

Aug. 19, 1969

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OXIDIZED CELLULOSE TOBACCO SUBSTITUTE COMPOSITION

Original Filed June 8, 1965

2 Sheets-Sheet 1

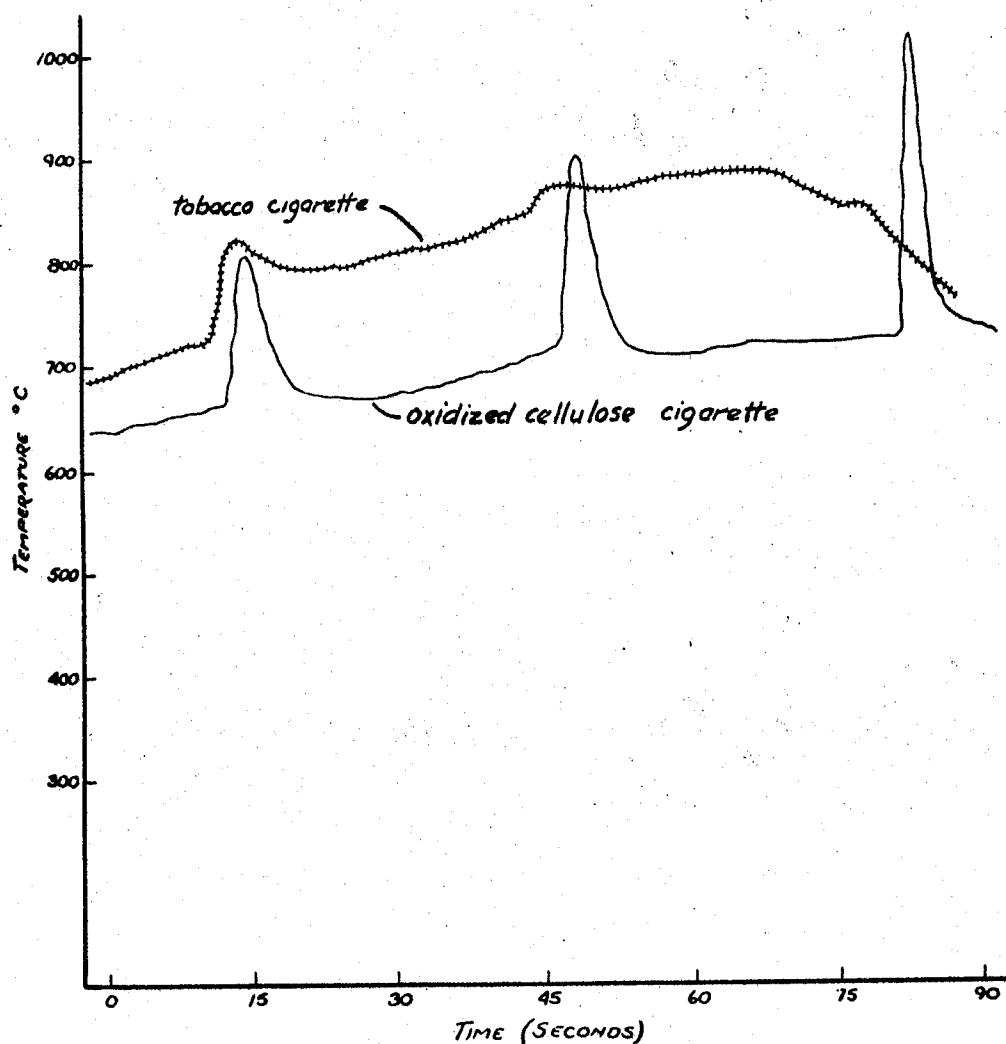


FIG. 1



FIG. 2

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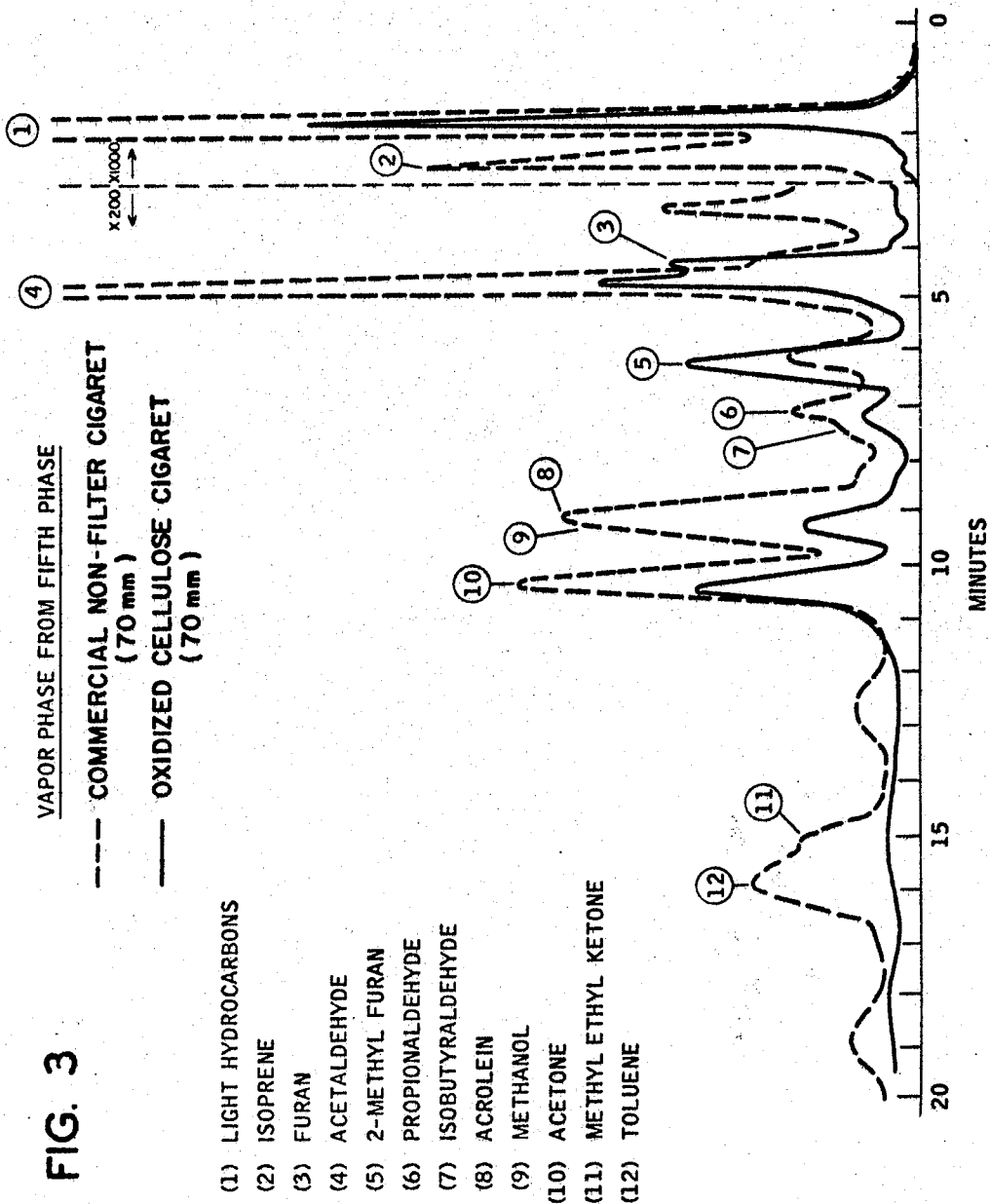
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OXIDIZED CELLULOSE TOBACCO SUBSTITUTE COMPOSITION

Earl Vance Kirkland, Wappingers Falls, N.Y., assignor
to Celanese Corporation, New York, N.Y., a corporation
of Delaware

Continuation of application Ser. No. 550,059, May 13,
1966, which is a continuation of application Ser. No.
462,319, June 8, 1965, which in turn is a continuation-
in-part of application Ser. No. 9,761, Feb. 19, 1960.
This application June 30, 1967, Ser. No. 650,258

Int. Cl. A24b 3/14

U.S. Cl. 131—2

3 Claims

ABSTRACT OF THE DISCLOSURE

A tobacco substitute material made principally from oxidized cellulose gauze or pulp which may, if desired, be blended with other form of cellulose, polymers or tobacco. The oxidized cellulose is combined with minor amounts of a hydrated metal compound and manifests reduced smoke condensate phenols, as well as some of the major molecular components reported as harmful in conventional tobacco smoke.

This application is a continuation of application Ser. No. 550,059 filed May 13, 1966, which in turn is a continuation of application Ser. No. 462,319 filed June 8, 1965, and which in turn is a continuation-in-part of application Ser. No. 9,761 filed February 19, 1960, all now abandoned.

The present invention relates broadly to smoking materials, and is more particularly concerned with a novel cigarette having as the base thereof oxidized cellulose.

It is an important aim of the present invention to provide a novel synthetic smoking material particularly suitable for cigarettes.

Another object of this invention lies in the provision of a base for a smoking material which produces in the smoke when smoked less total condensate and total phenols than do conventional cigarettes, and which displays in vapor phase analyses relative lesser amounts of the major molecular components reported to be harmful substances in the smoke of conventional non-filter cigarettes.

Still another object of the instant invention is to provide a base for a smoking material, which when smoked is mild, pleasant and agreeable.

A further object of this invention lies in the provision of a smoking material base of oxidized cellulose which may be combined with an unoxidized cellulose or a polymeric substance to impart more body thereto, and which also may be blended with conventional tobacco.

Other objects and advantages of the present invention will become more apparent during the course of the following description, particularly when taken in connection with the accompanying drawings.

In the drawings:

FIGURE 1 is a graph showing burning temperature profiles of cigarettes;

FIGURE 2 is a view of a cigarette; and

FIGURE 3 is a chart showing the results of vapor phase analyses on a conventional non-filter cigarette and the cigarette of the present invention.

Briefly stated, it has been discovered that a particularly advantageous smoking material is provided by oxidized cellulose exemplified by a copolymer of anhydroglucuronic acid and anhydroglucose or a polymer of anhydroglucuronic acid. Preferably, the oxidized cellulose is mixed with a hydrater metal compound to modify the burning

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rate thereof, and illustrative compounds for this purpose are hydrated magnesium sulfate and magnesium citrate.

It has been discovered that when oxidized cellulose is used in whole or in part in a cigarette the product is mild and is unexpectedly less irritating than when cellulose itself is so employed. To illustrate, cellulose in the form of shredded high alpha cellulose filter paper when used as a tobacco substitute in a cigarette, burns rapidly with a characteristic yellow flame and an odor resembling that of burning rags. The addition of hydrated magnesium sulfate in an exemplary amount of about 10% based on the weight of the product causes the burning rate of the cellulose to approach that found in ordinary cured tobacco leaves, produces a side stream odor and main stream taste which are much more pleasant, provides a differentially colored coal, and there results an ash which is dense, self-supporting and much lighter in color than the ash of the unmodified cellulose cigarettes. However, the resulting smoke does contain some volatile sulfur compounds.

Quite in contrast, when the cellulose is replaced in whole or in part by oxidized cellulose comprising polyanhydroglucuronic acid in the same formulation containing hydrated magnesium sulfate, the smoke is even milder and is believed to be practically or entirely free of sulfur oxides. This is quite surprising since oxidized cellulose comprising a polymer of anhydroglucuronic acid is a cation-exchange material and thus would not ordinarily be expected to take up, or remove, oxides of sulfur.

The oxidized cellulose comprising polyanhydroglucuronic acid may be obtained conveniently by the reaction of cellulose with nitrogen dioxide. This reaction and the products thereof are discussed by Kenyon et al. in "Industrial and Engineering Chemistry," vol. 41, p. 2 et seq. (1949). For purposes of this invention, the extent of oxidation may be varied considerably depending upon the manner in which the oxidized cellulose is to be further processed in the production of cigarettes. The extent of oxidation may be controlled so that the molar proportion of anhydroglucuronic acid units to anhydroglucose units in the product is illustratively about 1:9 to 4:1, or as may be stated otherwise, the extent of oxidation may range from 10 to 80%, depending on the manner in which the oxidized cellulose is to be further treated prior to the preparation of cigarettes. The mentioned range of the extent of oxidation produces in the final product from 5.68 to 45.44 meq. carboxyl groups per 100 grams of material. The extent of oxidation when stated herein as a specific percentage assumes that all carboxyl groups resulted solely from oxidation of the pendant hydroxy methyl groups of cellulose.

Another aspect of this invention relates to the use of other salts to modify the burning characteristics of cigarettes comprising oxidized cellulose comprising a polymer of anhydroglucuronic acid and hydrated magnesium sulfate. When large amounts of the hydrated magnesium sulfate are present it may be desirable to add inorganic compounds, e.g. salts, which promote sustained burning of the cigarette. Examples of such burning-sustainers are potassium chloride, magnesium chloride, potassium nitrate and magnesium nitrate. On the other hand, when magnesium citrate is employed as the burning rate controller, a burning rate suppressor such as alumina may be added.

The flavor of the cigarette may be improved by the incorporation of flavoring agents. These may be of the type used commercially for the flavoring of tobacco, such as menthol, tonka bean, powdered deer tongue, licorice or the proprietary mixtures known as "Alva" G-1, G-5, G-6, G-16, G-189, G-321 and G-327 supplied by Van Ameringen-Haebler, Inc., Division of International Flavors and Fragrances Inc. Vanillin has an excellent effect

on the flavor and odor of the cigarette, the usual household vanilla extract may be incorporated in the cellulose for this purpose.

Another aspect of this invention relates to the incorporation of a carbohydrate ether, particularly a combustible alkyl ether of a carbohydrate, e.g. ethyl cellulose or methyl cellulose, in the synthetic smoking material. I have found that the addition of the ether serves to bond the other additives firmly to the oxidized cellulose throughout the processing and burning thus insuring that there will be intimate contact between the oxidized cellulose and these additives during the burning process. Also the ether melts and flows over the burning material, leading to a more even distribution of the burning area. Another effect of the cellulose ether, particularly when larger amounts thereof are present, is to stiffen the tobacco substitute, giving a firmer cigarette, which is desirable for some purposes.

In the practice of my invention I have found it desirable to have a humectant present in order to prevent the tobacco substitute from drying out unduly. Any of the usual humectants used in cigarette manufacture may be employed; for example, sorbitol, which is preferred, another humectant polyhydric alcohol, e.g. glycerol may be used. The moisture content of the tobacco substitute is desirably in the range of about 5 to 25%, e.g. about 10 to 15%, exclusive of the moisture present as water of hydration. The preferred level of humectant in the finished smoking material is generally between 1 and 10%.

Still another aspect of this invention relates to the incorporation of nicotine or other alkaloid in the synthetic smoking material. I find that the presence of the alkaloid gives an increased feeling of satisfaction to the users of my synthetic smoking material. The nicotine may be supplied, for example, as such or in the form of its sulfate, or citrate or citrate-sulfate, malonate, or malate. Preferably, the amount of nicotine used is insufficient, in itself, to impart any pronounced color to the synthetic smoking material; its effect in this respect is at most a slight tinting of the product.

I may also incorporate an ammonium compound in the synthetic smoking material. Thus, compounds such as ammonium sulfate, ammonium carbonate, ammonium persulfate and ammonium perchlorate act to release ammonia and thus raise the pH of the side stream. The presence of the ammonia thus formed is also believed to have an effect in inhibiting the production of undesirable 3,4-benzpyrene during smoldering. The use of ammonium compounds also results in the formation of a whiter ash.

To enhance the appearance of our tobacco substitute a coloring agent may be incorporated. Although the color is preferably a tobacco-like brown, colors such as purple and pink may be used. Among the colors are those certified by the Food and Drug Administration such as F.D. and C. (Food, Drug and Cosmetic Act) Yellow #5; F.D. and C. Chocolate Brown, New, Shade B; C.I. 17590; Brown PG; 20170 Brown Y; 30045 Yellow-Brown K.

As was earlier stated, it is a further important aspect of this invention to blend or mix the oxidized cellulosic base with wood pulp and/or a water based polymeric emulsion to impart to the smoking material improved body, and when smoked, a noticeably milder smoke. The cellulose used is preferably a high alpha cellulose such as acetate grade or viscose grade cellulose wood pulp containing 92% or more of alpha cellulose. However, if desired, there may be used craft pulp (which contains about 75% alpha cellulose and gives a smoke having a harsher odor) or sulfite, both of which may be in the bleached, unbleached or semi-bleached condition. Desirably, the high alpha cellulose is beaten until its Canadian Standard Freeness is in the range of about 400 to 700 ml. as is disclosed in application Ser. No. 397,364, filed Sept. 14, 1964, now abandoned, in the name of Howard

J. Davis, which application is commonly assigned. Since in the present invention the alpha cellulose functions as a binder for the oxidized cellulosic base, it is generally preferred that the beating be continued until its freeness is less than 400 ml. The high alpha cellulose may be blended with the oxidized cellulose in an amount ranging from 1 to 25%, and preferably between about 6 and 10%.

When employed, the polymeric additive may be employed as an emulsion or solution and may be provided by polyacrylamid, polyacrylic acid or polyethylacrylate, the latter being at present preferred. The polymeric material may be present in an amount up to about 10% by weight, however, relatively smaller amounts are presently preferred and test investigations to date indicate that about 1% polymer is quite satisfactory.

My invention makes it possible to produce a cigarette in which the burning temperature during smoking is in the critical range of about 750 to 900° C. for only a very small fraction of the total smoking time. It is known that burning temperatures in the aforesaid critical range promote the formation of certain polycyclic aromatic compounds, such as 3,4-benzpyrene, which are carcinogenic. In conventional cigarettes the burning temperature is in the critical range for much longer times. This is readily demonstrated by standard burning temperature profiles, such as are shown in FIGURE 1.

Burning temperature profiles of cigarettes are obtained, in a standard manner, by continuously recording the temperature at a fixed point of the cigarette while the cigarette is being smoked in a standard manner, as described by G. P. Touey and R. C. Mumpower, Tobacco 144, 18 (1957). More particularly a platinum/87% Pt, 13% Rh fine wire thermocouple is placed at a point 25 mm. back from that end of the cigarette which is to be lit. The junction of the thermocouple is at the longitudinal axis of the cigarette while the two fine wires leading to the junction are at right angles to that axis and pass, through the cigarette paper, on opposite sides of the junction, the paper being suitably sealed about the wires to prevent entrance of air and movement of the thermocouple. The cigarette is smoked by means of an achine which draws air through the lit cigarette and then expels the indrawn gas and smoke into the atmosphere. More particularly, in the work described in this application, the machine has a piston operating in a cylinder connected to the cigarette through a trap cooled by a Dry Ice-acetone mixture. The volume displaced by movement of the piston in the cylinder is 35 ml., and the cylinder is maintained at room temperature (25° C.). The smoking machine is operated on a 30 second cycle, in which: air is drawn through the lit cigarette and into the cylinder, by movement of the piston, for two seconds; the gas in the cylinder is then expelled to the room, by movement of the piston, for two seconds; and the apparatus then remains stationary for 26 seconds, so that the cigarette is in the resting stage for 28 seconds. With this arrangement a standard tobacco cigarette, 70 mm. long and 22-26 mm. in circumference and having no filter tip, will smoke down to a 25 mm. butt in about 12 to 14 cycles. Alternatively, I may use a 60 second cycle, having a resting stage of 58 seconds, with similar two second intake strokes and two second exhaust strokes.

The instrument used for measuring temperature must have a high speed of response. For this purpose I have used a Sargent Multi-Range Recorder (Cat. No. S72151, E. H. Sargent & Co.) having a temperature response characteristic of 1/4 seconds for the full scale of recording, the set-up being such that the full scale of recording covers 1150° C.

As can be seen from FIGURE 1 in a conventional tobacco cigarette, during each puff of the smoking cycle (that is, during the 2-second intake of the gas) the temperature at the thermocouple junction rises as the cigarette burns back towards the junction. The temperature at

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the thermocouple drops slightly after each puff, at the beginning of each rest period, but when the temperature during the puff rises into the critical temperature range the resting temperature stays within the critical range. There is a long period of time when the temperature in a substantial portion of the cigarette, extending back from the lit end, is in the critical range.

In FIGURE 1 the time scale is expressed in seconds, the zero of the scale being chosen arbitrarily to show the time period during which the temperature of the thermocouple reaches a maximum.

FIGURE 1 also shows the temperature profile of a typical cigarette of tobacco substitute made in accordance with this invention. It will be apparent from the figure that the temperature drops off sharply after each puff and even after the puff temperature has come into the critical temperature range, the resting temperature is well outside that range. In addition, only a very small part of the cigarette is at a temperature in the critical range during the smoking cycle. For example, in the time cycle just before the cigarette burns back to the thermocouple, the thermocouple temperature is in the critical range for less than 50%, preferably less than 10%, and more preferably less than 5%, of the time. The initial slope of the curve descending from each peak temperature within the critical range is much higher than that of the tobacco cigarette, being sharper than about $-3000^{\circ}\text{C./min.}$

The slope of the curve ascending to each peak temperature within the critical range is also much higher than that of the tobacco cigarette, being well above $3000^{\circ}\text{C./min.}$ The difference between the peak temperature and the next succeeding minimum of the resting temperature during the two time cycles starting one puff before the highest temperature puff is at least about 50°C. , preferably at least about 150°C.

The best results are attained by the use of magnesium citrate as the hydrated metal compound to lower the burning rate of the oxidized cellulose tobacco substitute. Other hydrated metal compounds are magnesium sulfate heptahydrate, sodium sulfate, hydrated alumina and calcium tartrate. It will be understood that, like magnesium citrate, the other burning-inhibiting hydrates may be used with burning-sustainers, flavoring agents, carbohydrate ethers, humectants, nicotine, ammonium compounds, or other modifying agents, individually or in any combination.

In the practice of this invention, the proportion of the hydrated magnesium sulfate or magnesium citrate is desirably in the range of about 2 to 25%, preferably about 5 to 12%, based on the total air dry weight of the tobacco substitute. The proportion of the salt which is a burning-sustainer is desirably in the range of about $\frac{1}{2}$ to 5%, preferably about 1 to 4%, based on the total air dry weight of the tobacco product. The amount of flavoring agent is desirably in the range of about 0.001% to 10%. The amount of flavor formulation to be added is determined organoleptically, by trial, and may be readily distinguishable or not apparent. In the latter case, the cigarette may be more agreeable as a result of the added flavor even though it is not identifiable. The proportion of carbohydrate ether, when used, is desirably in the range of up to about 20%, preferably about 5 to 10%, based on the total air dry weight of the product. The proportion of humectant is desirably in the range of about 1 to 10%, based on the total air dry weight of the product. The proportion of nicotine, when used, is desirably in the range of up to no more than 2%, preferably about $\frac{1}{100}$ to $1\frac{1}{2}\%$, based on the total air dry weight of the product. The amount of the ammonium compound, when used, is desirably in the range of about $\frac{1}{2}$ to $2\frac{1}{2}\%$, preferably about $\frac{1}{2}$ to 1%, calculated as NH_3 , based on the total air dry weight of the product. A suitable proportion of coloring agent, when used, is desirably in the range of about 0.1 to 3% preferably about $\frac{1}{5}$ to 1%, based on the total air dry weight of the product.

The oxidized cellulose should be combined intimately, preferably impregnated, with the additive or additives to be

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employed. This may be done conveniently by impregnating a sheet of oxidized cellulose with a solution, dispersion or emulsion of the additives, which may be applied separately or all together, followed by drying and shredding the sheet or cutting it into strips. If desired, a sheet may be cut into strips or shreds and sprayed with a solution or dispersion of the additive or additives and then aged or tumbled to assist in the uniform distribution of the additive material on the cellulose, and thereafter dried. All or any part of the additive material may be incorporated into the oxidized cellulose in the course of a paper-making operation. One convenient way of doing this is by incorporating the water-soluble additive material into a slurry of oxidized cellulose, then forming the slurry into a sheet on a conventional paper-making machine, thereafter treating the sheet, preferably while still wet, with a solution or emulsion of non-water soluble materials and of the more expensive water-soluble constituents (e.g. nicotine), followed by drying and shredding. Alternatively a mass of oxidized cellulose may be blended directly with the additive material, in dissolved, emulsified, or finely divided dry condition, the mixture being then formed into the desired shape (e.g. by extrusion), dried and cut.

For best results, freshly prepared oxidized cellulose should be used.

The cut or shredded tobacco substitute may be processed like tobacco on the usual cigarette-making machines, such as those shown in U.S. Patent Nos. 1,787,551; 2,190,032; 2,208,504; 2,247,413; 2,236,579; and 2,671,452.

The cut or shredded tobacco substitute may be smoked by itself, however, it may also be blended with cured tobacco, with tobacco extract, or with any of the various reconstituted tobaccos. This blending may be effected by any of a variety of ways known in the tobacco blending art. The proportion of tobacco thus blended with tobacco substitute may be in the range of about 5 to 75%, for example. When the proportion of tobacco is considerable, e.g. over 50%, it may be desirable to decrease the proportion of nicotine, flavoring agents and carbohydrate ether used in the tobacco substitute.

By practice of this invention I have been able to make cigarettes which when smoked produces in the smoke less total condensate and total phenols as compared with conventional non-filter cigarettes, and which displays in vapor phase analyses relatively lesser amounts of the major molecular components reported to be harmful substances in the smoke of conventional non-filter cigarettes. A series of tests have been conducted which ably demonstrate the improvement made by my cigarettes in these respects, one series of tests being determination of phenolic compounds in the smoke condensate, and the other series being vapor phase determinations from a predetermined puff. The cigarettes employed in these determinations were prepared essentially as is described in Example I appearing hereinafter using substantially the formulation appearing therein.

The phenol determinations were conducted using generally the techniques described by D. Hoffman & E. L. Wynder, *Beitrage zur Tabakforschung*, No. 3, pp. 101-106 (1961), and a smoking machine substantially as disclosed by A. O'Keefe and R. Lieser, *Tobacco Science*, 2, 73 (1958) was employed therein. A 2-second puff of 35 cc. volume every 30 seconds was employed. The mainstream cigarette smoke was condensed on a glass fiber filter pad at room temperature, located between the smoking machine cigarette holder. All cigarettes, regardless of length, were smoked to a 25 millimeter butt, and also were conditioned and smoked at 60 percent relative humidity at 72°F.

The cigarettes were screened by weight prior to smoking; cigarettes weighing within ± 0.03 gram of the average cigarette weight were selected. Each determination of phenol in the smoke consisted of smoking 5 cigarettes on a single smoking machine position, and collecting the total condensable material in a single trap. The total condensate weight was obtained from the difference in pad weight

before and after smoking. Aqueous sodium hydroxide solution (5% NaOH) was then added to the pad to remove the condensate.

A Perkin-Elmer Model 226 Gas Chromatograph was used in the analysis of the phenolic fraction of the smoke condensate. This unit is equipped with a flame ionization detector. Chromatograph separation of the phenolic fraction of the condensate was achieved with a 100 foot Golay (capillary) column having a 0.02 inch internal diameter coated with a 85/15 mixture of Cellulube 550/Empol Dimer Acid.

Like procedures were followed with a quantity of known non-filter cigarettes, and the following tabulation clearly demonstrates the markedly lower total phenol and cresol content, as well as the lower total condensate, of the instantly disclosed smoking material:

Compound	Conventional non-filter cigarette	Oxidized cellulose cigarette
Phenol.....	78	7.5
o-Cresol.....	17	1
p-Cresol.....	28	1
m-Cresol.....	14	1
Total phenol plus cresols.....	137	-----
Condensate, total (wet).....	45	15

In the above table, the value for total phenol and cresols is measured in micrograms per cigarette, while condensate is measured in milligrams per cigarette. The total wet condensate is collected and weighed at room temperature and includes water of combustion.

The second series of determinations, namely vapor phase analyses from puffs comparable to the fifth puff from a conventional cigarette were conducted by locating a sampling valve in the line between the glass fiber filter pad and the chromatograph.

The results of these extensive studies are summarized in the chart of FIGURE 3 of the present application drawings. This is a precise reproduction of typical chromatograms obtained from the vapor phase of the smoke from the two types of cigarettes discussed herein. The major molecular components are listed thereon, and the relative amounts present in the substantially comparable puffs are proportional to the peak areas displayed.

It is observed that the light hydrocarbons such as methane, ethane and the like are much lower than a commercial non-filter cigarette, which is indicative of a more complete combustion epoch. Notably, isoprene is barely detectable. This highly reactive compound in both chemical and physiological systems, is a known precursor of known toxins, as well as carcinogenic polynuclear substances. Similarly, a much lesser amount of acetaldehyde was found to be present. As is known, acetaldehyde has been reported to have a synergistic effect with acrolein, which is a harmful component of cigarette smoke in inhibiting normal ciliary activity. A publication on this point is Inhibitory Effects of Tobacco Smoke on the Ciliary Activity of the Respiratory Epithelium and the Nature of the Compounds Responsible by R. Guillermin, R. Badre and B. Vignon.

The following examples are given to illustrate this invention further.

EXAMPLE I

A synthetic smoking material was made from oxidized cellulose ("Oxycel" sold by Parke, Davis & Co. and described in Kenyon et al., Industrial and Engineering Chemistry 41, 2 et seq. (1949)). The oxidized cellulose in gauze form impregnated with an aqueous solution of magnesium sulfate, potassium chloride, glycerol, ammonium sulfamate, and an F. D. & C. certified brown color, followed by drying, then impregnated with a solution of ethyl cellulose (Dow Ethocel standard, 48-49.5% ethoxy, 7 cps. viscosity) and nicotine, dissolved in a mixture of 80% toluene and 20% ethanol (by volume). The product was air-dried and conditioned at 71% R. H. The

analysis of the resulting product (on an oven-dry basis, excluding water of hydration) was

	Percent
Oxycel	69.1
MgSO ₄	8.6
KCl	5.2
Ammonium sulfamate	1.5
Glycerol	3.0
Ethyl Cellulose	11.3
Nicotine	1.3

The conditioned product was shredded by hand to form fibers 4-8 mm. in length and rolled into a standard size cigarette weighing 0.9 g. and 70 mm. long. The smoke was mild; analysis of the tar from the cigarette main stream smoke gave no indication of sulfate present, using a method whose detection limit was about 0.02 mg. of SO₄.

EXAMPLE II

Example I was repeated, except that household vanilla extract and Alva G-327 (a commercial tobacco flavoring agent sold by Van Ameringen-Haebler Ind.) were incorporated into the aqueous and organic impregnating solutions, respectively.

EXAMPLE III

Cellulose gauze was oxidized with nitrogen dioxide until the oxidized cellulose had a carbon content of 36.2%, a hydrogen content of 4.97% and an oxygen content (by difference) of 58.5%; the solubility of this material was such that when 2% thereof were added to a 0.5 molar aqueous solution of magnesium sulfate at room temperature a clear colloidal solution was formed. This oxidized cellulose was treated, to make a cigarette, in the manner described in Example I.

EXAMPLE IV

100 parts of "Oxycel" gauze (as in Ex. I) was dipped in a toluene-ethanol (80-20) solution containing 4% Ethocel (as described in Ex. I) 2% nicotine and 2% of a Havana tobacco flavor (Sheinker & Son). After air drying the weight of the resulting gauze was 158.8 parts. The product was shredded and rolled in cigarettes. The smoke was pleasing and especially mild. The product was also blended with an equal weight of cured tobacco. A cigarette made from this blend had a pleasing smoke.

EXAMPLE V

Example IV was repeated, using half the amount of KCl and no ammonium sulfate.

EXAMPLE VI

Example V was repeated using as the flavoring agent "Apple Tobacco" (Sheinker & Son) and "Blackberry bark extract" (Amend Drug & Chem. Co.) respectively.

In the above examples, the cigarette paper used was a standard non-porous cigarette paper (e.g. "Yorkshire" paper sold by Sears, Roebuck and Co.). If desired micro-perforated cigarette paper, well known to the cigarette art, may be used instead.

In the above specification the proportions are given in terms of the compounds supplied, disregarding any possible reactions between said compounds.

EXAMPLE VII

25 grams of wood pulp was heated in one liter of carbon tetrachloride, the water trapped from the azeotropic reflux, the slurry was cooled to about 14° C., a solution of nitrogen tetroxide in carbon tetrachloride was added and the slurry was stirred for 24 hours at 14 to 15° C. The reaction was stopped with methanol and the oxidized pulp was washed thoroughly and dried. Since it is somewhat difficult to form such oxidized cellulose products into hand paper sheets because the fibers do not readily mat and stick together, a slurry of the pulp was made in a polyethyl acrylate emulsion containing about

1.6% solids, followed by pressing and drying. The hand sheets were then dipped in the following formulation:

	Wt. percent
Mg citrate·4H ₂ O	8.06
NH ₄ HCO ₃	1.2
KHCO ₃	0.9
Sorbitol (70%)	1.1
Nicotine	0.69
Color	0.32
Flavor	0.035
Water	88

The treated hand sheets were shredded and made into cigarettes. The cigarettes burned well and the smoke was found to be quite pleasant.

EXAMPLE VIII

A sample of oxidized cellulose in fibrous form was made by oxidation with nitrogen tetroxide at 160 C., following generally the procedure described in the preceding example. This contained 43.5 meq. carboxyl groups per 100 grams of material, and assuming that all carboxyl groups resulted solely from oxidation of the pendant hydroxymethyl groups of cellulose, this material is about 74.8% oxidized.

The oxidized cellulose was mixed with an equal amount on a dry basis of highly beaten wood pulp having a Canadian Freeness about 300 ml., and a slurry was formed with water. The 50:50 blends of cellulose and oxidized cellulose were made into small paper sheets measuring about 8½ x 8½ inches, and dried. The sheets had ample strength for normal handling, and the dried sheets contained 16.5 meq. carboxyl groups per 100 grams product, which is equivalent to 29.1% oxidation. The hand sheets were then dipped in an aqueous solution of the following additives, pressed between rubber rollers and dried. The formulation of the dipping solution was as follows:

Citric acid	g.	35.3
Mg.O	g.	11.3
Nicotine	g.	4.0
Brown color	g.	1.3
Yellow color	g.	0.5
Sorbitol (70%)	g.	40.0
Water	ml.	780

If desired, the wet strength of the sheets may be improved by dipping them in a solution of ethyl acrylate in methylene dichloride. Such a solution contains about 1.4 grams polyethyl acrylate per liter of solution. After dipping, the sheets were air dried and equilibrated with moisture by hanging in an environment having a relative humidity of about 3%. The product contained by weight 0.5 to 0.9% polyethyl acrylate, 14 to 17% additives, and about 82 to 85% of the cellulose and oxidized cellulose blend. The sheets were cut into strips about ⅛ inch wide and about ⅛ to ½ inch long, and after humidifying the material was rolled into cigarettes.

Two groups of cigarettes were made, one containing only the material described in this example and the other was a 50:50 blend by weight of this same material with tobacco taken from a conventional non-filter cigarette. The cigarettes were 70 mm. in length, each contained about 0.5 to 0.9 grams of smoking material, and the pressure drop was found to be about 30 to 100 mm. water at an air flow of 17.5 ml./second.

Both types of cigarettes were smoked and were found to be comparable to all-tobacco cigarettes in mildness.

EXAMPLE IX

Sheets were made which analyzed about 30% oxidized cellulose from two grades of pulp with and without polyethyl acrylate, and were made into cigarettes with and without tobacco (50-50 blends). The cigarettes were smoked by an organoleptic panel to evaluate the variation produced by pulp source and the effects of polymer addi-

tive, as well as the effects of the tobacco additive. Additives were incorporated by dipping the sheets in the solution of Example VIII. Polyethyl acrylate was added to some sheets prior to salt addition by dipping the sheets in a solution of polyethyl acrylate in methylene dichloride (1.5g. polymer per liter). The finished product was shredded and rolled into cigarettes. Some of the finished product, after shredding, was blended with an equal weight of shredded cured tobacco and rolled into cigarettes.

Cigarettes were submitted to the panel for smoking evaluation which were substantially alike except for the source of the pulp. The panel unanimously agreed that high alpha (96%) pulp is preferred to paper grade (85-87%) on basis of mildness of the smoke. The panel also felt that the addition of polyethyl acrylate contributes to the flavor and the smoke is not harsh. Further, the panel agreed that wholly synthetic cigarettes provide a smoke which is substantially less harsh than a 100% tobacco, and the 50-50 blend, while retaining some of the harshness of tobacco, gives a milder smoke.

In the above examples, the cigarette paper used was a standard non-porous cigarette paper exemplified by the "Yorkshire" paper sold by Sears, Roebuck & Co. If desired, micro-perforated cigarette paper well known to the cigarette art, may be used instead.

In the above specification the proportions are given in terms of the compounds supplied, disregarding any possible reactions between said compounds.

It is to be understood that the foregoing detailed description is given merely by way of illustration, and that many variations may be made therein without departing from the spirit of my invention.

The embodiments of the invention in which an exclusive property or privileged is claimed are defined as follows:

1. A tobacco substitute constituting a smoking composition consisting essentially of a non-tobacco oxidized cellulose derived from oxidized cellulose gauze or oxidized wood pulp and comprising a polymer of anhydroglucuronic acid, said oxidized cellulose carrying an impregnation of between 2 to 25% by weight of a non-toxic hydrated metal compound designed to control the burning rate of the composition, said smoking composition delivering upon combustion in cigarette form reduced amounts of light hydrocarbons, isoprene, acetaldehyde, phenols, creosol and less total condensate as compared to an average conventional non-filter tobacco cigarette.

2. The tobacco substitute of claim 1 in which the hydrated metal compound is selected from the group consisting of magnesium citrate, magnesium sulphate, hydrated alumina and calcium tartrate.

3. The tobacco substitute of claim 1 in which the composition include a combustible alkyl ether of a carbohydrate which serves to bond the additive to the oxidized cellulose as well as to lead to a more even distribution of the burning area.

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MELVIN D. REIN, Primary Examiner

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