

PATENT SPECIFICATION

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(54) SMOKING MATERIAL

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London S.W.1., a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the manufacture of a smoking material for cigarettes, cigars, pipes and the like.

It is known that carbohydrates lose weight on heating, with the formation of simpler anhydro-sugars and/or the complete break up to small organic molecules such as acetaldehyde, formaldehyde formic acid, methane, carbon oxides, water and others. Cellulose in particular releases anhydroglucose units, particularly laevo glucosan.

Our British Patent No. 1,113,979 describes and claims a process for the preparation of a modified carbohydrate suitable for smoking mixtures which comprises subjecting carbohydrate to a catalysed degradation process at a temperature of 100° to 250°C until the weight of the degraded carbohydrate is less than 90% of the weight of the original carbohydrate. The degradation occurring in such a process is entirely different from that which occurs on heating a carbohydrate in the absence of a catalyst, and the products of the two processes are quite different.

It has hitherto been considered that if a carbohydrate was heated above 250°C, even in the presence of a catalyst, degradation would at least in part lead to the production of smaller molecules such as are obtained in the absence of any catalyst. This is not so, however, we have found that degradation to anhydro-sugar and smaller units does not occur to any significant extent at all when a carbohydrate

is heated in the presence of a catalyst, even at a temperature above 250°C.

In the accompanying drawings Curve A shows the weight loss achievable by heating α -cellulose at increasing temperatures, and Curve B shows the weight loss achievable by heating α -cellulose at the same temperatures in the presence of a catalyst (ammonium sulphamate, 5% by weight).

According to the present invention therefore we provide a process for the manufacture of a modified carbohydrate suitable for a smoking material which comprises subjecting carbohydrate material to a catalysed thermal degradation at a temperature above 250°C, preferably 250° to 300°C, until the weight of the solid residue is from 50 to 90%, preferably 65 to 90%, of the weight of the original carbohydrate material.

When operating at the relatively high temperatures used in the present process it is increasingly important to limit the duration of the heating in order that the weight of the residue does not fall below 50%, preferably 65% of the weight of the original carbohydrate material. The duration of the heating will depend very greatly upon the efficiency of the degradation catalyst employed. In general only short periods of heating will need to be employed, varying from a few minutes (e.g. about 5 minutes) at 250°C to only a few seconds at 300°C. The shorter heating times constitute a technical advantage over the process of our Patent No. 1,113,979, enabling higher production rates of equally satisfactory material to be maintained in continuous operation. At the higher temperatures, for example above 270°C, it may be desirable to operate in the absence of oxygen.

The carbohydrate material used in the present process is preferably cellulose.

[Price 33p]

Besides cellulose itself, other examples of carbohydrate material which may be used are cellulose derivatives such as methyl cellulose. Starch, e.g. rice, potato and maize starch, alginates, pectin, natural gums such as gum tragacanth, gum arabic and locust bean gum and simpler carbohydrates including mono- and di-saccharides for example glucose and sucrose are further examples of carbohydrate material which may be used.

Catalysts used in the thermal degradation step may be acidic or basic in nature, though preferably the former. Preferred catalysts are strong acids, and salts of strong acids with weak bases. Such catalysts include sulphamic acid, phosphoric acid, sulphuric acid, hydrochloric acid, perchloric acid, trichloroacetic acid, diammonium hydrogen phosphate, ammonium dihydrogen phosphate, ammonium sulphate, ferric chloride, zinc chloride, stannic chloride, aluminium chloride and especially ammonium sulphamate.

Basic catalysts include alkali hydroxides, e.g. sodium and potassium hydroxides, and alkali salts of weak acids, e.g. sodium and potassium carbonates, acetates and lactates.

To ensure that there is no substantial amount of degradation of the type represented by curve A in the accompanying drawings at least 1% by weight of catalyst should desirably be present, the preferred amount being from 2.5 to 20% by weight of the carbohydrate material.

Carbohydrate material may be subjected to the process of the invention in any convenient form, for example in powder or in sheet form. As for the process of Patent No. 1,113,979 carbohydrate material in sheet form may first be impregnated with a solution of the catalyst applied by immersion or spraying, and dried; or powdered carbohydrate material may be mixed with a solution of the catalyst and dried.

Upon subjection to the process of the invention the carbohydrate material becomes degraded to a black material. Should the black colour be considered undesirable in smoking materials, however, the colour may be bleached to brown, resembling that of a cigarette tobacco, by treatment with nitric acid, ammonia or hydrogen peroxide, preferably at elevated temperature.

The thermally degraded carbohydrate material, optionally after bleaching may then be fabricated into a form simulating tobacco, with the aid of a binder. This step in the process may be carried out by the techniques described in British Patent No. 1,113,979. Thus for example the material may be comminuted to a powder, mixed with a solution of a binder, for example a

water-soluble cellulose derivative e.g. methyl- or ethyl-cellulose, carboxymethyl cellulose or a salt thereof, starch, alginates, pectin, natural gums such as guar gum or locust bean gum, formed as a film and dried. Alternatively a mixture of the thermally degraded carbohydrate material and binder may be extruded as a filament or tape. The film, filament or tape may then be shredded to produce a tobacco-simulating material. Advantageously such material may be conditioned in a humid atmosphere to a moisture content of 5 to 15% by weight to make it more suitable for use as a filling for cigarettes or pipes.

Smoking materials manufactured by the process of the invention, like those prepared by the process of Patent No. 1,113,979 are superior in smoke quality and taste to the corresponding smoking materials made from untreated carbohydrates and they give a smoother, less irritating smoke. The smoke which they produce contains less 'tar' than tobacco smoke. These smoking mixtures may also be varied more widely in composition, and consequently in smoke properties, than mixtures containing untreated carbohydrates, and even than mixtures containing only tobacco. For example, by the incorporation of tasting and flavouring additives, the taste and flavour of the smoke can be varied to suit a wider range of consumer preferences. The proportion of nicotine which is a desirable constituent of smoking mixtures, may also be adjusted widely as desired.

It will be understood that the smoking materials of the invention may comprise, in addition to the modified carbohydrate, other materials which are normal constituents of smoking materials such as, for example, tobacco, untreated carbohydrate or other smoke-producing organic material and, as desired, any of the other modifying agents commonly used in such mixtures. For example, the smoking materials may comprise glow-promoting catalysts, materials to improve ash coherence and colour, nicotine, flavourants or medicaments. Numerous beneficial flavouring materials may be included. These include tobacco extracts, organic esters, essential oils, menthol, tonka bean or vanillin. Glycerol and glycols, such as, for example, ethylene glycol and di-, tri- and tetra-ethylene glycol are convenient humectants.

If desired inorganic fillers may also be incorporated in the smoking materials of the invention. It is particularly beneficial to incorporate in such material from 40 to 65% by weight of harmless inorganic filler wherein the combination of cations and anions is such as to impart an acceptable combustion rate to the mixture, as described in our British Patent No. 1,299,296. By this

means the amount of harmful smoke ingredients reaching the smoker is still further reduced. Conveniently mixtures of calcium and magnesium carbonate may be used for

5 this purpose.

The invention is illustrated but not limited by the following Examples in which the parts are by weight.

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Example 1

1.0 Part of sheeted α -cellulose pulp was immersed in a 5% aqueous solution of ammonium sulphamate and the pulp pressed

15 between rolls to leave 1 part of solution in the pulp. The pulp was dried and heat-treated for 100 seconds at 270°C. This process made the pulp black. The weight of degraded material was 75% of the original

20 weight of α -cellulose and ammonium sulphamate. The degraded material was then made into film and cigarettes as described in Example 12 of British Patent No. 1,113,979.

25 The sidestream and mainstream smokes produced from the cigarettes were milder and less irritating to the eyes and throat than those from an ordinary tobacco cigarette.

30 Example 2

1.0 part of α -cellulose pulp was impregnated with 7.0% aqueous solution of ammonium sulphamate and compressed to leave one part of solution in the cellulose.

35 The cellulose was dried at 165°C and then heated with air at 265°C for 2 minutes until the weight of material was 73% of the original weight and the colour changed to black.

40 26.9 parts of the black material were mixed with 6.7 parts of glycerol, 9.6 parts of sodium carboxymethyl cellulose, 21.3 parts of calcium carbonate and 35.5 parts of magnesite and the mixture processed to

45 make a film as described in Example 6 of our British Patent No. 1,299,296. The film was shredded and made into cigarettes. The sidestream and mainstream smoke were milder and less irritating to the eyes and

50 throat than that of an ordinary tobacco cigarette.

When the black material of the heating process was pyrolysed in a standard fashion at 600°C and the pyrolysis products swept

55 on to a gas chromatogram, the yields of acetaldehyde and acrolein, two particularly irritant species, were substantially lower than the yields from the parent cellulose.

Comparative yields in arbitrary units (peak

60 heights on the recorder traces) of acetaldehyde and acrolein were:

	Acetaldehyde	Acrolein
Cellulose	more than 250	148
65 Example 2 product	80	45

A similar black material was produced when Example 2 was repeated at 300°C for 1½ minutes instead of 165°C for 2 minutes.

Example 3

The process described in Example 2 was repeated except that the aqueous solution contained sulphuric acid. The air temperature was 280°C, heating time was 1½ minutes and weight of material was 75%.

Cigarettes were again less irritating to eyes and throat.

Comparative yields of acetaldehyde and acrolein were:

	Acetaldehyde	Acrolein
Cellulose	more than 250	148
Example 3 product	95	40

Example 4

The process described in Example 2 was repeated except that the aqueous solution contained sodium hydroxide. The air temperature was 275°C, heating time was 3 minutes and the weight of material was 80% of the original weight.

Cigarettes were again less irritating to eyes and throat.

Comparative yields of acetaldehyde and acrolein on 600°C pyrolysis were:

	Acetaldehyde	Acrolein
Cellulose	more than 250	148
Example 4 product	130	41

Example 5

The process described in Example 2 was repeated except that the aqueous solution contained 10% sodium carbonate. The air temperature was 270°, heating time was 4 minutes and weight of the residual material was 70% of the original weight of cellulose.

Cigarettes were again less irritating to eyes and throat.

Comparative yields of acetaldehyde and acrolein on 600°C pyrolysis were:

	Acetaldehyde	Acrolein
Cellulose	250	148
Example 5 product	125	40

Example 6

20 parts of sucrose were mixed with 20 parts of 10% aqueous solution of ammonium sulphamate. The resulting wet paste was dried at 60°C and then heated with air at 280°C for 5 minutes when weight of material was 71% that of original weight of sucrose.

Cigarettes were prepared as described in Example 2 and were again less irritating to eyes and throat.

Comparative yields of the irritant species acetaldehyde and acrolein on 600°C pyrolysis were:

	Acetaldehyde	Acrolein
Cellulose	more than 250	148
65 Example 2 product	80	45

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120

125

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	<i>Acetaldehyde</i>	<i>Acrolein</i>
Sucrose	More than 250	160
Example 6 product	110	47

5 Example 7

The process described in Example 6 was repeated except that the carbohydrate was glucose. The temperature of the heated air was 280°C, heating time was 5 minutes and weight was 73% that of the original weight of glucose.

Cigarettes were less irritating to nose and throat.

Comparative yields of acetaldehyde and acrolein on 600°C pyrolysis were:

	<i>Acetaldehyde</i>	<i>Acrolein</i>
Glucose	More than 250	150
Example 7 product	100	45

20 Example 8

The process described in Example 6 was repeated except that carbohydrate was starch. The temperature of the heated air was 275°C, heating time was 5 minutes and the weight was 75% that of the original weight of starch.

Cigarettes were less irritating to nose and throat.

Comparative yields of acetaldehyde and acrolein on 600°C pyrolysis were:

	<i>Acetaldehyde</i>	<i>Acrolein</i>
Starch	More than 250	155
Example 8 product	95	40

WHAT WE CLAIM IS:

1. A process for the manufacture of a modified carbohydrate suitable for a smoking material which comprises subjecting carbohydrate material to a catalysed thermal degradation at a temperature above 250°C until the weight of the solid residue is from 50 to 90% of the weight of the original carbohydrate material.

2. A process according to claim 1 wherein the catalysed thermal degradation is carried out at 250° to 300°C.

3. A process according to claims 1 or 2 wherein the weight of the solid residue is from 65 to 90% of the weight of the original carbohydrate.

4. Process according to any of the preceding claims wherein the carbohydrate material is cellulose.

5. Process according to any of claims 1-3 wherein the carbohydrate material is starch.

6. Process according to any of the preceding claims wherein the catalyst employed in the thermal degradation is a strong acid or a salt of a strong acid with a weak base.

7. Process according to claim 6 wherein the catalyst employed is ammonium sulphamate.

8. Process according to any of the preceding claims wherein the catalyst is present in an amount ranging from 1 to 20% by weight of the carbohydrate material.

9. Process according to any of the preceding claims wherein carbohydrate material in sheet or powder form is first impregnated with a solution of catalyst and dried.

10. The process according to claim 1 substantially as described in any one of the preceding Examples.

11. A modified carbohydrate manufactured by the process of any of the preceding claims.

12. A process for the manufacture of a smoking material comprising mixing a modified carbohydrate according to claim 11 with a binder and fabricating to produce a tobacco-simulating material.

13. A process according to claim 12 wherein the modified carbohydrate is first bleached.

14. A smoking material manufactured according to the process of either of claims 12 or 13.

15. A smoking material according to claim 14 incorporating from 40 to 65% by weight of harmless inorganic filler wherein the combination of cations and anions is such as to impart a commercially acceptable burning rate to the smoking material.

16. A smoking material according to claim 15 wherein the harmless inorganic filler comprises calcium and magnesium carbonates.

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Agent for the Applicants.

	<i>Acetaldehyde</i>	<i>Acrolein</i>
Sucrose	More than 250	160
Example 6 product	110	47

5 Example 7

The process described in Example 6 was repeated except that the carbohydrate was glucose. The temperature of the heated air was 280°C, heating time was 5 minutes and weight was 73% that of the original weight of glucose.

Cigarettes were less irritating to nose and throat.

Comparative yields of acetaldehyde and acrolein on 600°C pyrolysis were:

	<i>Acetaldehyde</i>	<i>Acrolein</i>
Glucose	More than 250	150
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20 Example 8

The process described in Example 6 was repeated except that carbohydrate was starch. The temperature of the heated air was 275°C, heating time was 5 minutes and the weight was 75% that of the original weight of starch.

Cigarettes were less irritating to nose and throat.

Comparative yields of acetaldehyde and acrolein on 600°C pyrolysis were:

	<i>Acetaldehyde</i>	<i>Acrolein</i>
Starch	More than 250	155
Example 8 product	95	40

WHAT WE CLAIM IS:

1. A process for the manufacture of a modified carbohydrate suitable for a smoking material which comprises subjecting carbohydrate material to a catalysed thermal degradation at a temperature above 250°C until the weight of the solid residue is from 50 to 90% of the weight of the original carbohydrate material.

2. A process according to claim 1 wherein the catalysed thermal degradation is carried out at 250° to 300°C.

3. A process according to claims 1 or 2 wherein the weight of the solid residue is from 65 to 90% of the weight of the original carbohydrate.

4. Process according to any of the preceding claims wherein the carbohydrate material is cellulose.

5. Process according to any of claims 1-3 wherein the carbohydrate material is starch.

6. Process according to any of the preceding claims wherein the catalyst employed in the thermal degradation is a strong acid or a salt of a strong acid with a weak base.

7. Process according to claim 6 wherein the catalyst employed is ammonium sulphamate.

8. Process according to any of the preceding claims wherein the catalyst is present in an amount ranging from 1 to 20% by weight of the carbohydrate material.

9. Process according to any of the preceding claims wherein carbohydrate material in sheet or powder form is first impregnated with a solution of catalyst and dried.

10. The process according to claim 1 substantially as described in any one of the preceding Examples.

11. A modified carbohydrate manufactured by the process of any of the preceding claims.

12. A process for the manufacture of a smoking material comprising mixing a modified carbohydrate according to claim 11 with a binder and fabricating to produce a tobacco-simulating material.

13. A process according to claim 12 wherein the modified carbohydrate is first bleached.

14. A smoking material manufactured according to the process of either of claims 12 or 13.

15. A smoking material according to claim 14 incorporating from 40 to 65% by weight of harmless inorganic filler wherein the combination of cations and anions is such as to impart a commercially acceptable burning rate to the smoking material.

16. A smoking material according to claim 15 wherein the harmless inorganic filler comprises calcium and magnesium carbonates.

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