the flavor and aroma when smoked of a cyclic ketone having the formula



wherein R is an aliphatic hydrocarbon group having from 4 to 29 carbon atoms and comprises a saturated alkane chain which is connected at both ends to the carbonyl group and which is substituted by members selected from the class consisting of hydrogen, saturated aliphatic hydrocarbon groups and unsaturated aliphatic hydrocarbon groups.

2. A tobacco composition having improved flavor and aroma comprising tobacco and an amount sufficient to improve the flavor and aroma of the tobacco when smoked of an inorganic salt of an aliphatic dicarboxylic acid having from about six to about thirty-one carbon atoms, said salt being a nontoxic salt of a bivalent metal.

3. A tobacco composition in accordance with claim 2 in the form of particulate smoking tobacco.

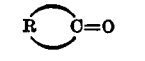
4. A tobacco composition in accordance with claim 2 in which the salt is calcium adipate.

5. A tobacco composition in accordance with claim 2 in which the salt is calcium suberate.

6. A tobacco composition in accordance with claim 2 in which the salt is calcium pimelate.

7. A tobacco composition in accordance with claim 2 in which the salt is thorium adipate.

8. A process for improving the flavor and aroma of smoking tobacco comprising incorporating with the smoking tobacco an amount sufficient to improve the flavor and aroma thereof when smoked of a cyclic ketone having the formula



wherein R is an aliphatic hydrocarbon group having from 4 to 29 carbon atoms and comprises a saturated alkane chain which is connected at both ends to the carbonyl group and which is substituted by members selected from the class consisting of hydrogen, saturated aliphatic hydrocarbon groups and unsaturated aliphatic hydrocarbon groups.

9. A process for improving the flavor and aroma of tobacco comprising incorporating with the tobacco an amount sufficient to improve the flavor and aroma thereof when smoked of a salt of an aliphatic saturated dicarboxylic acid having from about six to about thirty-one carbon atoms, said salt being a nontoxic salt of a bivalent metal.

10. A process in accordance with claim 9 wherein the said salt is a nontoxic salt of a bivalent metal.

11. A process in accordance with claim 9 wherein the salt is a calcium salt.

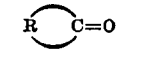
12. A process in accordance with claim 9 in which the salt is calcium adipate.

13. A process in accordance with claim 9 in which the salt is calcium suberate.

14. A process in accordance with claim 9 in which the salt is calcium pimelate.

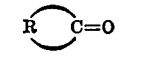
15. A process in accordance with claim 9 wherein the salt is thorium adipate.

16. A process for improving the flavor of tobacco smoke comprising incorporating with smoking tobacco a compound, which, upon pyrolysis of the smoking tobacco, introduces a cyclic ketone having the formula



wherein R is an aliphatic hydrocarbon group having from 4 to 29 carbon atoms and comprises a saturated alkane chain which is connected at both ends to the carbonyl group and which is substituted by members selected from the class consisting of hydrogen, saturated aliphatic hydrocarbon groups and unsaturated aliphatic hydrocarbon groups into the smoke resulting from pyrolysis.

17. A tobacco composition having improved flavor and aroma when smoked, comprising smoking tobacco and an additive, said additive serving, upon pyrolysis of the tobacco during smoking, to produce in the smoke resulting from pyrolysis a cyclic ketone having the formula



wherein R is an aliphatic hydrocarbon group having from 4 to 29 carbon atoms and comprises a saturated alkane chain which is connected at both ends to the carbonyl group and which is substituted by members selected from the class consisting of hydrogen, saturated aliphatic hydrocarbon groups and unsaturated aliphatic hydrocarbon groups.

18. A composition in accordance with claim 17 wherein the cyclic ketone is cyclohexanone.

19. A composition in accordance with claim 17 wherein the cyclic ketone is menthone.

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