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## METHOD FOR PREPARATION OF SMOKING PRODUCT WITH SELECTIVE REDUCTION FOLLOWING SELECTIVE OXIDATION

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11 Claims

### ABSTRACT OF THE DISCLOSURE

The preparation of a smoking product of a cellulosic material which has been selectively oxidized by the use of nitrogen dioxide and in which the oxidized reaction product is subjected to a selective reduction with borohydride or nascent hydrogen released by borohydride.

This is a continuation-in-part of our copending applications Ser. No. 595,622, filed Nov. 21, 1966, and entitled "Smoking Products," and Ser. No. 674,994, filed Oct. 12, 1967, and entitled "Smoking Products and Process for Making Such Products."

As used herein, the term "smoking products" is meant to refer to and to include filler material embodied in cigarettes, cigars and for use with pipes and the like, and mixtures thereof with various proportions of tobacco and including cigarette papers and wrappers used in the preparation of such cigars and cigarettes, and it includes cigarettes, cigars and the like products manufactured with such filler materials and wrappers.

In the aforementioned copending applications, description is made of the preparation of a smoking product suitable for use in cigarettes, cigars or with pipes wherein the smoking product is prepared of relatively pure cellulosic materials subjected to selective oxidation with liquid nitrogen dioxide to convert preferably more than 90% of the methylol groups in the cellulosic molecule to yield a product which can be referred to as an oxycellulose, or polyuronic acid. The oxidation reaction product is further processed by removal of liquid nitrogen dioxide by vaporization and preferably by washing the oxidized cellulosic product with water and/or alcohol and/or acetone or other solvent for removal of solubilized foreign material, including oils, waxes, latices and the like, which contribute undesirably to the taste and aroma when used as a smoking product in accordance with the practice of this invention.

As further described in the aforementioned copending applications, the oxidized and cleansed cellulosic derivative is further processed by a reduction reaction with borohydrides of an alkali or alkaline earth metal, such as sodium or lithium borohydride, for reduction of such nitrogen compounds, quinones, ketones, aldehydes and unsaturates as otherwise have a tendency to impart undesirable aroma and taste as the smoking product is burned. The product before or after reduction can be subjected to additional oxidation with a dilute peroxide solution as a means for eliminating further groupings which impart undesirable aroma or taste to the product.

The resulting smoking product is then formulated with mineralizing agents such as oxalates, glycolates, diglycolates, lactates, pivalates or tannates of such metals as calcium, magnesium, lithium, potassium, barium or strontium, preferably introduced to form the salt internally in the cellulosic derivative for purposes of providing desired ashing characteristics. Instead of forming the described

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salts internally in the cellulosic derivative, limited beneficial characteristics can be achieved by external application of such mineralizing agents. As described, the desired internal introduction is achieved by first wetting the cellulosic derivative with metal cation in dilute solution for absorption into the cellulosic derivative followed by exposure to the acid anion in solution to precipitate the metal salt in situ in the cellulosic material.

The treated cellulosic derivatives can be further processed to improve the burning, glow and smoking characteristics by formulation to include a potassium salt, such as potassium oxalate or by the addition of rubidium or cesium in the form of compounds thereof in amounts within the range of 0.1% to 10% by weight but preferably less than 1% by weight, as described in the copending application Ser. No. 623,528, filed Mar. 16, 1967, and entitled "Smoking Products and Process for Their Manufacture." Smoke generators for improving the appearance of the smoke generated by the product can be introduced, as by the introduction of various fatty acids, esters, ethers and the like and the aroma and pH characteristics can be achieved by the addition of volatilizable alkalyzing material such as ammonium oxalate, and the like.

The resulting product is suitable for use as a smoking product alone or in admixture with tobacco to produce a smoking product having good taste, good aroma and good appearance.

As the cellulosic raw material, use can be made of various forms of cellulose, such as wood pulp, alpha-cellulose, flax, fibrous carbohydrates, seaweed carbohydrates, bamboo filaments, cotton filaments, hemp, straw, refined paper, rice paper, filamentous gums and even plants and plant leaves and the like fibrous materials, from which non-carbohydrate components have been separated, all of which is hereinafter referred to as cellulosic material.

It is preferred to make use of a purified cellulosic material from which various of the sugars, proteins, chlorophylls, flavones, colors, lignins, oils, waxes, resins and latices have been removed since these contribute undesirable odors and tastes to the smoking product.

Purified cellulose is unsatisfactory for use as a smoking product from the standpoint of taste, aroma and burning characteristics. This is believed to stem from the acids and aldehydes that are evolved upon pyrolysis of the cellulose. It has been found that the presence of noxious gases from the combustion of pure cellulose can be greatly alleviated by conversion of the methylol groups to carboxyl groups to produce a product which readily pyrolyzes with complete burning of the cellulosic molecule into water vapor, and oxidation products of carbon, such as carbon dioxide and low molecular weight compounds, which readily volatilize. Thus the object is to achieve selective oxidation of the cellulosic material to convert methylol groups, primarily the methylol groups containing the C<sub>6</sub> carbon, to carboxyl groups, preferably with better than 90% conversion. There is no objection to further oxidation beyond 100% by conversion of secondary hydroxyl groups as on C<sub>2</sub> and C<sub>3</sub> to mono- and diketo groups so long as cleavage does not occur.

Selective oxidation without degradation of the cellulosic material is difficult to achieve with oxidizing agents such as peroxides, hypochlorites, permanganates, dichromates and the like. On the other hand, such selective oxidation for use in preparation of a smoking product from such cellulosic materials can be achieved with nitrogen dioxide.

Liquid nitrogen dioxide provides an oxidation reaction that has the desired selectivity and complete wetting of the cellulosic materials can be achieved almost instantaneously with liquid nitrogen dioxide with the result that oxidation reaction takes place substantially uniformly throughout the cross-section of the cellulosic material and

at a high reaction rate. Liquid nitrogen dioxide, when used in the most suitable proportions, operates as a quench immediately to dissipate heat generated by the exothermic reaction so as to avoid the formation of hot spots or non-uniformities in the reaction.

In our copending application Ser. No. 745,135, filed concurrently herewith and entitled "A Smoking Product and Method of Preparation," description is made of the oxidation of a cellulosic material by suspension in liquid nitrogen dioxide in the ratio of 1 part by weight cellulosic material to 5 to 1000 parts by weight liquid nitrogen dioxide and preferably 1 part by weight cellulosic material to 25 to 50 parts by weight of liquid nitrogen dioxide. The reaction therein is carried out at a temperature within the range of 15° to 65° C. and at an autogenous pressure when the reaction temperature exceeds 21° C. (the boiling point of nitrogen dioxide  $N_2O_4$ ).

In our copending application filed concurrently herewith and entitled "Preparation of Smoking Product of Cellulose Derivatives and Process," description is made of the selective oxidation of cellulosic material wherein the oxidation reaction, including reaction rate and the amount of conversion, is materially improved by formulation of the oxidation reaction medium to contain up to 8% by weight of water in the liquid nitrogen dioxide system and by carrying out the reaction at elevated temperature above 15° C. and preferably within the range of 20° to 45° C., depending somewhat upon the amount of moisture present in the reaction medium, whereby the reaction medium is rendered relatively non-electrically conductive so that the presence of water in the reaction medium will not result in attack or degradation of the cellulosic material to be oxidized and wherein the formulation to include aqueous medium in the reaction of liquid nitrogen dioxide operates also to adjust the specific gravity of the reaction medium in the direction towards the specific gravity of the cellulosic material whereby suspension of the cellulosic material in the reaction medium is easier to achieve and maintain. The result is a more rapid and uniform oxidation reaction of the cellulosic material to produce a better product at a more rapid rate.

In our copending application Ser. No. 745,134, filed concurrently herewith and entitled "Cellulosic Smoking Product and Method in the Preparation of Same," description is made of the selective oxidation of cellulosic material with liquid nitrogen dioxide, with or without water, and in which a molecular oxygen containing gas is introduced into the reaction medium, during the reaction, for reconversion of the nitrous acid and nitric oxide that is formed and for entering into the oxidation reaction in the presence of liquid nitrogen dioxide.

It has been found that even after thoroughly washing with water, a small amount of nitrogen, ranging from traces to as much as 0.5% to 1.0% by weight remains, perhaps in the form of nitro groups or nitric acid. The presence of even such small amounts of nitro groups in the oxidized cellulosic material has been found to be effective to impart an undesirable burning protein odor to the product when burned in a cigarette, cigar or pipe and the nitric acid imparts an irritating taste to the smoking product. In addition to such objectionable residual nitrogen groups, the oxidized cellulosic material will contain traces to small amounts of quinones unsaturates and aldehyde groups, other than on the  $C_2$  and/or  $C_3$  positions of the cellulosic molecule. These may be embodied in the impurities such as the lignins, waxes, natural resins or other residual impurities present during the selective nitrogen dioxide oxidation. Such quinone, ketonic and unsaturated impurities also contribute an irritating odor and taste when the smoking product is being used.

As a result, considerable effort has been expended towards the removal of such nitrogen groups from the oxidized cellulosic material and for the removal of nitro groups, quinone, ketonic and unsaturated groups from

lignins, waxes, natural resins and other organic impurities contained therein.

The use of the sulphur family of reducing agents for such purposes as reducing the nitro groups to amino groups, the quinone groups to hydroquinones, and the ketone or aldehyde groups to corresponding reduction reaction products has been found to be unsatisfactory for the reason that sulphur containing materials remain as residuals in the treated material. Such sulphur containing materials, including sulfates, produce bad burning odors especially in the presence of incandescent carbon and it has been found practically impossible to effect removal of such sulphurous residuals. Thus the reduction with the sulphur family of compounds often leaves the smoking product in a state which is more undesirable than before treatment.

Reduction with reduced metallic salts, as represented by stannous chloride and the like, leaves metallic ions which are absorbed by the oxidized cellulosic material and which are also difficult to remove. Such residual metallic ions impart an undesirable odor to the smoking product with the result that reduction with such metallic salts replaces one objectionable characteristic with another which may be even less desirable.

It is an object of this invention to produce and to provide a method for producing a cellulosic material selectively oxidized with nitrogen dioxide wherein residual nitrogen groups and/or quinone, ketone, aldehyde and unsaturated groups are removed by a reduction reaction to improve the odor and taste characteristics of the smoking products; in which such removal can be effected without substitution with other more undesirable odor or taste forming substances; in which the removal is effected by a selective reduction reaction which does not result in solution or degradation or attack of the selectively oxidized cellulosic material.

It has been found, much to our surprise, that improvements are secured from the standpoint of the odorless character and the mildness of the smoke generated by smoking products produced from the oxidized cellulosic material when the latter, after nitrogen dioxide oxidation, is subjected to treatment with a borohydride, such as an alkali metal, alkaline earth metal or ammonium borohydride, or a hydride such as calcium hydride, lithium aluminium hydride, or nascent hydrogen, in the presence of acidic medium.

Thus it is an object of this invention to provide a method and means for treatment of cellulosic materials after selective oxidation reaction with a reaction medium containing nitrogen dioxide to effect reduction of nitrogen containing groups, such as nitric acid esters and/or nitro groups, and to effect reduction of quinone, ketone and aldehyde groups, especially when other than ketones at the  $C_2$ - $C_3$  carbon atoms of the cellulosic molecule or in impurities present with the oxidized cellulosic material, and it is a related object to provide a method of the type described which does not substitute other undesirable components in the smoking product or cause attack or degradation of the oxidized cellulosic material.

While the reduction reaction hereinafter described is addressed to cellulosic materials oxidized with liquid nitrogen dioxide, it will be understood that beneficial results will be obtained by the described treatment when applied to cellulosic materials oxidized with gaseous nitrogen dioxide.

In accordance with the practice of this invention, the cellulosic material which has previously been oxidized with nitrogen dioxide is reacted with a dilute solution of a borohydride under conditions which operate to effect a reduction reaction. It is believed that the nitro groups are reduced to amino groups which are more soluble and can be removed by washing or which are less objectionable in the smoking product from the standpoint of taste and odor since such amino groups impart a neutralization of acid vapors upon volatilization during burn-

ing. Quinone groups are reduced to the more soluble corresponding hydroquinones and aldehyde and/or acetone groups are also reduced to more acceptable hydroxyl groups.

As the borohydride, use can be made of alkali metal and ammonium borohydrides or alkaline earth metal borohydrides, but it is preferred to make use of an alkali metal borohydride, such as the borohydride of sodium, potassium or lithium. Beneficial results are secured from solutions containing the borohydride dissolved in aqueous medium in an amount within the range of 0.05% to 5% by weight and preferably within the range of 0.1% to 1% by weight and when used in the ratio of 1 part by weight of the oxidized cellulosic derivative to 10 to 1000 parts by weight of the treating solution and preferably 1 part by weight of the oxidized cellulosic derivative to 20 to 100 parts by weight of the solution. The time of exposure for reaction is not critical since beneficial results can be secured with a residence time of 1 minute or more but it is preferred to make use of a reaction time, under the conditions to be described of from 5 to 60 minutes and more preferably about 10 to 30 minutes.

Solution of the borohydride in aqueous medium usually results in the formation of an alkaline solution having a pH above 7. When use is made of a borohydride solution having an alkaline pH, oxidized cellulosic material tends to be taken into solution. Thus, the usual practice which makes use of an alkaline solution of borohydride for reduction cannot be employed in the practice of this invention.

We have found that the desired reduction reaction, with a minimum amount of degradation or dissolution, using a borohydride solution can be achieved when the pH of the solution is adjusted to a pH below 7 but not below 3 and preferably within the range of 5 to 6.5. At a pH below 3, the borohydride tends to decompose at an excessive rate. pH adjustment to the desired level can be achieved with an organic acid, such as oxalic acid, acetic acid, glucuronic acid, oxidized cellulosic or the like water-soluble organic acid, or by an inorganic acid such as hydrochloric acid, nitric acid and the like. It is preferred to make use of an organic acid, especially oxalic acid, because otherwise subsequent treatments would be required to remove undesirable ions, such as  $\text{Cl}^-$  or the like materials introduced with the acid. In the preferred practice, any oxalic acid which might remain as a residue need not be removed since beneficial use can be made thereof in subsequent treatments to produce oxalates for mineralizing and for providing the desired ashing characteristics in the cellulosic smoking product.

Under the conditions described, the reaction can be carried out at a temperature above  $0^\circ\text{C}$ . but below  $30^\circ\text{C}$ . and preferably within the range of  $0^\circ$  to  $25^\circ\text{C}$ . At temperatures below  $0^\circ\text{C}$ ., the dilute aqueous solution is subject to freezing and at temperatures above  $30^\circ\text{C}$ ., the oxidized cellulosic material tends to go into solution. At temperatures close to freezing, the partial mercerizing of the oxycellulose is beneficial as regards permeability.

It is believed that the mechanism for reduction comprises the release of nascent hydrogen from the borohydride, possibly through the formation of  $\text{BH}_4$  ions as an intermediate. This is somewhat verified by corresponding reduction reaction achieved with nascent hydrogen released in the intermediate vicinity of the oxidized cellulosic material from the negative pole of an electrolytic cell wherein the freshly generated hydrogen gas almost immediately comes into reactive relationship with the oxidized cellulosic material to provide a reduction of the described groupings therein similar to the reduction achieved with metal hydrides, with an obvious improvement in smoke odor.

Having described the basic concepts of the invention, illustration will now be made by way of examples, which

are given by way of illustration and not by way of limitation of the practice of this invention.

#### EXAMPLE 1

Cellulosic material that has been oxidized with liquid nitrogen dioxide as in the aforementioned copending applications, after washing, is introduced into a 0.2% water solution of sodium borohydride in which the pH has been adjusted to a pH of 7 with oxalic acid. The materials are combined in the ratio of 1 part by weight of the oxidized cellulosic material to 100 parts by weight of solution and the reaction is continued at room temperature with continuous stirring for 30 minutes.

After 30 minutes, the solution is drained off and the oxidized cellulosic material is washed with one or more increments of water, preferably free of heavy metal ions, and the product is then dried. Absorbed sodium is removed by acid washing, unless a subsequent mineralizing treatment is relied upon for this purpose.

The resulting product finds better use as a smoking product than the oxidized cellulosic material before reduction reaction without borohydride but it is preferred subsequently to process the material by compounding to introduce one or more agents such as mineralizing agents in the form of calcium oxalate and the like, smoke generating agents, neutralizing agents such as ammonia or amines, glow supporting and burning rate controlling agents such as potassium, cesium or rubidium salts, coloring agents and the like, all as described in the aforementioned parent applications.

Others of the alkali metal and ammonium hydrides can be substituted, in whole or in part, for the sodium borohydride of Example 1 in the amount within the range of 0.1 to 1.0% by weight.

#### EXAMPLE 2

The oxidized cellulosic derivative used in Example 1 is placed between vertically separated, horizontally disposed poles, in the form of metal gauze or metal screen with the negative pole spaced below the positive pole and preferably with a plastic screen insulating the oxidized cellulosic material from the positive pole. A suitable screen may be formed of porous polyethylene. The poles are immersed in an electrolyte formulated of oxalic acid dissolved in aqueous medium in an amount within the range of 0.1% to 4% by weight and specifically about 1% by weight, and a current density of 5 to 50 amps per  $\text{cm}^2$  of screen area is passed between the poles while the bath is maintained at about ambient temperature.

Hydrogen gas, which is released at the negative pole, bubbles up through the oxidized cellulosic material and the freshly formed nascent hydrogen gas is effective to cause some reduction of nitro, quinone, keto and aldehyde groups, and unsaturates as previously described.

After treatment for about 10 to 30 minutes, the cellulosic derivative is removed, washed with water and dried for use as a smoking product having improved characteristics by comparison with the oxidized cellulose before treatment, or for subsequent processing into a smoking product, as described in Example 1, and as more fully described in the aforementioned parent applications.

It will be understood that use can be made of electrolytes formed of other acids or salts, preferably acids or salts which do not introduce groupings into the oxidized cellulosic material which might require subsequent removal. Oxalic acid and the like organic acids are preferred since that which remains in the product finds utility in the subsequent processing to form oxalates and the like salts.

It will be apparent from the foregoing that we have provided a simple and efficient means for selective reduction of undesirable components remaining in the cellulosic material following oxidation with nitrogen dioxide to improve the taste and aroma characteristics of the formed smoking product.

It will be understood that changes may be made in the details of formulation and operation without departing from the spirit of the invention.

We claim:

1. In the method of producing a smoking product from cellulosic material wherein the cellulosic material is subjected to a selective oxidation reaction with nitrogen dioxide, the steps of subjecting the oxidized cellulosic material to a reduction reaction by admixture of the oxidized cellulosic material with 1 to 1000 times its weight of an aqueous solution of a soluble borohydride.

2. The method as claimed in claim 1 in which the aqueous solution of borohydride is adjusted to a pH between 3-7.

3. The method as claimed in claim 1 in which the borohydride is present in a concentration of 0.05% to 5% by weight of the solution.

4. The method as claimed in claim 1 in which the borohydride is present in a concentration of 0.1% to 1% by weight of the solution.

5. The method as claimed in claim 1 in which the materials are admixed in the ratio of 1 part by weight oxidized cellulosic material to 20 to 100 parts by weight of the borohydride solution.

6. The method as claimed in claim 1 in which the borohydride is selected from the group consisting of an alkali metal borohydride, an alkaline earth metal borohydride, an ammonium borohydride and mixtures thereof.

7. The method as claimed in claim 1 in which the reaction is carried out with the materials at a pH within the range of 5 to 6.5.

8. The method as claimed in claim 1 in which the re-

duction reaction is carried out at a temperature within the range of 0° to 30° C.

9. The method as claimed in claim 1 in which the reduction reaction is carried out at a temperature within the range of 10° to 25° C.

10. The method as claimed in claim 1 in which the borohydride is selected from the group consisting of an alkali metal borohydride, an alkaline earth metal borohydride and ammonium borohydride and mixtures thereof in which the borohydride is present in an amount within the range of 0.05% to 5% by weight of the solution and in which the reaction is carried out at a temperature within the range of 10° to 25° C. with the reducing solution at a pH within the range of 5 to 6.5.

11. A smoking product formed of cellulosic material oxidized with nitrogen dioxide and then reduced by the process as described in claim 1.

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