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[54] CIGARETTE PAPER AND METHOD FOR PREPARATION

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[63] Continuation-in-part of Ser. No. 745,372, July 17, 1968, abandoned, which is a continuation-in-part of Ser. No. 595,622, Nov. 21, 1966, Pat. No. 3,447,539, and a continuation-in-part of 674,994, Oct. 12, 1967, abandoned.

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[58] **Field of Search**.....162/139, 157 C, 179; 131/2, 131/15; 260/212

[56] **References Cited**

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[57] **ABSTRACT**

Cigarette paper having improved taste and aroma during pyrolysis wherein the paper is loaded with an agent comprising up to 45 percent by weight calcium oxalate preferably formed in situ internally in the paper fibers and/or conversion of the cellulosic fibers by selective oxidation to convert preferably 40 to 60 percent of the methylol groups on the C_6 position to carboxylic acid groups and further treatments.

24 Claims, No Drawings

CIGARETTE PAPER AND METHOD FOR PREPARATION

This is a continuation-in-part of our copending application, Ser. No. 745,372, filed July 17, 1968 and titled "Cigarette Paper and Method for Preparation," now abandoned which in turn is a continuation-in-part of the copending application, Ser. No. 595,622, filed Nov. 21, 1966, and titled "Smoking Products," now Pat. No. 3,447,539 and Ser. No. 674,994, filed Oct. 12, 1967, and titled "Smoking Products and Process for Making Such Products" now abandoned.

In the aforementioned copending applications, description is made of the preparation of a smoking product suitable for cigarettes, cigars, or pipes, in which relatively pure cellulosic material is subjected to selective oxidation with liquid nitrogen dioxide to convert more than 90 percent of the free hydroxyl groups on the cellulosic molecule to carboxyl groups to yield a product which can be referred to as an oxycellulose. The oxidation reaction product is further processed by removal of the liquid nitrogen dioxide by vaporization and washing of the oxidized product with water and/or alcohol for removal of solubilized foreign materials and/or treatment with solvents, such as acetone for removal of oils, waxes, lattices and the like which contribute undesirably to the taste and odor when the product is used as a smoking product.

As further described in the aforementioned copending applications, the oxidized and cleansed cellulosic derivative is further processed by a reduction reaction with a hydride or borohydride of an alkali or alkaline earth metal, such as sodium, or lithium borohydride, for reducing groupings which otherwise have a tendency to evoke unpleasant odors or taste as the product is pyrolized. The product before or after being processed by the described reduction reaction can be subjected to oxidation with peroxide solutions as a means for eliminating further components which contribute undesirable aroma or taste to the product during pyrolysis.

The resulting oxidized and reduced cellulosic material is then formulated with mineralizing agents to the form of oxalates lactates, pivalates or tannates of such metals as calcium, magnesium, lithium, potassium, barium or strontium, preferably introduced internally, preferably within the cellulosic derivative for purposes of providing desirable ashing characteristics, although beneficial ashing characteristics of limited utility can be achieved by external application of such mineralizing agents to coat the fibers or for admixture with the fibers. As described, the desired internal application of the mineralizing agents can be achieved by first wetting the fibers with a solution of the desired metal ion for absorption into the cellulosic derivative, followed by exposure to a solution of the desired anion whereby the corresponding metal salt forms in situ with the cellulosic material.

Maintenance of glow and burning rate, characteristic of tobacco, is achieved by formulation to include a potassium salt, such as potassium oxalate, or by the addition of rubidium or cesium compounds in amounts within the range of 1 percent to 10 percent by weight but preferably less than 1 percent by weight, as described in the copending application Ser. No. 623,528, filed Mar. 16, 1967, and titled "Smoking Products and Process for Their Manufacture" now abandoned. Smoke generators can be added to increase the visual effect of the smoking product when burned.

The resulting product is suitable for use as a smoking product alone or in admixture with tobacco to produce a smoking product having better taste and less undesirable ingredients in the smoke.

The concept of this invention resides in the improvement of the paper or sheet material in which the tobacco or the smoking product is rolled in the fabrication of cigarettes, cigars, or the like smoking products.

To the present, use is made of cigarette paper formed of purified cellulose pulp loaded with about 20 percent to 30 percent by weight calcium carbonate with small amounts of other possible modifiers. Pyrolysis of this paper gives a most undesirable irritant odor which, though diluted with the smoke from the tobacco, undesirably affects the odor and taste of the smoking product. Many of the attributes obtained from the

improved smoking product prepared of cellulosic materials, as described in the aforementioned copending applications, are upset in part by the use of conventional cigarette paper or wrappers.

Thus, it is an object of this invention to product and to provide a method for producing a paper or wrapper of cellulosic material which is characterized by having improved odor, taste, and aroma during pyrolysis whereby cigars and cigarettes currently produced with tobacco can materially be improved, at least from the standpoint of taste and aroma, and wherein the balance of good taste and aroma of cigars and cigarettes produced in cellulosic materials in the manner described in the aforementioned applications are not materially upset by the wrapper or paper in which the smoking material is incorporated.

It is a further object of this invention to provide a number of methods and means which individually operate to provide a more desirable paper or wrapper from the standpoint of taste and aroma and which, in various combinations, offer still greater improvement when utilized as a part of a smoking product.

The invention will be described with reference to paper formed of purified cellulose or woodpulp, such as alpha-cellulose, but it will be understood that the term cellulose is intended to include other cellulosic fibers and materials of the type used in the making of paper and the like wrapping material.

First, with reference to cigarette paper as it is now prepared from purified cellulose loaded with 20 percent to 30 percent by weight calcium carbonate, considerable improvement is derived by the treatment of cigarette paper with a dilute solution of oxalic acid containing from 1 percent to 10 percent by weight oxalic acid in a dissolved state in an aqueous medium at a temperature within the range of room temperature to 80° C.

The oxalic acid solution operates to convert calcium carbonate to insoluble calcium oxalate. The latter is sufficiently stable thermally to remain while the cellulosic material is pyrolyzed during the smoking of the cigarette so that the effect of calcium on the odor is minimized and a cleaner tasting cigarette is obtained. During the final stages of the pyrolysis, the calcium oxalate breaks down to calcium oxide and calcium carbonate which remain as ash and carbon dioxide and/or carbon monoxide gas which goes off with the smoke and is substantially odorless and tasteless.

Treatment with oxalic acid does not interfere with the desirable characteristics of the paper for its intended use as a wrapper. Treatment with oxalic acid can be effected by passing the preformed paper web through an aqueous solution of oxalic acid at a rate to provide a residence time sufficient to achieve the desired transformation (about 2 to 10 minutes), after which the web is washed with water to remove excess oxalic acid or other solubles present in the processed paper.

Improvement in the smoking characteristics of the paper wrapper in cigarettes is achieved, in accordance with the practice of this invention when the calcium oxalate and/or magnesium oxalate or corresponding mineralizing agent, as described herein, is present in the paper in an amount greater than 5 percent by weight but it is undesirable to make use of an amount greater than 45 percent by weight and it is preferred to make use of a cigarette paper containing 10–40 percent by weight of such mineralizing agent.

It will be understood, of course, that the desired construction can be obtained by the substitution of calcium oxalate and/or magnesium oxalate for calcium carbonate in the finish or slurry of cellulosic pulp used in the original formation of the paper web.

Instead of oxalic acid, use can be made of pivalic acid or tannic acid to form the corresponding pivalate or tannate. Instead of calcium, use can be made of magnesium, barium, or strontium to provide the corresponding magnesium, barium, or strontium oxalate, pivalate, or tannate in the cigarette paper and it is preferred to make use of the combination of a

major proportion of calcium and a minor proportion of magnesium as the cation of which the filler is formed.

By way of modification of this initial concept, it has been found that still further improvement in the smoking characteristics of the paper can be obtained when a small amount of free pivalic, tannic and preferably oxalic acid is reintroduced or otherwise provided in the cigarette paper. The function of the free acid returned to the treater paper is to ensure that small amounts of ions of heavy metals, such as calcium, barium, strontium, magnesium, copper, cobalt, iron, and aluminum remaining in the paper or subsequently released are taken up to form the corresponding insoluble heat-stable oxalate, tannate or pivalate, as the case may be. For this purpose, it is undesirable to provide for more than 0.5 percent by weight acid since excessive amounts of oxalic or the like acids are objectionable from the standpoint of the taste and aroma which additional amounts thereof contribute to the product when it is smoked. When employed, it is preferred to introduce the oxalic or like acid in an amount within the range of 0.1 percent to 0.25 percent by weight. Reintroduction can be made by dissolving the calculated amount of acid in an aqueous medium to provide a solution containing 0.1 percent to 1 percent by weight of the acid and then spraying the solution onto the web or by passing the web through a solution followed by drying, or by mixing the solution with the pulp fiber slurry during the paper making.

The foregoing concepts will now be illustrated by way of the following examples.

EXAMPLE 1

Cigarette paper, already formed, is passed through a bath heated to 30° C. and formed of an aqueous solution containing 5 percent by weight oxalic acid. Passage is made at a rate to provide a residence time of about 5 minutes.

Upon emergence from the bath, the treated web is subjected to two or three washings with water to remove excess oxalic acid or other water solubles. A controller excess of oxalic acid is then applied by spraying the treated and washed and semidried paper with an aqueous solution containing 0.2 percent by weight oxalic acid in an amount to provide about 0.1 percent by weight free acid in the paper. The paper is finally dried to about 40 percent relative humidity.

Tannic acid can be substituted, in whole or in part, for the oxalic acid in equivalent amounts in Example 1.

EXAMPLE 2

Purified cellulose pulp is slurried with a mixture of calcium oxalate and magnesium oxalate in the ratio of about four parts by weight calcium oxalate to one part by weight magnesium oxalate with the total oxalate present in an amount to make up about 20 percent to 40 percent by weight of the solid of the fibrous slurry.

The slurry is used as a furnish in a conventional papermaking machine to produce a cigarette paper fabricated of cellulosic fibers containing 20 percent to 40 percent by weight of calcium and magnesium oxalate.

For the embodiment wherein calcium and/or magnesium oxalate is embodied in the paper, or in the fibrous materials with which the paper is formed, it is preferred to take advantage of the lapse of time between the admixture of the calcium cation and the oxalic acid anion to the precipitation of an insoluble calcium oxalate to achieve fuller penetration or impregnation of the cellulosic system. It appears that calcium oxalate remains in the dissolved state in a highly hydrated form for a length of time sufficient to enhance penetration of impregnation of the cellulosic system. It appears that calcium oxalate remains in the dissolved state in a highly hydrated form for a length of time sufficient to enhance penetration or impregnation of the cellulosic system, before precipitation of calcium oxalate in response to separation to water of hydration. This same effect is experienced with the combination of magnesium and oxalic acid, only at a slower rate.

In practicing this phase of the invention for introduction of calcium and/or magnesium oxalate, separate aqueous solutions are prepared containing the calcium cation in one solution in an amount within the range of 1–15 percent by weight and preferably 3–7 percent by weight, while the other aqueous solution contains the oxalic acid anion in equivalent amounts. The two solutions are admixed immediately prior to application with the cellulosic material or the separate solutions are applied substantially simultaneously to the cellulosic material or paper web, followed by drying.

Reapplication can be made a number of times until the desired concentration of ashing ingredients is inserted within the cellulosic system.

As in the preceding case, the calcium and magnesium can be substituted with barium or strontium and the oxalic acid can be substituted with tannic, pivalic, glycolic, diglycolic, or lactic acid.

The following example will illustrate the practice of this phase of the invention.

EXAMPLE 3

Purified cellulose pulp is slurried with 25 times its weight of a freshly prepared mixture of equal parts of 5 percent solution of calcium acetate and a 5 percent solution of oxalic acid. The slurry is cast on a screen in the usual manner for the formation of cigarette paper. The calcium acetate and oxalic acid do not immediately react to form an insoluble calcium oxalate, especially when the slurry is maintained at ambient temperature or below. As a result, the components are capable of soaking into the cellulose fibers before the calcium oxalate is precipitated to provide internal loading in situ in the fibers with the mineralizing agent. This pulp is then dried, the process repeated a number of times until the desired ash level is achieved. The calcium oxalate can be added as an insoluble compound for suspension with the pulp to provide a concentration within the range of 10 to 45 percent but best results are secured, especially from the standpoint of the characteristics of the ash, when the oxalate and the like mineralizing agent is formed internally within the pulp fibers. The formed paper is washed with water to remove water solubles including acetic acid formed upon replacement by oxalic acid and any excess oxalic acid or calcium acetate, as the case may be. Free oxalic acid can be reintroduced as in Example 1 or the free acid can be omitted.

When, instead of conventional cigarette paper, use is made of paper prepared as in Examples 1 to 3, a cigarette is produced having better aroma and taste when burned. When used in the preparation of a cigarette or cigar with a smoking product prepared of cellulosic material, as described in the aforementioned copending applications, the taste and aroma of the smoking product are upset less by the paper wrapper prepared in accordance with Examples 1 to 3 as compared with conventional cigarette paper.

This is an improvement which is important to the current field of smoking products since it provides for better taste and odor to current tobacco products as well as to synthesized smoking products of any type.

A second concept of this invention resides in the practice wherein the prepared cigarette paper, and preferably the purified cellulose pulp of which the cigarette paper is formed, is treated to effect selective oxidation of the methylol groups on the C_6 position of the cellulose molecule with permissible oxidation at the C_2 and/or C_3 position to produce a preferably partially oxidized cellulose hereinafter referred to as oxycellulose in which the oxidation reaction product may be comprised of polyuronic acids and their derivatives.

In the practice of this modification of the invention, the amount of oxidation of the cellulosic material should be limited to within the range of 15 to 95 percent calculated on the conversion of the methylol group on the C_6 position of the cellulose molecule. It is preferred to provide for an oxycellulose in which the level of oxidation has been limited to within

the range of 40 to 60 percent. Below the level of 15 percent oxidation the improvement of odor and taste during pyrolysis of the paper is not significant. Above an oxidation level of 60 percent, the oxycellulose tends to lose some of its fibrous characteristics such that the oxycellulose pulp becomes less capable of being interfelted and therefore less suitable for use in the preparation of a paper of sufficient strength and integrity for use as a cigarette wrapper. Previously formed paper oxidized to a level beyond 60 percent similarly becomes less suitable for use. When the oxycellulose is characterized by more than 60 percent oxidation, the oxycellulose can be blended with conventional pulp for use in the fabrication of cigarette paper but it is important to have a blend in which at least 15 percent of the total methylol groups have been oxidized in order to achieve significant improvements. Within the preferred range of 40 to 60 percent oxidation, the oxycellulose retains sufficient of its fibrous characteristics to enable use of the already formed cigarette paper or to enable use of the oxycellulose pulp in the preparation of cigarette paper by conventional paper-forming machines.

In effecting the desired level of selective oxidation, it is preferred to make use of nitrogen dioxide as the oxidizing medium. Since the preferred level of oxidation is substantially less than that for complete oxidation, it is possible to make use of gaseous nitrogen dioxide as the oxidizing medium. However, from the standpoints of oxidation rate, uniformity of oxidation and process control, it is preferred to make use of liquid nitrogen dioxide, especially in the treatment of previously formed cigarette paper. The oxidation reaction will hereinafter be described with reference to the use of liquid nitrogen dioxide as the oxidizing medium but it will be understood that corresponding results can be achieved by the use of gaseous nitrogen dioxide.

Liquid nitrogen dioxide offers a number of advantages over gaseous nitrogen dioxide or other oxidizing agents in that liquid nitrogen dioxide gives the desired selectivity in oxidation of methylol on the C_6 position of the cellulose molecule. Liquid nitrogen dioxide operates immediately and completely to wet the cellulosic fibers so that all of the cellulosic material is subject to immediate and uniform oxidation. Further, liquid nitrogen dioxide is available to quench hot spots whereby heat generated by the exothermic oxidation reaction is immediately dissipated thereby to avoid the creation of hot spots which might otherwise lead to combustion.

Still further, it is possible to effect modifications in the use of liquid nitrogen dioxide whereby the reaction rate can be increased to levels suitable for continuous processing. When use is made of liquid nitrogen dioxide as the oxidizing medium, treatment can be made with an amount of liquid nitrogen dioxide, one to one thousand times the cellulosic material and preferably 25 to 50 times the cellulosic material on a weight basis. The oxidation reaction should be carried out with the materials at a temperature within the range of 15° to 65° C. and under autogenous pressure. Reaction at temperatures below 15° C. is too slow for commercial practice and reaction at temperatures in excess of 65° often leads to undesirable side reactions and the production of an unstable product under the conditions of use.

Within the defined range of reaction conditions, oxidation is continued until the desired level of oxidation is achieved, as measured by titration to determine the amount of conversion of methylol to carboxyl groups. At 20° C., the desired level will be obtained in about 4 days for 90 to 95 percent oxidation and in about 1 day for 40 to 60 percent oxidation. At higher reaction temperatures of 40° to 45° C., the reaction time will be reduced to the matter of an hour or less for 40 to 60 percent oxidation and about 1 day for 90 to 95 percent oxidation.

It is possible to modify the liquid nitrogen dioxide system to include water in the reaction medium provided that the temperature of the reaction is maintained at a level sufficiently high to counteract excessive ionization in the medium, as measured by its electrical conductivity. It is believed that when the medium is conductive, the water in the nitrogen dioxide is in the form of nitric (and nitrous) acid which is capable of attacking and/or degrading the fibrous cellulosic material. Thus it is desirable to avoid formation of nitric or nitrous acids in the oxidizing medium. We have found that the electrical conductivity of a liquid nitrogen dioxide solution containing as little as 1 percent by weight water is very high at 0° but that the solution becomes substantially nonconductive at 20° C. The conversation range from conductivity to nonconductivity rises in temperature with increased concentration of water in the reaction medium. However, when oxidizing to a level of 95 percent, it is undesirable to make use of more than 8 percent by weight water in the liquid nitrogen dioxide system and when oxidizing to a level within the preferred range of 40 to 60 percent, an upper limit of about 10 percent by weight water in the oxidizing medium is established before the oxycellulose tends to be taken into solution.

On the other hand, the presence of water in the liquid oxidizing medium, which is rendered relatively nonconductive by going to elevated temperature, is effective to accelerate the rate of oxidation so that the combination of water and elevated temperature permits the desired level of oxidation to be achieved in a fraction of the time required for the liquid nitrogen dioxide alone. Thus means are provided to reduce the residence time of the fibrous cellulosic materials to achieve the desired level of oxidation.

In the preferred practice of this concept, it is desirable to make use of an oxidizing medium of liquid nitrogen dioxide containing 0.5 to 5 percent by weight water and preferably 1.5 to 3.5 percent by weight water. At a temperature of 40° to 45° C., an oxidation level of 40 to 60 percent can be reached in a matter of minutes to hours thereby to permit oxidation as a continuous operation by passage of the paper continuously through the oxidizing medium under autogenous pressure.

By way of still further modification, dependent upon the use of liquid oxidizing medium, such as liquid nitrogen dioxide, with or without water, the rate and uniformity of oxidation can still further be improved by means of introduction into the reaction medium of gaseous oxygen or a molecular oxygen-containing gas, such as air or oxygen-enriched air, but in which any gas in which the oxygen is included is an inert gas. The oxygen not only serves as a means to agitate or stir the ingredients, but, more importantly, it provides an oxidizing function of its own in the presence of nitrogen dioxide thereby to contribute to the oxidation and the rate of oxidation of the cellulosic fibers. It operates further in the system to oxidize formed nitric oxide to nitrogen dioxide thereby to maintain the level of oxidizing medium in the system. When used, the amount of oxygen used should range from equimolecular proportions with the cellulosic segments making up the cellulosic material (such as glucose or hexose) to about twenty times the theoretical amount, as described in our copending application Ser. No. 745,134, filed July 16, 1968, titled "Cellulosic Smoking Product and Method in the Preparation of Same," now U.S. Pat. No. 3,478,752.

The presence of calcium oxalate or other corresponding mineralizing agent heretofore described does not interfere with the reaction of oxidation of the cellulosic fibers, whether in the form of paper or pulp. As a result, the described oxidation reaction can be carried out with pulp or paper embodying calcium oxalate or other mineralizing agent or it can be carried out with paper or pulp in the absence of such mineralizing agent.

Having generally described the basic concepts of the modification for providing a pulp for the manufacture of paper or a paper of oxycellulose, examples will now be given by way of illustration, but not by way of limitation, of the practice of this concept of the invention.

EXAMPLE 4

Cigarette paper, previously formed of purified woodpulp, is immersed in 100 times its weight of liquid nitrogen dioxide and maintained at a temperature of 20° C. until 50 percent of

the C_6 methylol groups have been oxidized to carboxyl groups (about 2 days). During this period, air is bubbled through the reaction vessel at a rate of 5 to 50 parts by weight per part by weight of cellulosic material, spread over the reaction time. The oxidized cellulosic material still retains its fibrous characteristics such that the paper still has strength and integrity and can be passed through two to three water washes wherein deionized water is flushed through the oxidized paper. The paper is dried to about 40 to 50 percent relative humidity and calendered for subsequent use in the conventional manner as cigarette paper.

EXAMPLE 5

Purified woodpulp is introduced into a pressure vessel with 50 times its weight of liquid nitrogen dioxide containing 1.5 percent by weight water. The mixture is maintained under a constant state of agitation by recirculating a small stream of the liquid oxidizing medium from the bottom to the top of the reaction vessel. The reactants are maintained at a temperature of about 35° to 40° C. and the autogenous pressure and reaction is continued until 40 to 60 percent of the methylol groups on the C_6 position have been oxidized (about 2 hours). When reaction is completed, the liquid oxidizing medium is drawn off and the oxycellulose is washed several times with water.

The oxycellulose can be suspended in aqueous medium to form a slurry which can be employed in the conventional manner to form cigarette paper since the oxycellulose still retains sufficient of its fibrous characteristics for interfelting by the paper forming machine to produce a cigarette paper which can be processed and used in the conventional manner.

EXAMPLE 6

The process of Example 5 is repeated with the cellulosic pulp of Example 3 containing 10 to 45 percent by weight of internally formed calcium oxalate.

EXAMPLE 7

Purified cellulose pulp is introduced into a pressure vessel with 30 times its weight of liquid nitrogen dioxide containing 2 percent by weight water. The reaction is carried out under 30 p.s.i. with the materials maintained at a temperature of 35° C. until more than 90 percent of the methylol groups on C_6 have been oxidized (about 4 to 5 hours). When oxidation has been completed, the liquid oxidizing medium is drawn from the vessel and the oxycellulose is washed first with anhydrous nitrogen dioxide to remove moist nitrogen dioxide and soluble impurities such as gums, waxes, lignins, natural resins, and the like. After evaporation of the anhydrous nitrogen dioxide, the material is then washed with water to wash out nitric acid and water-soluble components. Unlike Examples 4 to 6 wherein the oxycellulose retains fibrous characteristics sufficient to enable interfelting to form cigarette paper, the cellulosic material oxidized to better than 90 percent no longer retains sufficient of its fibrous characteristics to enable fabrication into a paper of sufficient strength or integrity for use as cigarette paper.

The oxycellulose of Example 7 is admixed in the ratio of one part by weight oxycellulose to 0.5 to 1 part by weight of unmodified, purified papermaking wood pulp and the materials are slurried in aqueous medium having a pH below 7 and preferably within the range of 4 to 6 to prevent solution of the oxycellulose. Powdered calcium oxalate is included in the slurry in amount sufficient to give an ash of 23 percent in the finished paper. The slurry is processed in the conventional manner for paper making by casting on a Fourdrinier screen for interfelting of the oxycellulose and pulp fibers in uniform distribution for paper formation. The paper after being dried and calendered can be used as cigarette paper in the preparation of cigarettes, cigars and the like.

The papers of Examples 1 to 7 can be used in the conventional manner as cigarette paper or cigarette wrappers with smoking products of the type produced in accordance with the aforementioned copending application or with tobacco or with mixtures thereof, or with other materials capable of use as a filler for smoking in cigarettes and cigars.

A remarkable difference will be observed from the standpoint of a markedly improved and milder odor, aroma and taste when cigarette paper of Examples 4 to 7 is employed instead of conventional cigarette paper in cigarettes, cigars, and the like. This vast difference can be detected when conventional cigarette paper is pyrolyzed alone in a closed vessel to seal in the odor for comparison with the pyrolysis of cigarette paper produced in accordance with Examples 4 to 7, representative of the practice of this invention.

Further modification, additionally to improve the taste and aroma of cigarette paper and smoking products formed thereof, can be achieved by subsequent treatments of the oxycellulose produced in accordance with the practice of this invention, as by subjecting the cellulosic material selectively oxidized with nitrogen dioxide to a reduction reaction with a borohydride or nascent hydrogen, as described in our copending application filed concurrently herewith and titled "Method for Preparation of Smoking Products with Selective Reduction Following Selective Oxidation."

For this purpose, the cellulosic fibers, which have previously been oxidized with nitrogen dioxide (gaseous or liquid) are reacted in a dilute aqueous solution of a borohydride under conditions which operate to effect a reduction reaction. As the borohydride, use can be made of alkali metal and ammonium borohydride 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 with solutions containing the borohydride dissolved in aqueous medium in an amount within the range of 0.5 to 5 percent by weight and preferably within the range of 0.1 to 1 percent by weight. With such solutions, it is desirable to carry out the reaction with materials present in the ratio of one part by weight of the oxidized cellulosic derivative to 10 to 1,000 parts by weight of the solution and preferably 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 within the range of 5 to 60 minutes.

Solution of the borohydride in aqueous medium usually results in an alkaline solution having a pH above 7. When use is made of a borohydride solution having an alkaline pH, there is a tendency for the oxidized cellulosic material to be taken into solution.

We have found that the desired reduction reaction with a minimum of degradation or dissolution can be achieved by adjustment of the solution of the borohydride to a pH of 7 or below but not below 3 and preferably within the range of 6 to 7. At a pH below 3, the borohydride becomes too unstable. The pH adjustment to the desired level can be achieved with an organic acid, such as oxalic acid, acetic acid or glucuronic acid, oxidized cellulose or the like water soluble organic acid or by the use of an inorganic acid such as hydrochloric acid and the like. It is preferred to make use of an organic acid such as oxalic acid, otherwise subsequent treatment would be required for removal of undesirable ions, such as the chloride ions and the like materials introduced by the acid. In the preferred use of oxalic acid, any of the latter which remains as a residue need not be removed since beneficial use can be made of oxalic acid to produce oxalates for mineralizing the smoking product and to neutralize heavy metal ions which might otherwise be present.

Under the conditions described, the reaction can be carried out at a temperature within the range of 0° to 30° C. and preferably within the range of 0°to 25° C.

This concept will now be illustrated by way of example.

EXAMPLE 8

Cellulosic paper fibers previously oxidized, as in Examples 4 to 7, are immersed in a 0.2 percent water solution of sodium borohydride in which the pH has been adjusted with oxalic acid to within the range of 6.5 to 7. Exposure in the ratio of about one part by weight oxycellulose to 100 parts by weight of solution is continued for from 1 to 10 minutes. Thereafter, the solution is drained from the oxidized cellulosic material and the treated fibers are rinsed with one or more increments of deionized water.

Others of the alkali metal and ammonimum hydrides or borohydrides can be substituted, in whole or in part, for the sodium borohydride of Example 8 in solution in concentrations within the range of 0.1 to 1 percent by weight.

Instead of borohydride reduction, a beneficial reduction reaction can be achieved by the use of hydrogen freshly released from the negative pole of an electrolytic cell in which the oxidized cellulosic material is immersed, as illustrated by the following example. This example finds beat use in the treatment in a continuous operation of an endless web of cigarette paper previously oxidized as in the manner of Example 4.

EXAMPLE 9

The oxidized cellulosic cigarette paper is passed between horizontally disposed, vertically spaced-apart poles of an electrolytic cell with the negative pole lowermost in the form of a metal gauze or metal screen. A plastic screen such as porous polyethylene is positioned to separate the oxidized cellulosic paper from the positive pole. Use is made of an electrolyte formulated of oxalic acid dissolved in aqueous medium in an amount within the range of 0.1 to 40 percent by weight and a current having a density of 5 to 50 a./cm.^{2} of screen area is passed between the poles while the electrolyte is maintained at ambient temperature.

Hydrogen gas bubbles up from the negative pole through the web of oxidized cellulosic material as it is advanced continuously through the cell. The freshly formed nascent hydrogen is effective to reduce at least some of the nitro, quinone, keto or aldehyde groups and unsaturates in the oxidized cellulosic paper fibers. Upon issuance from the electrolyte, the treated web is rinsed with one or more increments of water and dried.

The reduction treatment described is not essential to the preparation of an improved cigarette or cigar wrapper but it will be found that such reduction still further improves the taste and aroma upon pyrolysis of the paper, whereby an improved smoking product can be secured.

By way of a still further modification, instead of introducing the mineralizing or ashing ingredients prior to oxidation, some advantage can be derived from the introduction of the ashing components after oxidation has been carried out whereby, with or without reduction, calcium and/or magnesium oxalate or the like ashing ingredients can be embodied as an internal component formed in situ within the cellulosic system, although limited benefits are derived when the ashing ingredients are applied externally onto the oxidized cellulosic fibers. It appears, at present, that the use of calcium or magnesium oxalate is preferably since such oxalates, when incorporated within the fibers of the oxidized cellulosic material, are effective ash-producing agents. Moreover, the oxalates do not have the side effects of producing undesirable odors or of affecting the combustion rate of the material. It is believed that the oxalate anion is sufficiently refractory to maintain the calcium or magnesium as an oxalate while the oxidized cellulose is undergoing pyrolysis. This prevents the immediate formation of calcium or magnesium polyuronate and the corresponding pyrolytic odor effects, reminiscent of ketones as produced by the pyrolysis of organic calcium salts.

The aforesaid oxalates are insoluble and therefore the problem is to provide means whereby such normally insoluble ash-forming materials may be incorporated into the fibers of the oxidized cellulose. We have discovered a number of ways in which such mineralizing materials can be introduced into the fibers of the oxidized cellulosic material.

For example, if oxidized cellulose is the starting product, incorporation of the oxalate into the fibers can be achieved by first soaking the oxidized cellulose in a soluble mineral salt solution such as a dilute solution of calcium acetate. The cation readily incorporates itself into the oxidized cellulosic material to form the calcium salt of the oxidized cellulose which can be described as a calcium polyuronate. This treatment is followed by a soaking in a solution of oxalic acid whereby the calcium polyuronate reacts with the oxalic acid which regenerates the polyuronic acid and produces insoluble calcium oxalate as an internal component inside the oxidized cellulosic fibers. Acetic acid which is formed during the replacement reaction and any excess oxalic acid is removed from the treated cellulosic material by means of a water wash.

The calcium can be introduced in the dissolved state in an aqueous medium in which the oxidized cellulosic material is suspended and wherein the calcium ion is made available for reaction to form insoluble calcium polyuronate. For this purpose, the calcium may be introduced as a water soluble salt such as calcium acetate, calcium chloride, calcium glucuronate, calcium bicarbonate, or the like, but it is preferred to make the calcium available for reaction with the oxidized cellulosic material by means of dissolving chalk or lime (slaked lime or preferably quicklime) in an acidic aqueous medium into which the oxidized cellulosic material is introduced to take up calcium to form insoluble calcium polyuronate. Thereafter oxalic acid is added whereby the oxalic acid which diffuses into the fiber is taken up by the calcium to form the calcium oxalate in situ within the cellulosic fiber, and thus to regenerate the oxidized cellulosic material in its original acidic condition.

When use is made of lime as the source of calcium, the acidic aqueous medium to which the calcium is added can be formulated from an organic or inorganic acid, such as acetic acid, nitric acid, hydrochloric acid, glucuronic acid and the like, with the acid present in an amount to provide an acidic solution having a pH less than 7 and preferably a pH within the range of 4 to 5. With hydrochloric acid or with acetic acid, the desired level can be obtained with the acid present in the aqueous medium in an amount within the range of 0.1 to 2 percent by weight. The pH of the solution into which the oxidized cellulose is introduced should not exceed 6.5, otherwise the oxidized cellulosic material will tend to dissolve therein. As a result, lime should not be added in an amount which will operate to raise the pH above 6.5 and it is preferred to add lime in an amount to raise the pH of the acidic aqueous medium to within the range of 4 to 6, and preferably about 5. For this purpose, lime can be added in an amount within the range of 0.01 to 4 percent by weight and preferably in an amount within the range of 0.01 to 1 percent by weight and still more preferably in an amount within the range of 0.02 to 0.05 percent by weight. Calcium oxide readily dissolves in the acidic aqueous medium to form the corresponding calcium salt. The addition of lime will operate to raise the pH of the solution. To avoid localized effects, it is preferred to conduct the calcium replenishment in a portion of the liquid separate from the portion containing the oxidized cellulose.

The oxidized cellulosic material, after taking up a suitable quantity of calcium ion, is then reacted with at least a stoichiometric amount of oxalic acid in solution in aqueous medium at a pH within the range of 2 to 7 and preferably within the range of 3 to 5. Calcium is taken from the calcium polyuronate to form the corresponding calcium oxalate in situ in the oxidized cellulosic fibers. Calcium oxalate is comparatively stable by comparison with the oxidized cellulosic material so that it will remain while the cellulosic material is being pyrolyzed during smoking of the smoking product.

The reaction to form the calcium oxalate is not critically dependent upon temperature. However, it is preferred to carry out the described reaction at a temperature within the range

of 0° to 40° C. with a reaction time of 5 to 10 minutes. Longer times can be used but will be unnecessary.

Instead, the mineralizing agents can be introduced into the oxidized cellulosic material in the manner previously described by introduction into the paper or cellulosic fiber and as illustrated in Examples 1 to 3, but with the oxidized cellulosic material substituted for the cellulosic paper or pulp.

The foregoing concepts of mineralizing the cellulosic material after oxidation reaction are illustrated by the following examples.

EXAMPLE 10

Oxidized cellulose, prepared in accordance with Examples 4 to 7, or oxidized cellulose which has been reduced in accordance with Examples 9 and 10 is introduced into a reaction vessel with sufficient water to provide mobility of the slurry upon stirring. Acetic acid is added to provide a concentration of 2 percent by weight and the lime is added in an amount to provide an ash level of about 5 percent when completely absorbed by the oxidized cellulosic material. The pH of the solution will rise from 4 to about 5 and as the calcium cation is taken up by the oxidized cellulose, the pH of the solution will fall back to about 4. After about 5 minutes at ambient temperature, oxalic acid is added in a stoichiometric amount with a drop in pH to about 3. As the oxalic acid is absorbed into the fibers by reaction with calcium to form calcium oxalate, the pH of the system will rise again to about 4.

The foregoing cycle may be repeated a number of times to produce an oxidized cellulosic material containing calcium oxalate internally dispersed with the fibrous system in an amount corresponding to 5 to 45 percent by weight calculated on calcium carbonate ash level.

After the final cycle, the treated oxidized cellulosic material is thoroughly washed with deionized water to remove excess oxalic acid and the resulting cellulosic material is dried.

The cellulosic pulp which has been oxidized and ashed can be suspended in aqueous medium to form a funish used in the preparation of paper.

EXAMPLE 11

The process of Example 10 is repeated except that the paper that is formed and dried is subsequently wet with an aqueous solution containing 0.25 percent by weight oxalic acid to reintroduce oxalic acid into the formed paper.

EXAMPLE 12

The process of Example 10 is repeated but instead of treating the oxidized cellulosic material with lime dissolved in acetic acid, the oxidized cellulosic material is treated directly with an aqueous solution containing about 0.1 percent by weight calcium acetate followed by the introduction of the solution of oxalic acid.

EXAMPLE 13

The procedure of Examples 10, 11, and 12 is followed except that magnesium, strontium or barium oxide or acetate are substituted in equivalent amounts for the calcium oxide and instead of making use of oxalic acid, tannic acid is substituted to form the corresponding tannate.

EXAMPLE 14

A 5 percent solution of calcium acetate is provided in one container and a 6 percent solution of oxalic acid is provided in another and the two solutions are mixed one with the other and immediately applied by spraying onto the oxidized cellulosic material. Application is made while the materials are maintained at a temperature within the range of 0° to 10° C. to provide the oxidized cellulosic material with calcium oxalate which remains soluble for a period of time to enable penetration into the oxidized cellulosic system and which thereafter precipitates out upon loss of water of hydration. After aging the material for 10 to 30 minutes to allow precipitation to be completed, the oxidized cellulosic material is washed with water to remove soluble salts and the resulting product is dried. The application can be made a number of times to provide the desired ash level. The foregoing applications may be made with the oxidized cellulose in the form of pulp or in the form of paper to incorporated the desired ashing ingredients. When in the final form, the dried paper of ashed and oxidized cellulosic material may be treated with a 0.1 to 0.5 percent by weight solution of oxalic acid in deionized water to incorporate up to 5 percent by weight of oxalic acid into the fibrous system.

The cellulosic materials and paper formed thereof in accordance with the foregoing description may be further processed in the manners described in the aforementioned copending applications to incorporate various agents such as agents for controlling the burning rate by the addition of potassium, rubidium or cesium salts, or the addition of agents to provide neutralization of the smoke, such as by the addition of ammonia, or amine salts or nicotine, or by the introduction of agents for generation of increased amounts of smoke as by the introduction of fatty acids, esters and ethers, and the introduction of coloring agents, all as described in the aforementioned copending parent application.

It will be apparent from the foregoing that we have provided a cigarette paper and method and means for producing same wherein the taste and aroma of the cigarette paper during pyrolization and during the burning of the smoking product wrapped therein are markedly improved. Such papers or wrappers, produced in accordance with the practice of this invention, find beneficial use with current smoking products or smoking products of the type fabricated of cellulosic materials or other synthesized smoking products.

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

We claim:

1. In the method of producing a cellulosic wrapper for smokable material in the fabrication of cigarettes and cigars, the steps of providing a paper of cellulosic fiber for wrapping smokable material in the fabrication of cigarettes and cigars, uniformly distributing throughout the cellulosic fibers of the paper 5 to 45 percent by weight of an ashing ingredient in the form of a salt having a cation in the form of an alkaline earth metal and an anion selected from the group consisting of oxalic acid, tannic acid, pivalic acid, glycolic acid, diglycolic acid and lactic acid, sheeting the paper before or after treatment to wrapper form, and packaging the smokable material within the treated wrapper to produce the cigarette or cigar.

2. The method as claimed in claim 1 in which the cation is selected from the group consisting of calcium, magnesium, strontium, and barium.

3. The method as claimed in claim 1 in which the ashing ingredient comprises a mixture of calcium oxalate and magnesium oxalate present in the ratio of one part by weight magnesium oxalate to one to four parts by weight calcium oxalate.

4. The method as claimed in claim 1 in which the ashing ingredient is introduced by the steps of wetting the cellulosic material with the salt while in a solubilized state in aqueous medium and aging the treated fibers to precipitate the salt in situ within the cellulosic fibrous structure.

5. The method as claimed in claim 4 comprising the steps of providing one aqueous solution containing the cation and a second aqueous solution containing the anion and substantially simultaneously wetting the cellulosic material with the solutions.

6. The method as claimed in claim 5 in which the solutions are admixed immediately prior to wetting the cellulosic material.

7. The method as claimed in claim 5 in which the solutions are separately applied substantially simultaneously onto the cellulosic material.

8. The method as claimed in claim 1 in which the ashing ingredient is introduced into the cellulosic fibers prior to paper formation and which includes the step of forming the cellulosic fibers into a thin paper wrapper and rinsing the formed paper with water to remove water solubles and then drying the paper.

9. The method as claimed in claim 8 which includes the step of introducing an acid into the treated paper in an amount up to 0.5 percent by weight of the paper in which the acid is selected from the group consisting of oxalic acid, tannic acid, pivalic acid, glycolic acid, diglycolic acid, and lactic acid.

10. The method as claimed in claim 8 in which the acid is oxalic acid.

11. The method as claimed in claim 1 in which the salt is present in an amount of at least 5 percent by weight of the cellulosic fibers and the remainder making up the ashing component is a filler selected from the group consisting of perlite, talc, alumina, silica, and calcium carbonate.

12. The method as claimed in claim 1 which includes the additional step of oxidizing the cellulosic material with nitrogen dioxide selectively to oxidize methylol groups on the C_6 position of the cellulosic molecule by an amount within the range of 15 to 60 Percent.

13. The method as claimed in claim 12 in which the nitrogen dioxide oxidizing medium is liquid nitrogen dioxide and which includes the step of separating the liquid oxidizing medium from the oxidized cellulosic fiber upon completion of the oxidation reaction.

14. The method as claimed in claim 12 in which the cellulosic material is oxidized by an amount insufficient to destroy the fibrous characteristics of the cellulosic material.

15. The method as claimed in claim 12 in which the cellulosic material is oxidized by an amount within the range of 40 to 60 percent.

16. The method as claimed in claim 13 which includes the step of bubbling an oxygen containing gas through the liquid nitrogen dioxide during the oxidation reaction.

17. The method as claimed in claim 12 in which the liquid oxidizing medium contains up to 8 percent by weight water.

18. The method as claimed in claim 17 in which the amount of water is within the range of 0.5 to 5 percent in the oxidizing medium.

19. The method as claimed in claim 13 in which the oxidation is carried out at a temperature within the range of 15° to 65° C.

20. The method as claimed in claim 13 which includes the step of rinsing the oxidized fibers with anhydrous liquid nitrogen dioxide after separating the liquid oxidizing medium from the oxidized cellulose fibers.

21. The method as claimed in claim 12 which includes the step of subjecting the oxidized cellulosic material to a mild reduction reaction.

22. The method as claimed in claim 21 in which the reduction reaction is carried out with a reducing agent selected from the group consisting of freshly prepared hydrogen and a borohydrate.

23. The method as claimed in claim 12 which includes the step of adding an acid to the dried oxidized cellulosic material in an amount up to 5 percent by weight and in which the acid is selected from the group consisting of oxalic acid, tannic acid, pivalic acid, glycolic acid, diglycolic acid, and lactic acid.

24. The method as claimed in claim 23 in which the applied acid is oxalic acid.

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