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3,478,752

CELLULOSIC SMOKING PRODUCT AND METHOD IN THE PREPARATION OF SAME

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No Drawing. Continuation-in-part of applications Ser. No.
595,622, Nov. 21, 1966, and Ser. No. 674,994, Oct. 12,
1967. This application July 16, 1968, Ser. No. 745,134
Int. Cl. A24b 15/04; A24d 1/00

U.S. Cl. 131—2

14 Claims

ABSTRACT OF THE DISCLOSURE

The preparation of a smoking product in the form of
a cellulosic derivative which includes the step of selec-
tively oxidizing a cellulosic material with liquid nitro-
gen dioxide, with or without water, and the introduction
of an oxygen containing gas for control of the oxidation
reaction and acceleration thereof.

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

As used herein, the term "smoking products" is meant
to refer to and to include filler material embodied in ciga-
rettes, cigars and for use with pipes and the like, and mix-
tures thereof with various proportions of tobacco and in-
cluding cigarette papers and wrappers used in the prepara-
tion of such cigars and cigarettes, and it includes ciga-
rettes, cigars and the like products manufactured with
such filler materials and wrapper.

In the aforementioned copending applications, descrip-
tion is made of the preparation of a smoking product
suitable for use in cigarettes, cigars or with pipes where-
in 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 oxy-
cellulose or polyuronic acid. The oxidation reaction prod-
uct is further processed by removal of liquid nitrogen
dioxide by vaporization preferably by washing the oxi-
dized 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 deriva-
tive 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 un-
desirable 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

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which impart undesirable aroma or taste to the product.

The resulting smoking product is then formulated with
mineralizing agents such as oxalates, glycolates, diglyco-
lates, lactates, pivalates or tannates of such metals as
calcium, magnesium, lithium, potassium, barium or stron-
tium, preferably introduced to form the salt internally in
the cellulosic derivative for purposes of providing desired
ashing characteristics. Instead of forming the described
salts internally in the cellulosic derivative, limited benefi-
cial characteristics can be achieved by external applica-
tion of such mineralizing agents. As described, the de-
sired internal introduction is achieved by first wetting
the cellulosic derivative with metal cation in dilute solu-
tion 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 pro-
cessed to improve the burning, glow and smoking char-
acteristics 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 prefer-
ably less than 1% by weight, as described in the copend-
ing application Ser. No. 623,528, filed Mar. 16, 1967,
and entitled "Smoking Products and Process for Their
Manufacture." Smoke generators for improving the ap-
pearance 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 char-
acteristics can be achieved by the addition of volatiliz-
able alkalyzing material such as ammonium oxalate, nico-
tine 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.

This application will be addressed to the process for
treatment of the cellulosic material with liquid nitrogen
dioxide for selective oxidation of methylol groups in
forming an oxidized cellulosic derivative which is more
suitable for use as a smoking product than the purified
cellulose and which finds excellent use in the preparation
of a smoking product.

The features of this invention reside in the conversion
of a cellulosic material to a product which is desirable
for use in smoking and which finds wide acceptance as
a smoking product from the standpoint of taste, aroma,
appearance, burning characteristics and relative absence
of harmful ingredients or undesirable reaction products.

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

It is preferred to make use of a purified cellulosic
material from which various of the sugars, proteins,
chlorophylls, flavors, colors, lignins, oils, waxes, resins
and latices have been removed since these contribute un-
desirable 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 many of the defects 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 breakup 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_6 carbon, to carboxyl groups, with better than 30% and preferably with better than 90% conversion. There is no objection to further oxidation beyond 100% by conversion of secondary hydroxyl groups as on C_2 and C_3 to mono- and diketone groups so long as cleavage does not occur.

Selective oxidation of cellulosic material 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.

Gaseous nitrogen dioxide has been found to be impractical for this purpose since the resulting oxidation reaction is too slow and difficulty is experienced in achieving complete access to the entire cross-section of the cellulose derivative with the result that it is difficult to achieve high conversion at a commercial rate and conversion is not uniform thereby resulting in an undesirable product for smoking. Further, the reaction of oxidation of the cellulosic material is an exothermic reaction that is accompanied by the generation of heat which is not easily dissipated with the use of gaseous nitrogen dioxide. As a result, hot spots can develop in various areas of the treated material to cause degradation and sometimes a combustion of the cellulosic material.

On the other hand, it has been found that liquid nitrogen dioxide yields an oxidation reaction that has the desired selectivity and that complete wetting of the cellulosic materials can be achieved almost instantaneously with liquid nitrogen dioxide with the result that the oxidation reaction takes place substantially uniformly throughout the cross-section of the cellulosic material and at a much more rapid rate whereby a more uniformly and more completely oxidized product is obtained in less time. Furthermore, liquid nitrogen dioxide, when used in the proportions most suitable for the practice of this invention, operates as a quench immediately to dissipate heat generated by the exothermic reaction so as to avoid the formation of hot spots or non-uniformity in the reactions.

It has been found that the course of the oxidation reaction and the treatment of the oxidized cellulosic material can be influenced by a number of very important factors which cannot be translated into reactions with gaseous nitrogen dioxide but which can be employed in the oxidation of the cellulosic material with liquid nitrogen dioxide thereby greatly to enhance the oxidation process including increase in reaction rate, increase in the amount of conversion, uniformity of oxidation, as well as purification and subsequent treatment of the oxidized reaction product, as will hereinafter appear.

In our copending application Ser. No. 745,221, 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 autog-

enous pressure when the reaction temperature exceeds 21° C. (the boiling point of nitrogen dioxide).

In our copending application Ser. No. 745,135, 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. Liquid nitrogen dioxide containing small amounts of moisture becomes non-electrically conductive at elevated temperature so that the presence of water in the reaction medium will not result in attack or degradation of the cellulosic material to be oxidized. 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.

The concepts of this invention are addressed to the further discovery that when oxygen, or a molecular oxygen, or a molecular oxygen containing gas, such as air or oxygen enriched air, is bubbled through, or otherwise introduced into the reaction medium formulated of liquid nitrogen dioxide, with or without water, during the selective oxidation of the cellulosic material, and oxidized cellulosic material more desirable for use as a smoking product is obtained and the rate of oxidation of the cellulosic material is noticeably increased.

There is reason to believe that the oxygen containing gas is capable of entering into the oxidation reaction of the cellulosic material in the presence of liquid nitrogen dioxide to enhance the desired selective oxidation. There is also reason to believe that the oxygen is effective to convert nitrous acid that is formed to nitric acid in situ in the reaction and to reconvert nitric oxide that is formed to nitrogen dioxide, with corresponding reduction in undesirable by-product formation. One or more of the above reactions can take place markedly to improve the reaction rate and product.

In addition to the direct effect obtained from the presence of oxygen gas in the oxidizing medium, it has been found that considerable benefits are derived indirectly from the introduction of the oxygen containing gas in that introduction, in the form of fine bubbles, operates to provide agitation of the mixture and uniform suspension of the cellulosic material in the liquid reaction medium thereby more uniformly to expose the cellulosic materials to the oxidation reaction. This not only provides for exposure of greater surface area of cellulosic material to the reaction medium but it also provides for the maintenance of uniform reaction conditions throughout the mass to provide a more uniformly oxidized cellulosic product which is better suited for use or processing as a smoking product.

The amount of oxygen introduced or the feed flow rate is not critical since only a small amount of nitric oxide is produced at a fairly slow rate. Thus, it will be sufficient if the oxygen, in the form of pure oxygen or air, is introduced in the weight ratio of 1 part by weight oxygen or 5 parts by weight air per 5 parts by weight of cellulosic material and it is preferred to introduce an amount of oxygen or air up to ten times the minimum or up to 10 parts by weight of oxygen or 50 parts by weight of air per 5 parts by weight cellulosic material, over the total time of the reaction.

Introduction of the oxygen containing gas can be made

through an inlet in the bottom portion of the reaction vessel with distributors for dispersing the gas throughout the cross-section of the reaction medium whereby the gas rises in fine bubbles through the reaction medium and the cellulosic material contained therein.

Having described the basic concepts of this invention, examples will now be given by way of illustration, but not by way of limitation, of the practice of this invention.

EXAMPLE 1

A highly purified commercial grade of wood pulp, formed into thin paper, is shredded into strands of about 2 mm. width and immersed in approximately one hundred times its weight of liquid nitrogen dioxide. Reaction is carried out for six to eight days while maintaining the temperature of the reaction medium at about 20° C. and with the introduction of air through an inlet in the bottom of the reaction vessel covered with a screen of porous polyethylene for distribution of the air throughout the cross-section of the reactor and through which the air rises as fine bubbles. Air is introduced in an amount to provide 10 parts of weight of air per part by weight of cellulosic material until the reaction is completed (better than 90% conversion of methylol groups).

The liquid reactant is then drained from the reaction vessel and the oxidized cellulosic derivative is washed with aqueous medium for removal of solubles and nitrogen dioxide from the oxidized product.

EXAMPLE 2

A highly purified wood pulp, fabricated into a thin paper, is shredded into strands of about 2 mm. width and loaded into a pressure vessel with liquid nitrogen dioxide containing 2% by weight water and in which the liquid reaction medium is introduced in the ratio of 1 part by weight of pulp to 25 parts by weight of the liquid oxidizing medium. The reaction medium is heated to a temperature within the range of 40° to 45° C., and the reaction is carried out at its autogeneous pressure of about 50 p.s.i.

Throughout the reaction, one-fifth of the reaction medium is bled from the system and replaced with anhydrous nitrogen dioxide to compensate for the amount of water which is released during the oxidation reaction so as to maintain the water content in the reaction medium at about 2% by weight.

During the reaction cycle, which takes about 20 hours, oxygen is bubbled through the reaction mass to a total amount corresponding to about 1 part by weight of oxygen to 5 parts by weight of the cellulosic material. After 24 hours of reaction, the oxygen is shut off and the liquid reaction medium is drained from the reactor and the oxidized cellulose is first rinsed with anhydrous liquid nitrogen dioxide and then dried and then rinsed with water to remove solubles and residual nitrogen acids.

It will be found that the cellulosic material is oxidized by an amount greater than 90%, when calculated on the basis of conversion of the C₆ methylol group.

EXAMPLE 3

Alpha-cellulose is suspended in a pressure vessel with one hundred times its weight of liquid nitrogen dioxide containing 1.5% by weight of water. The reaction medium within the vessel is maintained at 20° C.

Through a distributor at the bottom of the vessel, air in an amount totalling at least 1 part by weight of air per part by weight of cellulosic material is introduced into the reaction vessel by bubbling through the reaction medium and the cellulose. The reaction is continued for three to five days. Unreacted air and nitrogen is allowed to escape through a chilled condenser to return nitrogen dioxide vapors to the vessel. At the completion of the reaction, the air is shut off and the liquid reaction medium is drained from the reaction vessel leaving the solids in the form of an oxidized cellulosic material which is first

washed with anhydrous nitrogen dioxide and then dried and then washed with water to remove solubles and residuals in the form of nitrogen acids.

The product resulting from Examples 1 to 3 will be found to have improved smoking characteristics from the standpoint of taste and aroma, as compared to the cellulosic material prior to the described selective oxidation treatment. However, it is preferred further to process the oxidized cellulosic derivatives of Examples 1 to 3, as described in the aforementioned copending applications, to effect one or more additional processing steps such as reduction in the presence of a dilute solution of borohydride for reduction of residual nitro groups to amino groups and/or for reduction of residual quinone, ketones, aldehydes or unsaturates to corresponding hydroquinone, hydroxyl or saturated groups and to introduce one or more agents such as a mineralizing agent, represented by calcium oxalate, smoke generating agents, neutralizing agents such as ammonium or amine salt, glow or burning agents such as salts of potassium, cesium or rubidium, coloring agents and the like, as described in the aforementioned copending applications.

It will be apparent from the foregoing that a process for selective oxidation of cellulosic materials with liquid nitrogen dioxide is provided wherein the oxidation reaction is carried out more uniformly and at a higher rate to produce a more desirable oxidation reaction product of the cellulose derivative at less expense.

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 process for preparation of a smoking product from cellulosic materials, the steps of reacting the cellulosic material with a liquid oxidizing medium formed of liquid nitrogen dioxide selectively to oxidize the cellulosic material, and introducing an oxygen containing gas for passage through the liquid oxidizing medium during the oxidation reaction.

2. The process as claimed in claim 1 in which the liquid oxidizing medium is present in the ratio of 5 to 1000 parts by weight of the liquid oxidizing medium per 1 part by weight of the cellulosic material.

3. The process as claimed in claim 1 in which the liquid oxidizing medium is present in the ratio of 25 to 50 parts by weight of the liquid oxidizing medium per 1 part by weight of the cellulosic material.

4. The process as claimed in claim 1 in which the oxidation reaction is carried out with the materials at a temperature within the range of 15° to 65° C.

5. The process as claimed in claim 1 in which the oxidation reaction is carried out with the materials at a temperature within the range of 25° to 45° C.

6. The process as claimed in claim 1 which includes the step of separating the oxidized cellulosic derivative from the liquid oxidizing medium, and drying the oxidized cellulosic derivative at elevated temperature to volatilize off volatilizable nitrogen oxides.

7. The process as claimed in claim 1 in which the oxidizing medium contains water in an amount up to 8% by weight.

8. The process as claimed in claim 1 in which the oxidizing medium contains water in an amount within the range of 0.5% to 5% by weight.

9. The process as claimed in claim 1 in which the oxidizing medium contains water in an amount within the range of 1.5% to 3% by weight.

10. The process as claimed in claim 1 in which the oxygen containing gas is introduced in an amount of at least 1 part by weight of oxygen per 5 parts by weight of cellulosic material.

11. The process as claimed in claim 1 in which the oxygen containing gas is introduced in an amount of up to 50 parts by weight of oxygen per 1 part by weight of cellulosic material.

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12. The process as claimed in claim 1 in which the oxygen containing gas is air.

13. The process as claimed in claim 12 in which the air is introduced into the liquid oxidizing medium in an amount within the ratio of 5 to 50 parts by weight of air per 1 part by weight of cellulosic material.

14. An oxidized cellulosic derivative for use in the preparation of a smoking product prepared by the process of claim 1.

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U.S. Cl. X.R.

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