

- [54] **TOBACCO SUBSTITUTE SMOKING MATERIAL**  
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[22] Filed: **Mar. 18, 1971**  
[21] Appl. No.: **125,810**

- [30] **Foreign Application Priority Data**  
Mar. 23, 1970 Great Britain ..... 13865/70  
[52] **U.S. Cl.**..... 131/2, 131/17, 131/144  
[51] **Int. Cl.**..... **A24b 15/00**, A24b 15/04  
[58] **Field of Search**..... 131/2, 17, 140-144

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[57] **ABSTRACT**

Tobacco substitute based smoking mixture with added protein and phenyl acetic acid and/or 2-phenyl ethanol. The protein serves to reduce or eliminate the intensity of the off-odours and off-flavours of the smoke from the substitute smoking material and imparts a tobacco-like flavour and after-taste to the smoke.

The phenyl acetic acid and/or 2-phenyl ethanol serve to mask any off-notes arising from the protein. The tobacco substitute base utilized is preferably a carbohydrate material which has been subjected to a catalytic degradation at a temperature of at least 200° C. to a point at which it constitutes about 90 percent or less of the dry weight of the original carbohydrate.

**5 Claims, No Drawings**

## TOBACCO SUBSTITUTE SMOKING MATERIAL

This invention relates to a smoking mixture suitable for incorporation in cigars, cigarettes and smoking pipes, in total or partial replacement of the tobacco constituent of the mixtures normally used.

Smoking mixtures normally consist mainly of, or contain a high proportion of natural tobacco and the opinion is now widely held that the smoking of tobacco, especially in cigarette form, increases the incidence of lung cancer and bronchitic ailments. The replacement of tobacco in smoking mixtures by cellulose and other smoke-producing materials has been proposed but such proposed mixtures have not been acceptable to smokers because the smoke flavour was excessively different from that of tobacco smoke.

It is an object of this invention to provide a smoking mixture comprising an organic combustible material as smoke producing fuel which will give a smoke resembling tobacco smoke in flavour.

In copending U.S. application Ser. No. 125,812, filed on even date herewith, we described how this object can be fulfilled to some extent by the inclusion of protein in the smoking mixture. The protein serves to reduce or eliminate the intensity of the off-odours and off-flavours of the smoke from the substitute smoking material and also imparts a tobacco-like flavour and after-taste to the smoke. Such an improved smoking mixture containing protein to mask the unpleasant character of the smoke produced therefrom is not, however, entirely satisfactory since the protein itself can give rise to off-notes or odours.

It is a further object, therefore, of this invention to improve on the protein-containing smoking mixtures of our aforesaid application Ser. No. 125,812 by including an ingredient which masks the protein off-notes of the smoke from said mixtures.

According to the present invention there is provided a smoking mixture comprising an organic combustible material as smoke producing fuel, protein and phenyl acetic acid and/or 2-phenyl ethanol.

The amount of protein to smoke-producing fuel is in the range 1:1 to 1:60, preferably 1:8 to 1:30.

The smoking mixture of the invention may comprise a minimum of 25 percent by weight of the aforesaid smoke-producing fuel up to 7 percent by weight of protein, up to 0.02 percent of phenyl acetic acid and/or 0.2 percent of 2-phenyl ethanol.

The organic combustible material may be a smoke-producing carbohydrate.

The smoke-producing carbohydrate may advantageously comprise  $\alpha$ -cellulose, cellulose derivatives, sugars, starch, alginate, pectin or natural gum.

The organic combustible material may be a modified carbohydrate.

The modified carbohydrate may advantageously be prepared as disclosed in our U.S. Pat. No. 1,113,979 by subjecting it to a catalysed degradation process at a temperature of 100°–250°C until the weight of the degraded material is less than 90 percent of the dry weight of the original carbohydrate.

Preferred degradation catalysts include sulphuric acid, sulphamic acid and ammonium sulphamate.

A preferred modified carbohydrate is thermally degraded cellulose.

The modified carbohydrate may also be oxidised cellulose. The organic combustible material may be a solid

condensate as described in co-pending U.S. application Ser. No. 31014, filed Apr. 22, 1970, and now U.S. Pat. No. 3,705,589 of Dec. 12, 1972, and produced by acid or based catalysed condensation of a compound of the formula  $R^1COCH_2CH_2COR^2(1)$  (or a precursor thereof), wherein  $R^1$  and  $R^2$ , which may be the same or different, each represents a hydrogen atom, or an alkyl, hydroxyalkyl or formyl group. Said condensate may be prepared from succinaldehyde, acetonyl acetone or a precursor of (1) which is a compound containing a furan ring structure.

The protein should preferably be pure and it is desirable, but not essential, that any residual fat should be removed from the protein, for example, by extraction with an organic solvent. Especially valuable proteins include animal protein, for example, albumin, casein, gelatine, peptone, haemoglobin or wool protein and vegetable proteins, for example, protein from maize (zein) wheat (glutin and gliadin), soyabean or groundnut. Protein acid hydrolysates and protein enzyme hydrolysates, particularly casein acid hydrolysate and casein enzyme hydrolysate, are also suitable.

The smoking mixtures of the invention will, in addition to protein and the smoke-producing constituent and phenyl acetic acid and/or 2-phenyl ethanol contain other ingredients such as are normally used in smoking mixtures to impart desired physical properties and burning characteristics. For example, the mixtures may comprise glow-controlling catalysts, materials to improve ash coherence and colour, nicotine, flavourants, medicaments and humectants or film-forming binding agents. The mixtures may also contain tobacco as part of the smoke-producing material. Such added tobacco could be in the form of comminuted tobacco or tobacco shred.

Alkali metal compounds may advantageously be used as glow-controlling catalysts and salts of ammonia, alkali metals or alkaline earth metals may be used as ash improvers.

Alkali or alkaline earth carbonates or porous fillers may be incorporated in the smoking mixtures to give an open texture and facilitate combustion.

More particularly, additional compounds may comprise:

1. Fillers - e.g., calcium carbonate, magnesium carbonate.
2. Humectants - e.g., glycerol, ethylene glycol, polyethylene glycol.
3. Film-forming agents - e.g., methyl cellulose, sodium carboxymethyl cellulose, pectins, gums.
4. Glow-controlling catalysts - e.g., potassium citrate, calcium carbonate, magnesium carbonate.
5. Ash cohesion agents - e.g., citric acid, sodium hydrogen phosphate, tobacco extracts.
6. Solanesol, other similar unconjugated polyisoprenoids and derivatives thereof (e.g., esters, acids and hydroxyl derivatives), may be added to obtain a sweetish aroma from the burning mixture and to give a pleasant after-note in the mouth of the smoker.

The smoking mixture containing modified carbohydrate or aldol condensation product may additionally contain as a minor component one or more carbohydrate materials such as cellulose fibre, starch or sugar, to improve flavour and physical properties.

The smoking mixture is preferably prepared in a form simulating tobacco. Thus it is preferred to form the mixed ingredients into a sheet and cut or shred into the

physical form required. If the smoke-producing material used is already sheeted, the smoking mixture may be prepared by merely treating the sheet with the remaining ingredients. In the usual case, where the smoke-producing material is in divided form, the ingredients may be admixed and subsequently sheeted. To facilitate sheeting, it is advantageous to incorporate a solution of a binding agent, for example, water-soluble cellulose ether, polyvinyl alcohol or a water-soluble gum, in the mixture.

The invention is further illustrated by the following Examples in which all parts and percentages are by weight.

The Examples illustrate that the desired effect can be achieved by adding phenyl acetic acid or 2-phenyl ethanol to the smoking mixture or by adding both compounds together to the mixture. The Examples also illustrate that the addition of these compounds has little positive influence on the flavour of tobacco substitute material if protein is absent. The effect is thus synergistic between the substitute compounds and protein. In each of the Examples the flavour and after-taste of the product were assessed by a panel of smokers. Furthermore, in each Example, those ingredients which are not soluble, are to be considered as being finely divided.

#### EXAMPLE 1

2.8 parts glycerol, 0.8 part citric acid and 1.0 part potassium citrate were dissolved in 20 parts distilled water and the resultant solution added to a stirred solution of 2 parts of sodium carboxymethyl cellulose in 80 parts hot distilled water. 1.27 parts casein (fat-free) 2 parts calcium carbonate and 10.13 parts of a material made by heating  $\alpha$ -cellulose impregnated with 0.51 part of ammonium sulphamate for 4 hours at 200°C, were added to the above solution and the slurry stirred until homogeneous (approximately 1 hour).

The slurry was cast on glass plates to form a film 0.006 in. thick which was shredded. The shred was sprayed with an ether solution containing 0.004 part of phenyl acetic acid, the ether removed by evaporation and the shred made into cigarettes. When smoked, the cigarettes had a tobacco-like flavour and after-taste. This effect was superior to that from a similar cigarette without phenyl acetic acid added.

In a similar composition in which the casein was replaced by ammonium sulphate, thus eliminating any protein flavour effect yet keeping the smoke pH the same as before, phenyl acetic acid produced a smoke in which no tobacco flavour was evident.

#### EXAMPLE 2

2.8 parts of glycerol, 0.8 part citric acid and 1.0 part potassium citrate were dissolved in 20 parts distilled water and the resultant solution added to a stirred solution of 2 parts of sodium carboxymethyl cellulose in 80 parts hot distilled water. 0.88 part casein (fat-free), 2 parts of calcium carbonate and 10.52 parts of a material made by heating  $\alpha$ -cellulose impregnated with 0.51 part of ammonium sulphamate for 4 hours at 200°C, were added to the above solution and the slurry stirred until homogeneous (approximately 1 hour).

The slurry was cast on glass plates to form a film 0.006 in. thick which was shredded. The shred was sprayed with an ether solution containing 0.004 part of phenyl acetic acid, the ether removed by evaporation and the shred made into cigarettes. When smoked, the

cigarettes had a tobacco-like flavour and after-taste. The same result was obtained when the 0.004 part of phenyl acetic acid was incorporated into the slurry mix instead of spraying on to the shred.

This Example illustrates the desired effect with a lower proportion of casein included in the smoking mixture.

#### EXAMPLE 3

2.8 parts of glycerol, 0.8 part citric acid and 1.0 part potassium citrate were dissolved in 20 parts distilled water and the resultant solution added to a stirred solution of 2 parts of sodium carboxymethyl cellulose in 80 parts hot distilled water. 0.88 part casein (fat-free), 2 parts of calcium carbonate and 10.52 parts of a material made by heating  $\alpha$ -cellulose impregnated with 0.51 part of ammonium sulphamate for 4 hours at 200°C, were added to the above solution and the slurry stirred until homogeneous (approximately 1 hour).

The slurry was cast on glass plates to form a film 0.006 in. thick which was shredded. The shred was sprayed with an ether solution containing 0.002 part of phenyl acetic acid, the ether removed by evaporation and the shred made into cigarettes.

When smoked, the cigarettes had a tobacco-like flavour and after-taste.

This Example illustrates the desired effect being obtained with a lower proportion of phenyl acetic acid in the smoking mixture.

#### EXAMPLE 4

2.8 parts glycerol, 0.8 part citric acid and 1.0 part potassium citrate were dissolved in 20 parts distilled water and the resultant solution added to a stirred solution of 2 parts of sodium carboxymethyl cellulose in 80 parts hot distilled water. 0.88 part casein (fat-free), 2 parts of calcium carbonate and 10.52 parts of a material made by heating  $\alpha$ -cellulose impregnated with 0.51 part of ammonium sulphamate for 4 hours at 200°C, were added to the above solution and the slurry stirred until homogeneous (approximately 1 hour).

The slurry was cast on glass plates to form a film 0.006 in. thick which was shredded. The shred was sprayed with an ether solution containing 0.02 part 2-phenyl ethanol, the ether removed by evaporation and the shred made into cigarettes.

When smoked, the cigarettes had protein off-notes and rank notes reduced with tobacco-like after-taste and a hint of tobacco flavour present.

#### EXAMPLE 5

2.8 parts glycerol, 0.8 part citric acid and 1.0 part potassium citrate were dissolved in 20 parts distilled water and the resultant solution added to a stirred solution of 2 parts of sodium carboxymethyl cellulose in 80 parts hot distilled water. 0.88 part casein (fat-free), 2 parts of calcium carbonate and 10.52 parts of a material made by heating  $\alpha$ -cellulose impregnated with 0.51 part of ammonium sulphamate for 4 hours at 200°C, were added to the above solution and the slurry stirred until homogeneous (approximately 1 hour).

The slurry was cast on glass plates to form a film 0.006 in. thick which was shredded. The shred was sprayed with an ether solution containing 0.008 part of 2-phenyl ethanol, the ether removed by evaporation and the shred made into cigarettes.

When smoked, the cigarettes had a faint tobacco-like flavour and tobacco-like after-taste. Rank protein off-notes were considerably reduced compared to the same composition without 2-phenyl ethanol.

#### EXAMPLE 6

2.8 parts glycerol, 0.8 part citric acid and 1.0 part potassium citrate were dissolved in 20 parts distilled water and the resultant solution added to a stirred solution of 2 parts of sodium carboxymethyl cellulose in 80 parts hot distilled water. 0.88 part casein (fat-free), 2 parts of calcium carbonate and 10.52 parts of a material made by heating  $\alpha$ -cellulose impregnated with 0.51 part of ammonium sulphamate for 4 hours at 200°C, were added to the above solution and the slurry stirred until homogeneous (approximately 1 hour).

The slurry was cast on glass plates to form a film 0.006 in. thick which was shredded. The shred was sprayed with an ether solution containing 0.002 part phenyl acetic acid and 0.02 part 2-phenyl ethanol, the ether removed by evaporation and the shred made into cigarettes.

When smoked, the cigarettes had a sweet tobacco-like flavour and tobacco-like after-taste. The flavour was superior to the similar composition without 2-phenyl ethanol (Example 4) and protein off-odours were not so readily detected.

#### EXAMPLE 7

2.8 parts glycerol, 0.8 part citric acid and 1.0 part potassium citrate were dissolved in 20 parts distilled water and the resultant solution added to a stirred solution of 2 parts of sodium carboxymethyl cellulose in 80 parts hot distilled water. 0.56 parts casein (fat-free), 2 parts of calcium carbonate and 10.84 parts of a material made by heating  $\alpha$ -cellulose impregnated with 0.51 part of ammonium sulphamate for 4 hours at 200°C, were added to the above solution and the slurry stirred until homogeneous (approximately 1 hour).

The slurry was cast on glass plates to form a film 0.006 in. thick which was shredded. The shred was sprayed with an ether solution containing 0.001 part of phenyl acetic acid and 0.01 part 2-phenyl ethanol, the ether removed by evaporation and the shred made into cigarettes.

When smoked, the cigarettes had weak tobacco-like flavour and tobacco-like after-taste.

#### EXAMPLE 8

1.34 parts of glycerol and 0.78 part of potassium citrate dissolved in 4 parts distilled water were mixed with 1.92 parts of sodium carboxymethyl cellulose dissolved in 96 parts hot distilled water. 6.72 parts of magnesium carbonate (magnesite), 3.86 parts of calcium carbonate, 0.2 part of protein casein (extracted for 48 hours with petroleum ether at 30°C) and 5.18 parts of a material made by heating  $\alpha$ -cellulose with ammonium sulphamate for up to 4 hours at 200°C, were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates to give a film 0.006 in. thick which was dried, removed from the plates, cut and shredded. This shred was sprayed with a solution of 0.0002 part of phenyl acetic acid and 0.0004 part of 2-phenyl ethanol in 50 parts of ether and the solvent allowed to evaporate.

When the treated shred was made into cigarettes in a 50:50 blend with flue-cured tobacco shred and smoked in comparison with a similar blend with the two additives missing, there was a marked preference for the former cigarette because of the presence of a fuller flue-cured tobacco flavour.

Assimilar result was obtained in similar exercises using either 70:30 or 85:15 shred/shred blends of the modified cellulose mixture and flue-cured tobacco respectively.

#### EXAMPLE 9

1.34 parts of glycerol and 0.78 part of potassium citrate dissolved in 4 parts distilled water were mixed with 1.92 parts of sodium carboxymethyl cellulose dissolved in 96 parts hot distilled water. 6.72 parts of magnesium carbonate (magnesite), 3.86 parts of calcium carbonate, 0.2 part of protein casein (extracted for 48 hours with petroleum ether at 30°C) and 5.18 parts of a material made by heating  $\alpha$ -cellulose with ammonium sulphamate for up to 4 hours at 200°C, were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates to give a film 0.006 in. thick which was dried, removed from the plates, cut and shredded. This shred was sprayed with a solution of 0.0002 part of phenyl acetic acid, 0.0004 part 2-phenyl ethanol and 0.01 part of carotene (as a mixture of isomers 85 percent  $\beta$ -, 15 percent  $\alpha$ -carotene) in 35 parts of carbon tetrachloride and the solvent allowed to evaporate.

When the treated shred was made up into cigarettes in a 50:50 blend with flue-cured tobacco shred and smoked in comparison with a similar blend with phenyl acetic acid and 2-phenyl ethanol missing, there was a marked preference for the former cigarette because of the presence of a fuller flue-cured tobacco flavour.

A similar result was obtained in similar exercises using a 70:30 shred/shred blend of modified cellulose mixture and flue-cured tobacco respectively.

#### EXAMPLE 10

1.34 parts of glycerol and 0.78 part of potassium citrate dissolved in 4 parts of distilled water were mixed with 1.92 parts of sodium carboxymethyl cellulose dissolved in 96 parts hot distilled water. 6.72 parts of magnesium carbonate (magnesite), 3.86 parts of calcium carbonate, 0.38 part of the protein casein (extracted for 48 hours with petroleum ether at 30°C) and 5.0 parts of rice starch were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates to give a film 0.006 in. thick which was dried, removed from the plates, cut and shredded. The shred was sprayed with a solution of 0.0002 part of phenyl acetic acid and 0.002 part of 2-phenyl ethanol in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarette with the additives because of its improved tobacco character.

#### EXAMPLE 11

1.34 parts of glycerol and 0.78 part of potassium ci-

trate dissolved in 4 parts of distilled water were mixed with 1.92 parts of sodium carboxymethyl cellulose dissolved in 96 parts hot distilled water. 6.72 parts of magnesium carbonate (magnesite), 3.86 parts of calcium carbonate, 0.38 part of the protein casein (extracted for 48 hours with petroleum ether at 30°C) and 5.0 parts of  $\alpha$ -cellulose were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates to give a film 0.006 in. thick which was dried, removed from the plates, cut and shredded. The shred was sprayed with a solution of 0.0002 part of phenyl acetic acid and 0.002 part of 2-phenyl ethanol in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarette with the additives because of its improved tobacco character.

#### EXAMPLE 12

1.8 parts of glycerol dissolved in 4 parts of distilled water were mixed with 2.4 parts sodium carboxymethyl cellulose dissolved in 96 parts distilled water. 5.98 parts of magnesium carbonate (magnesite), 3.44 parts of calcium carbonate, 0.3 parts of zein protein, 1 part bentonite and 5.08 parts of a material made by heating  $\alpha$ -cellulose with ammonium sulphamate were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates and dried to give a film 0.006 in. thick. The film was removed, shredded and the shred was sprayed with a solution of 0.001 part of phenyl acetic acid and 0.002 part of 2-phenyl ethanol, in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked, in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarettes with the additive because of improved tobacco character.

#### EXAMPLE 13

1.8 parts of glycerol dissolved in 4 parts of distilled water were mixed with 2.4 parts sodium carboxymethyl cellulose dissolved in 96 parts distilled water. 5.98 parts of magnesium carbonate (magnesite), 3.44 parts of calcium carbonate, 2.69 parts of casein protein and 1 part of bentonite and 2.69 parts of a material made by heating  $\alpha$ -cellulose with ammonium sulphamate were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates and dried to give a film 0.006 in. thick. The film was removed shredded and the shred was sprayed with a solution of 0.001 part of phenyl acetic acid and 0.002 part of 2-phenyl ethanol in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarettes with the additive because of improved tobacco character.

#### EXAMPLE 14

1.8 parts of glycerol dissolved in 4 parts of distilled water were mixed with 2.4 parts sodium carboxymethyl cellulose dissolved in 96 parts distilled water. 5.98 parts

of magnesium carbonate (magnesite), 3.44 parts of calcium carbonate, 0.088 parts of casein protein, 1 part bentonite and 5.21 parts of a material made by heating  $\alpha$ -cellulose with ammonium sulphamate were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates and dried to give a film 0.006 in. thick. The film was removed, shredded and the shred was sprayed with a solution of 0.001 part of phenyl acetic acid and 0.002 part of 2-phenyl ethanol in 50 part ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarettes with the additive because of improved tobacco character.

#### EXAMPLE 15

1.8 parts of glycerol dissolved in 4 parts of distilled water were mixed with 2.4 parts sodium carboxymethyl cellulose dissolved in 96 parts distilled water. 5.08 parts of magnesium carbonate (magnesite), 2.92 parts of calcium carbonate, 1.4 parts of casein protein and 1 part bentonite and 5.38 parts of a material made by heating  $\alpha$ -cellulose with ammonium sulphamate were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates and dried to give a film 0.006 in. thick. The film was removed, shredded and the shred was sprayed with a solution of 0.004 part of phenyl acetic acid and 0.04 part of 2-phenyl ethanol in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarettes with the additive because of improved tobacco character.

#### EXAMPLE 16

1.8 parts of glycerol dissolved in 4 parts of distilled water were mixed with 2.4 parts sodium carboxymethyl cellulose dissolved in 96 parts distilled water. 5.98 parts of magnesium carbonate (magnesite), 3.44 parts of calcium carbonate, 0.3 parts casein and 1 part bentonite and 5.08 parts of a condensate of succinaldehyde (see U.S. Pat. application Ser. No. 31014) were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates and dried to give a film 0.006 in. thick. The film was removed, shredded and the shred was sprayed with a solution of 0.001 part of phenyl acetic acid and 0.002 part of 2-phenyl ethanol in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarettes with the additive because of improved tobacco character.

#### EXAMPLE 17

1.8 parts of glycerol dissolved in 4 parts of distilled water were mixed with 2.4 parts sodium carboxymethyl cellulose dissolved in 96 parts distilled water, 5.98 parts of magnesium carbonate (magnesite), 3.44 parts of calcium carbonate, 0.3 parts of soya protein, 1 part bentonite and 5.08 parts of a material made by heating  $\alpha$ -cellulose with ammonium sulphamate were added to

the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates and dried to give a film 0.006 in. thick. The film was removed, shredded and the shred was sprayed with a solution of 0.001 part of phenyl acetic acid and 0.002 part of 2-phenyl ethanol in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with a similar cigarette not containing the two sprayed-on additives, there was a marked preference for the cigarettes with the additive because of improved tobacco character.

#### EXAMPLE 18

0.34 parts glycerol were dissolved in 4 parts distilled water and mixed with 6.6 parts sodium carboxy-methyl cellulose dissolved in 96 parts water. 6.2 parts dolomite (Dolodust), 5.6 parts diatomaceous earth (celite), 0.22 part charcoal, 0.34 part octanol and 0.4 part casein protein were added to the above mixture and the whole stirred until homogeneous (about 1 hour).

The slurry was cast on glass plates and dried to give a film 0.006 in. thick. The film was removed, shredded and sprayed with a solution of 0.0004 parts phenyl acetic acid and 0.0008 parts 2-phenyl ethanol in 50 parts ether and the solvent allowed to evaporate. When the treated shred was made into cigarettes and smoked in comparison with similar cigarettes not containing the two sprayed on additives there was a marked preference for the cigarettes with the two sprayed on additives because of improved taste and after-taste which

had a cigar/pipe tobacco nature.

What I claim is:

1. A smoking mixture comprising a thermally degraded carbohydrate tobacco substitute as the essential smoke-producing fuel, a protein selected from the group consisting of casein, groundnut protein, soya-bean protein, zein, albumin or gliadin, the amount of protein to smoke-producing fuel being in the range 1:8 to 1:60 and a sufficient amount of a member of the group consisting of phenyl acetic acid and 2-phenyl ethanol to mask any off-notes from the protein, said thermally degraded carbohydrate being obtained by subjecting a carbohydrate material to a catalysed degradation process at a temperature of at least 100° C. until the weight of the degraded material is approximately 90 percent or less of the dry weight of the original carbohydrate.

2. A smoking mixture as claimed in claim 1 wherein the amount of protein to smoke-producing fuel is in the range 1:8 to 1:30.

3. A smoking mixture as claimed in claim 1 consisting essentially of the smoke-producing fuel, up to 7 percent by weight of protein, up to 0.02 percent of phenyl acetic acid and/or 0.2 percent of 2-phenyl ethanol.

4. A smoking mixture as claimed in claim 1 wherein the modified carbohydrate comprises thermally degraded cellulose.

5. A smoking mixture as claimed in claim 1 wherein the protein is pure protein free of residual fat.

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