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[54] **METHOD FOR PRODUCING SMOKING PRODUCT OF OXIDIZED CELLULOSIC MATERIAL**
13 Claims, 2 Drawing Figs.

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[50] **Field of Search** ..... 260/212; 8/116, 120; 131/2, 17, 15, 140—144

[56] **References Cited**
UNITED STATES PATENTS

2,448,892	9/1948	Kenyon et al.	8/116
2,537,979	1/1951	Eberl	(8/116UX)
3,461,879	8/1969	Kirkland	131/2

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ABSTRACT: The method for rapidly and uniformly effecting selective oxidation of cellulosic materials used in the preparation of a smokable product embodying the sequence of steps of soaking the cellulosic material with liquid nitrogen dioxide and then exposing the cellulosic material to hot gaseous nitrogen dioxide for oxidation reaction and wherein the liquid nitrogen dioxide may contain up to 8 percent by weight water.

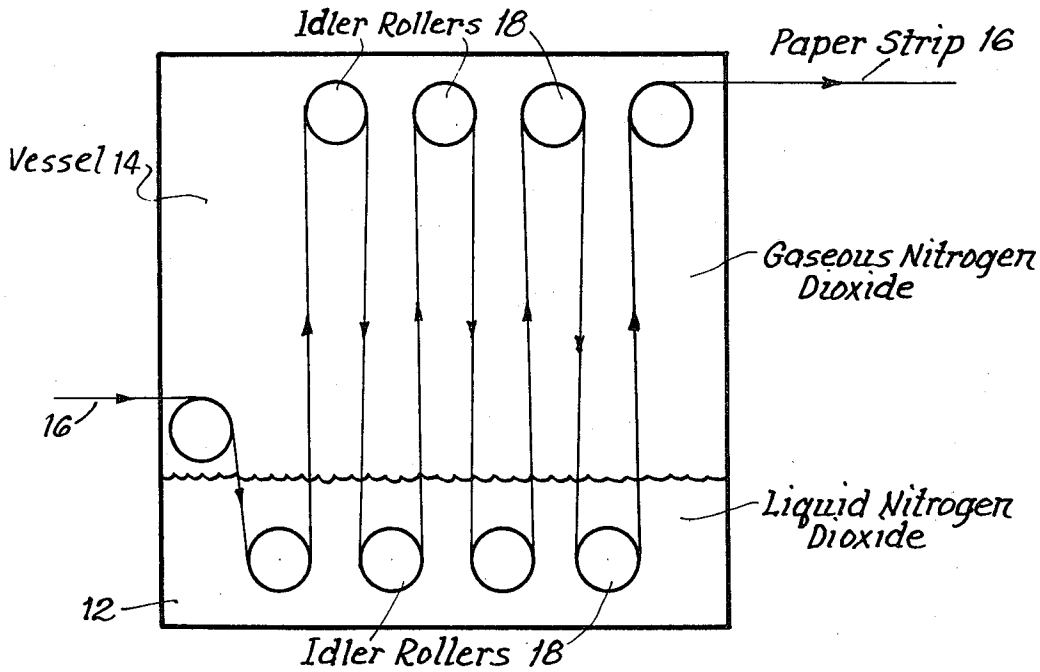


FIG. 1

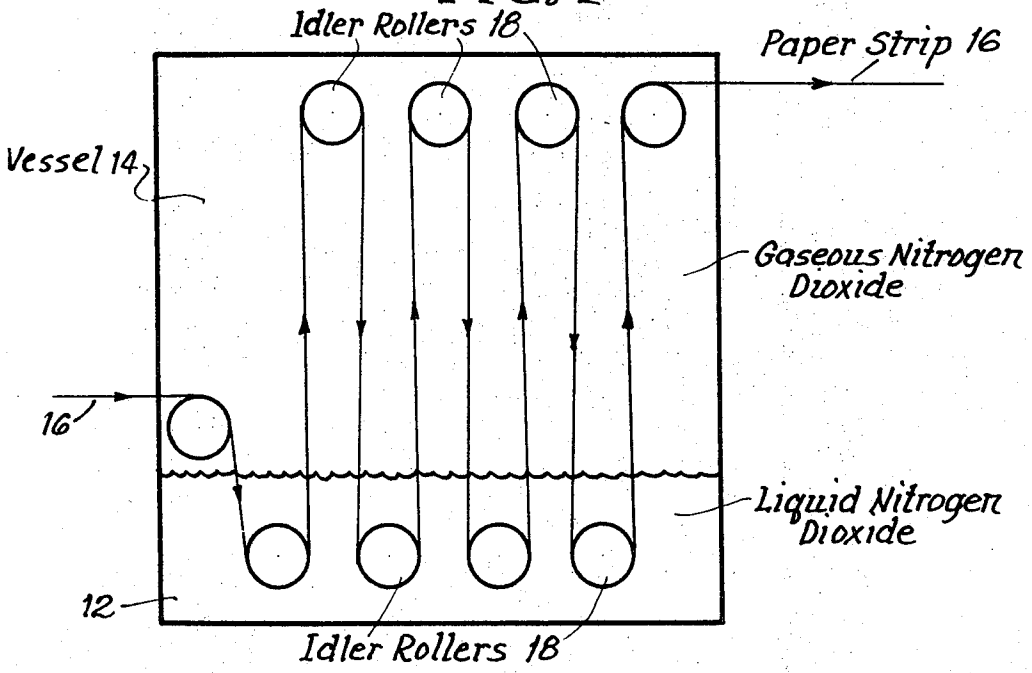
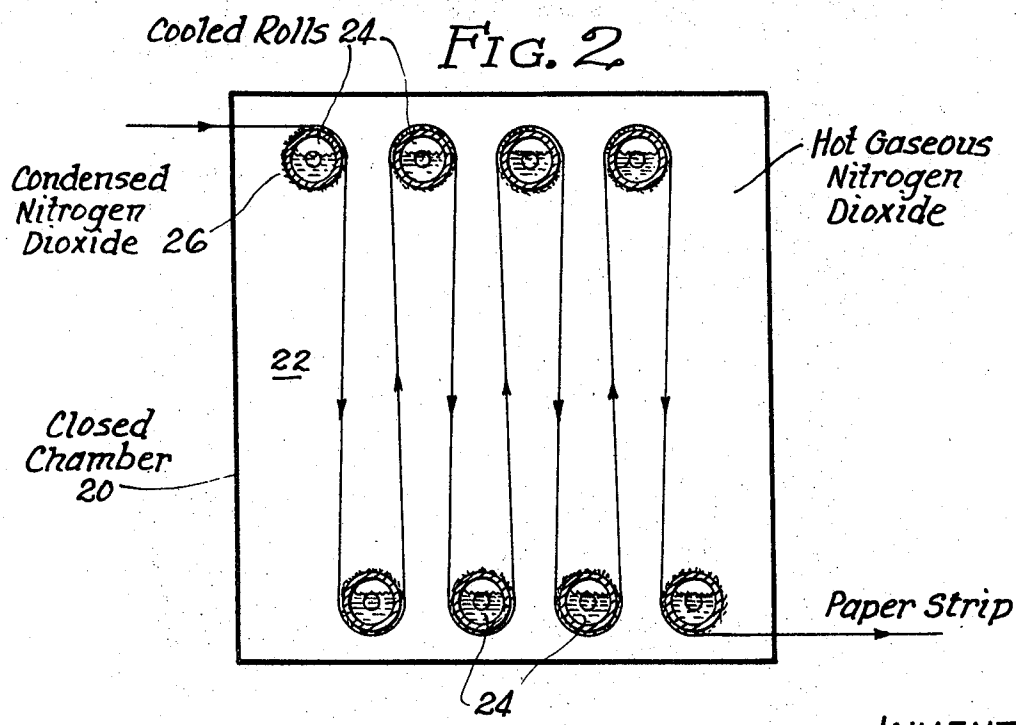


FIG. 2



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METHOD FOR PRODUCING SMOKING PRODUCT OF OXIDIZED CELLULOSIC MATERIAL

This invention relates to a smokable product produced of oxidized cellulosic materials and to a smoking product produced thereof.

As used herein, the term "smoking product" is meant to include filler material for use in cigarettes, cigars, pipe tobacco and the like, cigarette papers and wrappers used in the preparation of cigarettes, cigars and the like.

Purified cellulosic materials have been found to be unsatisfactory for use as a smokable product because of the irritating acids and aldehydes which are evolved during pyrolysis.

It has been found that such defects can be substantially eliminated by oxidation of the methylol groups of the cellulose molecule to carboxyl groups, preferably by conversion of at least 90 percent. To preserve the strength of the product, it is desirable to preserve the polymeric structure of the cellulose by selective oxidation of the methylol groups and by avoiding hydrolysis of the cellulose.

In the copending applications Ser. No. **595,622**, filed Nov. 21, 1966, and entitled "Smoking Product," now U.S. Pat. No. 3,447,539, and Ser. No. 674,994, filed Oct. 12, 1967, and entitled "Smoking Product and Process for Making Such Products," description is made of the preparation of a smokable product suitable for use in cigarettes, cigars, pipes and the like wherein the smokable product is prepared of relatively pure cellulosic materials subjected to selective oxidation with liquid nitrogen dioxide to convert preferably more than 90 percent of the methylol groups in the cellulosic molecule to yield a product which can be referred to as oxycellulose. The oxidation reaction product is further processed by removal of nitrogen oxides by vaporization and washing and by extraction with one or more organic solvents to remove undesirable impurities, such as oils, waxes, latexes and aromatics which have been released as a consequence of treatment with nitrogen dioxide.

As further described in the aforementioned copending applications, the oxidized and cleansed oxycellulose is further processed by a reduction reaction with a boro hydride or an alkali or alkaline earth metal, such as sodium borohydride, for reduction of nitro groups, quinones, ketones and aldehydes which otherwise might have a tendency to impart undesirable aroma and taste to the smoking product, when burned, or to reduce the stability thereof during storage.

The product, before or after reduction, can be subjected to additional oxidation with a dilute solution of peroxide further to eliminate groupings that contribute undesirable aroma or taste to the product. The need for such additional treatments naturally varies with the initial purity of the oxycellulose.

The refined oxycellulose is then formulated with mineralizing agents, such as oxalates, glycolates, diglycolates, lactates, pivalates or tannates of the alkaline earth metals, preferably in a manner to form such salts internally of the oxycellulose fibrils. As described, internal formation can be achieved by first forming the alkaline earth metal salt of the oxycellulose and then treating with a solution of the anion to precipitate the mineralizing salt in situ in the cellulosic material.

The treated oxycellulose can be further formulated to improve burning, glow and smoking characteristics by the use of potassium, rubidium or cesium salts, such as the oxalates thereof, 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 from the smoking product can be introduced by way of fatty acids and the like and suitable aroma can be achieved by the addition of volatilizable alkalyzing materials, such as ammonium oxalate, urea and the like.

In the aforementioned copending applications, processes are described in which use is made of liquid nitrogen dioxide to achieve the selective oxidation.

An important improvement sought to be secured with nitrogen dioxide oxidation of cellulose is to conduct the process in a continuous operation rather than in a batch process. This involves feeding the cellulosic material at one end and removing it at another. Since the reaction with liquid nitrogen dioxide is very slow, often requiring 5 to 8 days to achieve the desired level of conversion, and since large tonnages of material are required per day, the reactor would be of tremendous dimension and somewhat impractical from the standpoint of corrosive and explosive hazards that are involved.

In the aforementioned copending applications, it has been shown that a substantial improvement in the rate of oxidation can be achieved with liquid nitrogen dioxide under increased pressure and temperature and in the presence of some water.

It is an object of this invention to provide a new and improved method and means for carrying out the selective oxidation of cellulose with nitrogen dioxide in a more continuous high speed operation and to fabricate an improved smoking product thereof.

In the drawing,

FIG. **1** is a schematic elevational view of one system for treatment of paper strip, and

FIG. **2** shows a modified strip treating system.

The concept of this invention resides in the treatment of the cellulosic material to effect oxidation with gaseous nitrogen dioxide in a manner to achieve reaction speeds equivalent or superior to high temperature reaction in liquid nitrogen dioxide under pressure, but without the hazards of explosion.

As used herein, the term "cellulosic material" is meant to include various cellulose containing materials, such as alpha-cellulose, beta-cellulose, hydrocellulose, cotton, flax, hemp, wood, bamboo, rice straw, wheat straw, corncobs, cornsilk, ramie, bast, seaweed in various forms such as leaves, pulp, fibers and filaments from which the cellulosic material is separated, paper, shreds of paper and the like, all of which are relatively free of noncarbohydrate components. It is preferred to make use of purified cellulosic material from which salts, sugars, proteins, chlorophylls, xanthanes, flavones, lignins, oils, waxes, resins and latexes have been removed, since these are deleterious to the taste and odor of the smoking product.

One of the difficulties in the use of gaseous nitrogen dioxide for selective oxidation of cellulose is the rapid release of heat of absorption and the heat generated by the exothermic oxidation reaction when the cellulosic material is first exposed to gaseous nitrogen dioxide. Such localized heat effects can initiate conflagration of the material as well as generation of high pressures.

It has also been found that the oxidation reaction of cellulose by gaseous nitrogen dioxide starts off very rapidly and then, after a moderate level of conversion, the reaction rate falls off sharply, even when carried out at elevated temperature and/or pressure. For example, exposure of a purified grade of paper to gaseous nitrogen dioxide at 70 C. yields 4 percent oxidation almost immediately, 11 percent oxidation after 5 minutes, 16 percent oxidation after 10 minutes, 22 percent oxidation after 15 minutes, 27 percent oxidation after 30 minutes, and only 28 percent oxidation after 90 minutes. Thus a maximum of 30 percent oxidation is capable of being achieved with gaseous nitrogen dioxide at elevated temperatures and thereafter the oxidation reaction is relatively negligible.

The level of oxidation is not improved by any appreciable extent with the use of moist gaseous nitrogen dioxide as compared to dry gaseous nitrogen dioxide or with the use of cellulosic material having a certain amount of moisture as compared to dry cellulosic material.

The level of oxidation is improved somewhat by the presence of moisture in the paper or other cellulosic material. For example, in comparison with paper dried to 0 percent moisture content with one having 7 percent moisture, an asymptotic level of 19 percent oxidation was achieved with the dried paper after 30 minutes of exposure to gaseous

nitrogen dioxide as compared to an asymptotic level of 27 percent oxidation before the reaction became negligible.

Termination of the oxidation reaction at such relatively low levels stems from the exposure for reaction of the outermost portions of the cellulosic material and the relative inability of the oxidation to proceed in the innermost regions beyond the reacted phase, perhaps because of the inability of the gaseous nitrogen dioxide to gain access to such regions or because of other interfering factors arising in the oxidized cellulosic product. This condition seems to be aggravated by the shrinkage of the cellulosic fibers due to the heat generated during the initial reaction.

It has been found in accordance with an important concept of this invention that the level of selective oxidation of cellulosic materials with gaseous nitrogen dioxide can be markedly increased by wetting the cellulosic material with liquid nitrogen dioxide prior to exposure to gaseous nitrogen dioxide. While it is preferred to effect the exposure of the cellulosic material to gaseous nitrogen dioxide while the cellulosic material is still wet with liquid nitrogen dioxide, the marked improvement in level and uniformity of oxidation is achieved if a drying out period exists between the liquid treating step and the oxidation reaction with gaseous nitrogen dioxide. This can be illustrated by the following example:

EXAMPLE 1

Purified cellulose paper, in strip form, was dipped in liquid nitrogen dioxide at ambient temperature and atmospheric pressure and allowed to dry until it had a dry appearance. Thereafter, the paper was exposed to gaseous nitrogen dioxide at 70° C. at atmospheric pressure. A rapid reaction, similar to that obtained with liquid nitrogen dioxide under pressure and at 70° C. was obtained. A level of oxidation of about 25 percent was obtained in about 10 minutes before the rate of oxidation leveled off.

Repetition of the cycle of dipping in the liquid nitrogen dioxide, drying and exposure to gaseous nitrogen dioxide for 10 more minutes raised the level of oxidation to a conversion of 42 percent. A third cycle resulted in conversion of 55 percent, etc.

As a further concept of this invention, it was found that the presence of moisture in the liquid nitrogen dioxide with which the cellulosic material is wet greatly accelerated the oxidation rate as well as the level of oxidation achieved by the combination of steps of first wetting the cellulosic material with liquid nitrogen dioxide and then exposing the cellulosic material to hot gaseous nitrogen dioxide, as illustrated by the following examples:

EXAMPLE 2

Purified cellulosic paper was first dipped to wet the fibers in liquid nitrogen dioxide containing 1 percent by weight of water and then the cellulosic material wet with the liquid nitrogen dioxide was exposed to gaseous nitrogen dioxide at 100° C. After 7 minutes of exposure, an oxidation level of 44 percent conversion of the methylol groups was achieved. This is to be compared to only 11 percent conversion when treatment is carried out with the same materials and under the same conditions with dry liquid nitrogen dioxide.

EXAMPLE 3

Cigarette wrapping paper containing calcium carbonate as filler was treated with gaseous nitrogen dioxide at 70° C. without first wetting the paper with liquid nitrogen dioxide and also after first wetting the paper with liquid nitrogen dioxide. Conversions were measured by first fixing the calcium carbonate with oxalic acid to form the corresponding calcium oxalate, titrating the oxycellulose with sodium hydroxide solution and calculating the percent conversion after allowing for the calcium oxalate content, as calculated from an ash determination. The results secured were as follows: after 15 minutes exposure, the percent conversion without dipping was 11 percent whereas the percent conversion with the prior wetting of the paper with liquid nitrogen dioxide was 20 percent; after 30 minutes, the percent conversion without liquid nitrogen dioxide was 16 percent as compared 37 percent with the prior dipping in liquid nitrogen dioxide; after a second dip of the latter and a total of 90 minutes exposure to gaseous nitrogen dioxide, the percent conversion increased to 65 percent.

It will be apparent from the foregoing that, by means of a predip of the cellulosic material in liquid nitrogen dioxide followed by oxidation in hot gaseous nitrogen dioxide, and by appropriate spaced repetition of the cycle, selective oxidation of the cellulosic material can be achieved in the desired amounts and to the desired levels at relatively high speed. The repeated cycling of the cellulosic material through a station for wetting with liquid nitrogen dioxide and then through a station for reaction with the hot gaseous nitrogen dioxide is capable of arrangement for a continuous operation and/or for use with substantially endless strips of paper or other cellulosic material which can be cycled any number of times through the same stations or separately aligned stations to provide a continuous operation for selective oxidation of the cellulosic material until the desired level of conversion is achieved.

Treatment with liquid nitrogen dioxide can be carried out with the liquid nitrogen dioxide at a temperature within the range of −1° to 21° C. at normal pressure and at higher temperatures commensurate with the boiling point temperature of liquid nitrogen dioxide at such pressure. In a continuous cycle of operation, it is preferred to work at about normal pressure and at a temperature of about 15° C. to minimize the escape of fumes into the atmosphere.

Treatment in the gaseous phase can be carried out at a temperature within the range of 30° to 120° C. and preferably at a temperature within the range of 70° to 100° C.

For prewetting the cellulosic material, use can be made of liquid nitrogen dioxide having up to about 4 percent by weight water although the amount of water can be raised to 8 percent when the cellulosic material is in the form of cotton. It is preferred to make use of liquid nitrogen dioxide having a water content within the range of 0.5 percent to 1.5 percent by weight of water.

The pressure can be varied over a fairly wide range within the confines of the pressure-temperature curve for nitrogen dioxide. It is preferred, however, to operate at a pressure at or slightly below atmospheric pressure so that leakage will be inward instead of outward from the reaction chamber. Oxygen or an oxygen containing gas can be introduced for admixture with the gaseous nitrogen dioxide for purposes of regenerating nitrogen dioxide from the nitric oxide formed of the consumed nitrogen dioxide, thereby to maintain the level of nitrogen dioxide concentration in the reaction gases.

It has been found that when the cellulosic material is prewet with liquid nitrogen dioxide prior to exposure to hot gaseous nitrogen dioxide, the amount of heat generated by absorption of gaseous nitrogen dioxide is insignificant thereby to avoid the risk of burning or the formation of undesirable hot spots.

By reason of the prewet with liquid nitrogen dioxide, the reaction selectively to oxidize the methylol groups with gaseous nitrogen dioxide takes place uniformly throughout the cross section of the cellulosic materials instead of limiting the reaction to the surface. As a result, a higher conversion and a more uniformly oxidized cellulosic oxidized product is achieved whereby an improved product is secured by the practice of this invention.

In a typical system for continuous operation, use can be made of a glass lined vessel **10** partially filled with liquid nitrogen dioxide **12** with an open space above the liquid level which becomes filled with gaseous nitrogen dioxide **14** at elevated temperature. Substantially continuous strips of paper **16** can be trained about resistant rollers **18** for continuous travel of the strip of paper in a sinuous path between the liquid portion at the bottom and the gaseous portion thereabove to provide a number of cycles of first wetting with liquid nitrogen

dioxide and then exposure to gaseous nitrogen dioxide until the desired level of conversion has been achieved. The entrance and exit ducts for the paper strip can be provided in the form of Teflon lined slits.

It will be understood that the strip of paper introduced in a system of the type described might, for practical purposes, first pass through the gaseous phase into the liquid phase to effect the prewet. Under such circumstances, it is desirable to have the paper pass through the gaseous phase as quickly as possible whereby the liquid phase can operate as a quench for temperature control.

By way of modification, the strip of paper can be drawn through an elongate tubular member through which hot gaseous nitrogen dioxide is circulated with occasional spraying of the strip with liquid nitrogen dioxide at predetermined spaced intervals.

Another technique for exposure to gaseous nitrogen dioxide with intermittent wetting with liquid nitrogen dioxide embodies the displacement of a strip of paper through a chamber **20** filled with hot gaseous nitrogen dioxide **22** with rollers **24** for turning the direction of movement of the strip being cooled to a temperature to condense gaseous nitrogen dioxide **26** on the surfaces thereof to wet the strip as it passes over the rolls.

The above illustrate rapid and selective oxidation of cellulosic material in a continuous operation. It will be understood that the described treatment can be carried out on a batch principle with pulp, paper and the like.

Following oxidation, the treatments and modifications enumerated in the introduction and more fully described in the aforementioned copending applications may be used for cleaning, reduction and supplemental oxidation of the oxidized cellulosic material and for modifying the oxidized product by the addition of mineralizing agents, neutralizing agents, agents for controlling the burning rate, smoke generating agents and the like.

It will be apparent from the foregoing that we have provided a means for the efficient and uniform selective oxidation of cellulosic material wherein the oxidation reaction can be carried out in a continuous fashion to produce a product capable of use as a smokable material in the manufacture of cigars, cigarettes, and wrappers therefor.

It will be understood that changes may be made in the details of construction, arrangement and operation, without departing from the spirit of the invention, especially as defined in the following claims.

We claim:

1. In the method of rapidly and uniformly selectively oxidizing cellulosic material for use in the preparation of a smokable product, the sequence of steps of soaking a relatively pure cellulosic material with liquid nitrogen dioxide the said liquid nitrogen dioxide containing water in an amount of up to about 8 percent by weight and sufficient to improve the level of oxidation, and then reacting the cellulosic material which has been wet with liquid nitrogen dioxide with gaseous nitrogen dioxide.

2. The method as claimed in claim **1** in which the gaseous nitrogen dioxide reaction is carried out at elevated temperature.

3. The method as claimed in claim **2** in which the reaction is carried out at a temperature within the range of 30° to 220° C.

4. The method as claimed in claim **1** in which the reaction with gaseous nitrogen dioxide is carried out at a pressure of about atmospheric pressure to slightly less than atmospheric pressure.

5. The method as claimed in claim **1** in which the liquid nitrogen dioxide with which the cellulosic material is wet contains water in an amount up to 4 percent by weight.

6. The method as claimed in claim **1** in which the liquid nitrogen dioxide with which the cellulosic material is wet contains water in an amount within the range of 0.5 percent to 1.5 percent by weight.

7. The method as claimed in claim **1** in which the liquid nitrogen dioxide is at a temperature within the range of −1° to 21° C.

8. In the method of rapidly and uniformly selectively oxidizing cellulosic material for use in the preparation of a smokable product, the sequence of steps of wetting relatively pure cellulosic material with nitrogen dioxide, drying the cellulosic material after so wetting it and then wetting it and then reacting the cellulosic material which has been wet with liquid nitrogen dioxide with gaseous nitrogen dioxide.

9. The method as claimed in claim **8** which comprises repeating the cycle a number of times until the desired level of conversion of methylol groups has been achieved.

10. The method as claimed in claim **9** in which the cycle is repeated until more than 90 percent of the methylol groups have been converted by oxidation.

11. In the method of rapidly and uniformly selectively oxidizing cellulosic material for use in the preparation of smokable product, the sequence of steps of wetting relatively cellulosic material with nitrogen dioxide, and then reacting the cellulosic material which has been wet with liquid nitrogen dioxide with gaseous nitrogen dioxide, the said reaction being carried out in a vessel partially filled with nitrogen dioxide whereby liquid nitrogen dioxide is in the bottom portion of the vessel and the space above the liquid nitrogen dioxide is filled with gaseous nitrogen dioxide and in which a strip of cellulosic material is continuously advanced for alternate immersion in the liquid and exposure to the vapor.

12. In the method of rapidly and uniformly selectively oxidizing cellulosic material for use in the preparation of a smokable product, the sequence of steps of wetting relatively pure cellulosic material with nitrogen dioxide, and then reacting the cellulosic material which has been wet with liquid nitrogen dioxide with gaseous nitrogen dioxide with gaseous nitrogen dioxide, the said reaction being carried out in an elongate tubular member having a number of spray positions, through which a strip of cellulosic material is pulled, passing gaseous nitrogen dioxide through the tubular member, and intermittently spraying the strip with nitrogen dioxide.

13. In the method of rapidly and uniformly selectively oxidizing cellulosic material for use in the preparation of a smokable product, the sequence of steps of wetting relatively pure cellulosic material with nitrogen dioxide, and then reacting the cellulosic material which has been wet with liquid nitrogen dioxide with gaseous nitrogen dioxide, the said reaction is carried out by passing a strip of cellulosic material in a sinuous path about roller's within a chamber saturated with hot gaseous nitrogen dioxide, refrigerating at least some of the rollers to condense gaseous nitrogen dioxide on the periphery thereof to wet strip as it is passed thereabout.