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3,459,195

REINFORCED RECONSTITUTED TOBACCO SHEET

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1 Claim

ABSTRACT OF THE DISCLOSURE

The present disclosure relates to a reinforced reconstituted tobacco sheet comprising a web of treated cellulose having adhered thereto from 1 to 20 parts by weight of particulate tobacco per part of said treated cellulose, said reinforced reconstituted tobacco sheet being such that when it is incorporated into a cigarette said cigarette has a static burning rate of not less than 2 millimeters per minute and not more than 5 millimeters per minute, the treated cellulose comprising oxidized cellulose.

This invention relates to tobacco compositions and methods of producing such compositions. More particularly, the invention relates to improved reconstituted tobacco sheets which are reinforced in such a manner that their physical properties are greatly improved without the decreases in smoking qualities.

During the production and processing of tobacco products, including aging, blending, sheet forming, cutting, drying, cooling, screening, shaping and packaging, considerable amount of tobacco fines and tobacco dust are produced. It is known that such tobacco fines and dust can be combined with a binder to form a relatively coherent sheet, which resembles leaf tobacco and which is commonly referred to as reconstituted tobacco. Various methods have been employed for making reconstituted tobacco of this general character. For example, one method for making reconstituted tobacco is disclosed in United States Patent 2,734,510 wherein the tobacco fines and dust are applied to a binder made of carboxymethyl cellulose, carboxymethyl hydroxyethyl cellulose or a suitable salt thereof. Other patents, such as United States Patent 2,708,175 and United States Patent 2,592,554 described various other binders which may be used in the production of reconstituted tobacco. There are also numerous other methods which have been employed for the production of reconstituted tobacco.

All of the presently known methods for producing reconstituted tobacco, however, involve the production of reconstituted tobacco sheets which would be improved if there were some way of further increasing their strength, without deleteriously affecting any of their other desirable properties. Many reconstituted tobacco sheets, produced in accordance with the teachings of the prior art, have been found to be undesirably weak, both during the actual steps involved in their preparation and during the processing steps involved during their incorporation in smoking products.

One method which is used in the trade for producing sheet from tobacco scraps is to reduce the tobacco to dust, to lay down a layer of this dust, and to apply to it a layer of liquid binder solution or suspension, on top of which another layer of dust is laid. Sometimes, a second layer of binder and a third layer of dust are applied, the resulting sheet is lacking in strength and must be handled with great care. If it is made too

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thick, it will not have a tobacco-like appearance and is likely to burn improperly.

I have discovered that a reinforcing base in the form of a gauze or web may be used on which to apply tobacco dust, to form a reconstituted tobacco sheet of good strength and filling power and to result in a smoking product having an acceptable smoke flavor. I have also found that the novel products produced in accordance with my invention, when smoked, produce smoke which contains smaller amounts of certain of the less desirable components found in tobacco smoke than the smoke which results from the usual reconstituted tobaccos or the smoke which results from natural tobacco.

My invention comprises using, as a base for reconstituted tobacco sheets, a gauze or web of cellulose which has been treated in such a way that its combustion and pyrolysis characteristics are modified. This modification is evidenced by a reduction in the static burning rate of the resulting product, as will be discussed in more detail below.

Cotton (cellulose) gauze will burst into flame, under ordinary conditions, when it is ignited. By appropriate lowering of the burning rate of the cellulose, for example, by oxidizing the cellulose or by the application of certain flameproofing agents to the cellulose, or by impregnating the cellulose with tobacco solubles, the web of treated cellulose can be combined, as will be described in more detail below, with tobacco parts to make a reconstituted tobacco product which will glow or burn at a rate similar to the burning rate of ordinary tobacco filler.

The lowering of the burning rate of the treated cellulose web to be employed in accordance with the present invention, should be such that the static burning rate of a cigarette produced in accordance with the present invention, and including the treated cellulose in combination with tobacco in the amounts specified below, will be more than 2 millimeters per minute. The static burning rate of a cigarette (non-filter with an RTD of 1.8–2.8 inches of water) containing oxidized cellulose or cellulose treated with flame retardants, the cellulose not being in combination with tobacco, will be 2 millimeters per minute or less up to the point where no burning will occur. The static burning rate is the burning rate, without any puffing, of a standard size cigarette and is defined as the millimeters of cigarette which are burned per minute, when the test cigarette is statically burned in a controlled draft cabinet. By comparison, the static burning rate of commercially available cigarettes is approximately 4 to 5 mm. per minute.

While an excess of the treating reagent may be employed to reduce the static burning rate of the cellulose even further below the 2 mm. per limit level, it is preferred that only sufficient reagent be employed to decrease the static burning rate to approximately 2 mm. per minute.

Particulate tobacco, for example, tobacco which has been pulverized and which has been homogenized in water, or tobacco which has received an enzyme treatment in accordance with the teachings of U.S. Patent 3,240,214, or tobacco which has been slurried with an added binder, is applied to said gauze. The tobacco material may be applied to one or both sides of the base gauze by rolls, by a spray, or by a dip, after which the resulting sheet is dried.

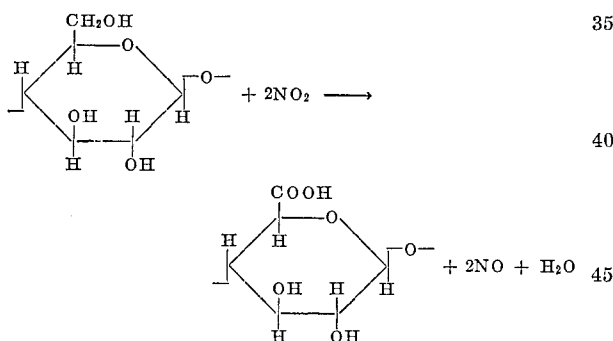
Such products have been found to be self-supporting even before drying. They can be cut into sheets for shredding into filler for smoking articles or rolled for use as cigar binder. They have also been found to have the strength to permit shredding, blending, cigarette making and any other necessary handling. They have good filling power, when shredded as cigarette filler, and good smoking qualities. They also provide a light, sweet smoke,

which may be less harsh than that of most commercial reconstituted tobacco.

The cellulose web which is employed in the present invention may be either woven or non-woven, but is preferably of a thin, open construction, having, for example, a weight of from 14 to 45 g./sq. yd., and having from 15 to 50 threads per inch, if woven. The mesh size of the gauze should be sufficiently coarse for a tobacco slurry to penetrate at least partially into the interstices of the web. This affords a more intimate mixture of the tobacco material with the cellulosic matrix and results in a better adhesion of the tobacco to the matrix. The mesh size also should be sufficiently fine so that reinforcement is still attained for the material in the shredded form. Each shred of the reinforced tobacco in a cigarette should, preferably, contain some reinforcing cellulosic material. If the weaves are too open, too many shreds containing no reinforcing matrix might result. One gauze which has been satisfactorily employed had 18 weaves per inch and weighed 18 g. per sq. yd., another gauze which has been satisfactorily employed had 42 weaves per inch and weighed 39 g. per sq. yd.

If oxidation of the cellulose is to be employed, an agent such as nitrogen dioxide is selected which will produce carboxyl groups without seriously affecting the mechanical properties of the material. The oxidation or other treatment may be applied either before or after the web is formed. The carboxyl content may be from 10 to 24% after oxidation.

The oxidation technique which may be employed is preferably the oxidation of cellulose by nitrogen dioxide which occurs mainly according to the following equation:



The following description is an illustration of the preparation of oxidized celluloses which are suitable for use in accordance with the present invention:

Commercial nitrogen dioxide was introduced into a reaction vessel containing cellulose. The ratio of NO_2 to cellulose was chosen between 1:1 and 7:1. The vessel was closed and the reaction was allowed to take place at room temperature for from one to 10 days. At the end of this time as much nitric oxide (NO) and excess nitrogen dioxide (NO_2) as possible were removed by evacuation. The oxidized cellulose was taken out of the vessel and plunged into distilled water, after which it was washed with numerous changes of distilled water and dried. Its nitrogen content was found to be between 0.05 and 1.0% and its carboxyl content was found to be between 10 and 22% by weight.¹ The theoretical maximum carboxyl content, assuming that only the one hydroxyl group per anhydroglucose unit in the above equation is oxidized, would be 25.6%. The procedure for the oxidation of cellulose by nitrogen dioxide has been described in the literature, for example, in *Methods in Carbohydrate Chemistry*, volume III, Roy L. Whistler, editor, Academic Press, New York 1963, pp. 168-172. One type of oxidized cellu-

¹ At a carboxyl content above 22% the oxidized gauze loses tensile strength.

lose which is commercially available may be obtained from Eastman Chemical Products Inc., Kingsport, Tenn.

Oxidized cellulose prepared in the above manner, and containing 20% carboxyl groups has been subjected to thermal degradation and the weight loss has been compared as a function of the temperature. The following procedure was followed. A 10 g. sample was weighed into an aluminum dish, placed in a vacuum oven, heated up to the desired temperature and kept one hour at this temperature. The sample was then removed from the oven and weighed again. The experiments were performed under vacuum or by passing air, nitrogen or argon, through the oven. The results of the experiments are summarized in Table I. As can be seen from Table I below, oxidized cellulose is converted at 200° mostly into volatile products, while the cellulose is barely degraded.

TABLE I

Material	Weight before experiment (g.)	Residual weight after one hour at 200° C. in air, nitrogen, argon or vacuum (g.)
Cellulose (Johnson & Johnson Co. Steripad-cotton gauze)-----	10	9.0-9.5
Oxidized cellulose 20% carboxyl (Eastman Co. gauze)-----	10	3.0-3.5

It can be seen from Table I that, unlike cotton cellulose, oxidized cellulose yields very little tar on pyrolysis. The gaseous products from the pyrolysis of oxidized cellulose have been identified as consisting mainly of H_2O , CO_2 and CO . It can also be concluded from Table I that oxidized cellulose, while conferring mechanical strength to the unlit product, is degraded at temperatures below the burning temperature of tobacco in a cigarette into more favorable volatile products and into less tar than cotton cellulose. For example, as is demonstrated in Example 5 which appears hereinafter, oxidized cellulose in a cigarette delivers less than half the amount of acetaldehyde and about a tenth the amount of benz(a)pyrene as compared to cellulose.

If flameproofing of the cellulose is to be employed, some of the flameproofing agents which may be used to treat the cellulose base, in accordance with the present invention, are diammonium phosphate, tetrakis (hydroxymethyl) phosphonium chloride (also referred to as THPC), phytic acid, ammonium sulfate, diammonium phosphate with urea, and pentaerythritol with phosphoric acid.

When cotton is treated with one of the many commercially available flame retardants, such as the retardants mentioned above, then shredded and blended with tobacco into a cigarette, it does not participate in the combustion and has many undesirable properties. For example, the cigarette does not burn evenly, the ash does not hold together. Cotton treated with flameproofing compounds and coated with tobacco and thereafter shredded, gives a more satisfactory smoke. The reason seems to be that the tobacco portion furnishes the heat for combustion while the cotton treated with flame retardants pyrolyzes in a manner different than untreated cotton. The various reaction mechanisms which take place are very complex. Flameproofing agents are believed to act by a coating effect, by a thermal effect, by a gaseous effect and/or by a chemical effect. In the context of this invention, it is of importance that the flameproofing compounds are nontoxic and do not produce undesirable or toxic volatiles upon pyrolysis. It is also of importance that the application of desirable flame retardants to cellulose decreases the amount of tar and increases the amounts of gas and char from the cellulose formed on pyrolysis. A desirable flame retardant according to my invention incorporates strength to the unlit reconstituted tobacco; during combustion the flame retardant increases the amount of ash, without causing the static burning of cigarettes made employing the flame retardant treated

tobacco to stop and without releasing undesirable gaseous or undesirable particulate compounds, i.e., tar. The following general classes of compounds may be employed as flame retardants within the context of my invention: Boric acid and borates; chlorides, phosphates, sulfates, bromides, fluorides, formates and carbonates of the following metals: calcium, magnesium, aluminum, lithium, zinc, potassium, sodium, barium and strontium, as well as ammonium. Organic flame retardants containing phosphorous may also be used.

When a flameproofing agent is used, it is applied to the cellulose in an amount comprising from about 1 to 30% by weight, based on the cellulose, and it may be applied by one of the many processes which are used for the flameproofing of cellulosic material. For example, a solution of the flameproofing reagent is added to the cellulose matrix by immersion of the cellulose into the solution, the excess solution is removed by squeezing or centrifuging, the product is dried at 45° to 109° C., and is then cured, if necessary, at 110° to 170° C. As an illustration, the cellulose-phosphate-urea reaction was brought about by following essentially the method described by A. C. Nuessle, F. M. Ford, W. P. Hall and A. L. Lippert (Textile Research Journal, volume 26, 1956, p. 32). The cellulosic fabric was immersed in a water solution containing between 4 and 40% urea and between 2 and 20% $(\text{NH}_4)_2\text{HPO}_4$, squeezed, dried and baked 10 min., at 150° C., washed in water to remove unreacted materials, and dried.

In other instances a solution of the reagent was added to the cellulose matrix by immersion, whereupon the treated cellulose was squeezed and dried at 45° C. in a forced air circulation oven before the application of tobacco. Other treatments will be described in the examples which appear later in this specification.

The flameproofing agent is not generally employed with oxidized cellulose, although combinations of flameproofed cellulose and oxidized cellulose may be employed.

If intimate mixing of the cellulosic matrix with tobacco solubles is to be employed, the cellulosic matrix can be immersed in tobacco solubles or the tobacco to be applied to the matrix can be processed as to release solubles into the matrix.

Tobacco solubles can be obtained by extracting tobacco with water, alcohol or other suitable solvents. Another way of releasing tobacco solubles besides extracting which I used was the treatment of tobacco material with enzymes that can break down the cell walls. It was found that by using catalytic amounts of enzyme, for example, preparations having cellulase, hemicellulase and pectinase activity, the tobacco solubles inside the cells are released and no unfavorable aroma is imparted to them. At the same time, a tobacco slurry is obtained that can easily be applied to a cellulosic matrix and adheres well after drying. When tobacco solubles are employed in accordance with the present invention, the water or alcohol soluble extract is obtained by washing tobacco at a temperature of from about room temperature to 100° C. for example, for a period of from about 5 to 120 minutes, and should be applied to the cellulose in amounts of from 1 to 20% by weight based on the cellulose. It may be applied by immersing the cellulose matrix in a solution of tobacco solubles, by spraying or the like.

The tobacco dust may be prepared from any stems, (i.e., tobacco leaf midribs), scraps, fines or combination of these, and is preferably pulverized to pass at least a 50-mesh screen but with no limit on fineness. With the proper choice of a coating system, larger mesh size, for example —10 mesh tobacco, could be utilized. The dust may be slurried in water with an enzyme having cellulase, hemicellulase, and pectinase activity, the pH being adjusted to 4.2–5.0, for example, with citric acid, if necessary, and the slurry may be digested either for 3 to 20 hours at room temperature or for ½ to 12 hours between about 45° C. and about 80° C. In a different

procedure, the tobacco slurry without enzyme may be homogenized, that is, milled to much finer dimensions (e.g., in a Manton-Gaulin homogenizer). Alternatively, a binder may be added to the slurry. Such binders as are commonly used in preparing reconstituted tobacco include natural gums, pectins, methyl cellulose and carboxymethyl cellulose. Usually, a humectant such as glycerol, propylene glycol, or triethylene glycol is added, but its presence is not essential; humectants from 0 to 10% of the tobacco weight may be used.

The tobacco slurry may be applied to the treated gauze by any of the known methods such as casting, rolling, spraying or dipping, and may be applied to one or both surfaces. The resulting tobacco-containing sheet may then be dried by conventional means, for example, in small scale operations by air at room temperature or by air drying at a more elevated temperature, such as 45° C. to 80° C., until the moisture content is brought to the proper level, which is approximately 11 to 14% by weight. In large scale commercial operations, with forced air circulation at a temperature of from about 315° C., a drying time of about one minute or less will, generally, be sufficient. The finished sheet appears uniform, smooth, medium to dark brown in color.

The finished product may be shredded by conventional means and, after being shredded, may be mixed with tobacco for use as cigarette filler. It may also be used unblended, in which case it is necessary that the treated cotton portion of the reinforced reconstituted tobacco sheet comprises 5 to 50% by weight and, preferably, from 10 to 35% by weight, according to the degree of resistance-to-burning possessed by the treated cotton, in order that the shredded reinforced reconstituted tobacco sheet support combustion. If the product is to be blended with tobacco, or used as a cigar binder, the proportion of reinforcement may be higher, up to 70% of the sheet.

The following examples are illustrative:

Example 1

Cotton gauze was oxidized by dry nitrogen dioxide by the method which has been described in the literature (E. C. Yackel and W. O. Kenyon, J. Am. Chem. Soc. 64, 121–127 (1942)). Cotton gauze, "Steripad" brand 50 g., produced by Johnson and Johnson Co. was packed loosely in a reaction flask. From a supply of about 100 g. of nitrogen dioxide, nitrogen dioxide vapor was circulated over the gauze in the reaction flask. The vapor leaving the reaction vessel passed to a water-cooled condenser and was returned as unreacted nitrogen dioxide to the supply flask. After an initial slight temperature rise, the reaction vessel returned to room temperature (23° C.). This procedure was continued for about 15 hours; nitrogen oxides were then removed from the gauze by a flow of air, and the product was rinsed rapidly in distilled water until the washings were no longer acidic, and dried in air.

A dust of pulverized tobacco containing stem and leaf was slurried in water with 0.1% of the tobacco weight of Cellulase 35 enzyme² and digested overnight. The slurry was stirred rapidly and was cast on oxidized cellulose gauze taped to a glass plate to give a sheet which, after drying to 12% moisture, contained 68% tobacco materials. This sheet, 0.017 in. thick, had a tensile strength of 4.0 kg./sq. in., an elongation of 7.8% and a work-to-break of 577 g. cm./sq. in. (Work-to-break is the work required to elongate and break a unit cross-section of sheet.) A commercial reconstituted tobacco product prepared from similar tobacco scrap was 0.012 in. thick, had 0.51 kg./sq. in. tensile strength, 2.8% elongation, an work-to-break of 22.4 g. cm./sq. in. Sheet cast from the treated tobacco dust without reinforcement was 0.007 in. thick, had a tensile strength of 0.39 kg./sq. in., an elongation of 5.0% and a work-to-break of 33.0 g. cm./sq. in.

² Cellulase 35 enzyme is produced by Rohm and Haas Co., Philadelphia, Pa. and is a mixture of polysaccharases including cellulase, pectinase and hemicellulase.

The reinforced sheet handled well, and shredded without excessive breakage to give a filler which, when smoked, had good aroma and mild taste.

It can be seen from the above that reconstituted tobacco reinforced by oxidized cellulose gauze has greater mechanical strength than the commercial reconstituted tobacco material presently used in cigarette filler. This mechanical strength is due to the cellulosic matrix rather than to the tobacco slurry which, when cast on glass plates, has been found to produce sheets of about the same mechanical strength as a commercial reconstituted tobacco material.

Example 2

In a one-gallon "Waring Blendor" container, 0.2 g. of Cellulase 35 enzyme was added to 2000 ml. of water. After brief stirring to dissolve, 200 g. of -50 mesh dust of tobacco by-products, composed of 50% bright stems and 50% leaf blend, was added and stirred to disperse. The pH was adjusted to the range of 4.2-5.0 by adding approximately one g. of citric acid monohydrate; of glycerine, 10 ml., was added as humectant. The slurry was allowed to stand three hours at room temperature. It was stirred at maximum speed for one minute and the thick slurry was diluted with water as required for casting.

A piece of commercial oxidized cellulose gauze (having a carboxyl content of 19%, and produced by Eastman Chemical Products, Inc., Kingsport, Tenn.) weighing 11.5 g. was stretched and taped on a glass plate.

A portion of the slurry of tobacco dust was cast on the gauze, and the combination was dried in a forced-air circulation oven at 45° C. for three hours. The finished sheet (comprising 33% cellulosic base) which was stripped off the glass plate weighed 34.5 g.

As control sheets were cast from another portion of the slurry without support and the sheets were dried at 45° C., the sheets were shredded and made into cigarettes each of which was 65 mm. in length and had a resistance-to-draw (RTD) of 1.8-2.2 in. of water. The resulting cigarettes were presented to a smoking panel consisting of five expert smokers. The panel found the product of the invention to have a very mild and sweet smoke. The comparative results which were found are given in Table II.

TABLE II.—SMOKING EVALUATION OF RECONSTITUTED TOBACCO CIGARETTES

	Enzyme-treated and cast tobacco dust, control	Enzyme-treated tobacco dust on oxidized cellulose
Percent cellulosic reinforcement.....	0	33
Cigarette wt., g.....	1.6	1.2
Resistance-to-draw (RTD) ¹ (inches water).....	1.8-2.2	1.8-2.2
Panel result.....	Very harsh	(²)

¹ RTD is defined as the pressure drop across a cigarette, expressed as inches of water, when air flows through the cigarette at a velocity of 1,050 ml./min. To determine this pressure difference, one end of the cigarette was inserted into a specially designed tube through which air was drawn. The pressure difference between the open and enclosed ends of the cigarette was measured.

² Very mild, high in basic sweet.

Example 3

In a similar manner to that described in Example 2, a tobacco slurry in enzyme solution was made up. A portion of the slurry was cast on "Steripad" cotton gauze weighing 20.0 g. to give a sheet which, when dry, weighed 107.5 g. A portion of the slurry was cast on commercial oxidized cellulose gauze weighing 14.5 g. to give a sheet weighing 51.0 g. when dry.

The resulting sheets were shredded and each was blended with an equal weight of a commercial cigarette tobacco. Cigarette rods made from these blends were 65 mm. long, weighed 1.1 g., and had resistance-to-draw of 2.0 to 2.2 inches of water. Commercial 20-mm. cellu-

lose acetate filters were attached to the rods and the resulting cigarettes were smoked unidentified in a paired comparison test by an expert panel of five members. The opinion of the panel was that the smoke from cigarettes made using oxidized cellulose was more tobacco-like and thinner than the smoke made from cigarettes using "Steripad" gauze. (See Table III.)

TABLE III.—SMOKING PANEL EVALUATION OF BLENDS OF RECONSTITUTED TOBACCO

	Enzyme-treated tobacco dust on cotton gauze and tobacco	Enzyme-treated tobacco dust on oxidized cellulose and tobacco
Percent cellulosic reinforcement.....	9	14
Panel result.....	More sour and woody, more overall harsh- ness.	More hay-tobacco, more thin- bodied, more metallic.

Example 4

Hand-made filter cigarettes of same make-up (identical filter, same RTD) were prepared and submitted to a panel of five expert smokers.

In one set of experiments increasing amounts of Whatman No. 1 cellulose powder was added to a homogenate of cigarette tobacco. In another set of experiments increasing amounts of Steripad cotton gauze shreds (cellulose) was added to cigarette tobacco. The results of the panel evaluation are summarized below. It can be seen that high amounts of cellulose powder intimately mixed with tobacco solubles can be tolerated while already small amounts of gauze shreds produce an undesirable harsh smoke.

COMPARISON OF SMOKE FLAVOR PROFILES

Control	Experimental
100 parts of homogenized tobacco blend, no added cellulose.	100 parts of homogenized tobacco blend 80 parts cellulose powder; less taste less burnt, less mouth harshness less astringent, more throat harshness.
100 parts of tobacco blend, no added cellulose.	100 parts of tobacco blend, 20 parts of cotton gauze shreds; more overall mouth, tongue and throat harshness, more penetrating, more hot, more acid.
Do.....	100 parts of tobacco blend, 80 parts of cotton gauze shreds; could not be smoked because too harsh.

These results show that intimate mixing of cellulose with tobacco solubles greatly decreases the harshness of smoke delivered from pure cellulose.

Example 5

Various hand-made non-filter cigarettes of identical length and RTD were examined for acetaldehyde delivery according to an infrared absorption procedure and for benzo(a)pyrene delivery. A commercial tobacco blend was used in the making of the cigarette. It was also used for producing an aqueous tobacco extract in which Steripad cotton gauze and oxidized cellulose were dipped. A cigarette containing 100% untreated cotton gauze burns with a flame; a cigarette containing 100% untreated oxidized cellulose gauze does not burn at all. The treatment with tobacco solubles decreases the burning rate of cellulose and increases the burning rate of oxidized cellulose to reach roughly the same rate (3 to 5 mm./min.). The acetaldehyde analyses of the smoke gas phase are summarized in the table below. The results indicate that cellulose in the form of gauze shreds or extract containing cotton gauze delivers about the same amount of acetaldehyde into smoke. Oxidized cellulose, however, on the same weight basis delivers less than half the amount of acetaldehyde than does untreated cellulose. Benzo(a)pyrene was isolated by column chromatography and paper chromatography of the particulate phase of cigarette smoke. The

quantitative readout was made by ultraviolet of fluorometric spectroscopy. The results indicate that extract-containing cotton gauze delivers about half the amount of benze(a)pyrene into smoke than the average tobacco blend, while extract-containing oxidized cellulose delivers about 30 times less the amount of benze(a)pyrene than the average blend.

Cigarette filler	Acetaldehyde, micrograms/cig.	Benzo(a)pyrene 10 ⁹ , g./cig.
100% tobacco blend.....	570	17.6
Blend of 60% tobacco blend and 40% untreated cotton gauze (cellulose) shreds.....	417	N.D.
Blend of 60% tobacco blend and 40% cotton gauze with 33% to- bacco solubles.....	437	N.D.
Cotton gauze (cellulose) with 6% tobacco solubles.....	554	8.0
100% oxidized cellulose (19% car- boxyl content) gauze with 6% tobacco solubles.....	186	0.5
Blend of 60% oxidized cellulose gauze containing 6% tobacco solubles and 40% tobacco blend.....	168	N.D.

N.D.—Not determined.

Example 6

Cotton gauze, "Steripad," weighing 25.0 g was treated with a flameproofing agent consisting of 20 g. urea and 10 g. diammonium phosphate in 100 ml. of water. The gauze was dried and cured 10 min. at 150° C.; a gain in weight of 8.8 g. was observed.

A slurry prepared from tobacco dust, as described in Example 2, was applied to one side of this gauze. The sheet which, after drying, contained 32% of reinforcing gauze was shredded. When made into cigarette rods, 65 mm. long, weighing 0.8 g. and having 2.1 inch RTD, and attached to a commercial cellulose acetate filter, it burned well and with a pleasant aroma. The smoke contained 18.7 mg. of total particulate matter (TPM) and 8.3×10^{-9} g. of benz(a)pyrene (0.44 p.p.m. in the TPM). A commercial cigarette of average benz(a)pyrene delivery, with the same length of rod and filter delivered 20.1 mg. of TPM and 11.7×10^{-9} g. of benz(a)pyrene (0.59 p.p.m.) The results show that the cigarette with the reinforced flameproof cotton matrix delivered less benz(a)pyrene into smoke than the control

Example 7

Cotton gauze (Steripad gauze), 51 g., was dipped into a solution containing 40 g. urea and 20 g. diammonium phosphate (DAP) dissolved in 100 ml. water. The wet gauze was squeezed, air-dried and cured for 10 min. in an oven heated at 150° C. A weight gain of 48 g. was observed. A double layer of DAP-urea-treated gauze was coated on one side with enzyme-converted tobacco dust slurry as previously described and air-dried. The sheet was composed of 39.6% DAP-urea-treated cotton and 60.4% tobacco material. This product was coded A. A portion of A, 52.5 g., was then coated with enzyme-converted tobacco slurry on the tobacco free-side, air-dried and weighed. The weight was 61.5 g.; its composition was 20.8 g. (33.8%) DAP-urea-treated cotton gauze and 40.7 g. (66.2%) tobacco material. The product was coded B.

Unmodified "Steripad" gauze, in double layers, was coated on one side with enzyme-converted tobacco dust slurry as previously described and air-dried. The final sheet was composed of 26.7% cotton and 73.3% tobacco material. It was coded C.

Enzyme-converted tobacco dust slurry was also cast on glass plates and air-dried. The resulting sheets were coded D.

The mechanical strength of the samples A through D

was determined on the Instron machine. The results are summarized in Table IV:

TABLE IV.—MECHANICAL STRENGTH OF REINFORCED RECONSTITUTED, TOBACCO MATERIAL AT 12% MOISTURE

Material	Sheet weight, g./ft. ²	Instron tensile, kg./in. ²	Elongation at break percent	Work, g. cm./in. ²
A.....	N.D.	1.6	16.8	259
B.....	28.1	2.6	15.1	396
C.....	13.2	2.4	8.5	274
D.....	10.0	0.4	5.0	33

N.D.—Not determined.

The results show a considerable increase in tear strength due to the various gauze reinforcements.

Example 8

A matrix support was prepared from cotton cheese cloth (Curity grade 90, manufactured by the Kendall Co., New York 18, New York) and phytic acid (70% aqueous solution, from Nutritional Biochemical Corporation, Cleveland, Ohio). Phytic acid (inositol hexaphosphoric acid, $C_6H_{18}O_{24}P_6$) occurs in nature usually in the form of the mixed calcium, magnesium and potassium salt. The product of commerce is mostly derived from corn steep liquor.

Cheese cloth (172.5 g.) was dipped into a solution of 70 g. phytic acid in 300 ml. water, squeezed and air-dried. The weight gain was 65 g. Onto the phytic acid-treated cloth was cast enzyme-treated tobacco slurry as described in Example 2. The dry material contained 30.5% phytic acid-treated cotton. This sheet was shredded and made into filter cigarettes. The cigarettes contained 1.0 g. filter per cigarette and had an RTD of 4.0 inches of water without and of 6.0 with filter. The cigarettes were coded A.

Cigarettes of the same weight and RTD as those coded A were also made from unmodified cheese cloth coated with the tobacco slurry. In this case, the filler was composed of 22.5% cotton. The filter cigarettes were coded B.

The values in Table V (below) are absorption values obtained from infrared analysis of the smoke gas phase. They are thus relative values. For comparison, a typical commercial filter cigarette (0.85 g. filler weight, RTD=4.7 inches with filter) was also analyzed. It was coded C.

TABLE V.—INFRARED ANALYSIS OF GAS PHASE OF SMOKE

Cigarette	Acetalde- hyde	Carbon monoxide	Isoprene	Acetylene	Methane
A.....	0.90	0.31	0.03	0.16	0.37
B.....	6.23	0.45	0.10	0.36	0.51
C.....	5.37	0.37	0.15	0.25	0.46

The cigarette with the phytic acid modified reinforcement has favorable smoke characteristics attributable partly to the reduction in acetaldehyde.

The cigarette samples A (phytic acid treated gauze) and B (unmodified gauze) were smoked by an experienced taste panel of five members. A comparison of the smoke aroma and smoke harshness is listed in Table VI.

TABLE VI.—DESCRIPTIVE PANEL SMOKING

Cigarette	Harshness	Flavor
A.....	Less harsh than B.....	Sweet, more acceptable flavor than B.
B.....	Hot to tongue and nose...	Burn vegetables, dusty.

Cigarette A was found to be less harsh and to have a sweeter, more acceptable flavor than B, which was hot and dusty.

Example 9

To 15 gal. of water 0.67 lb. of guar gum (General Mills, Minneapolis, Minn.) was added with stirring and the mixture was heated to 80° C. for 15 min. Then 0.67 lb. of "Methocel" MC (methyl cellulose, 4000 cps., Dow

Chemical Co., Midland, Michigan) was stirred in and the mixture was allowed to cool. The following were added in sequence: triethylene glycol, 0.6 lb.; carboxymethylcellulose 7 MP (Hercules Powder Co., Wilmington, Delaware) 0.67 lb.; and 17.4 lb. tobacco dust, —50 mesh. The mixture was blended in a Cowles dissolver for 10 minutes.

Cotton gauze prepared as in Example 8 by treatment with phytic acid was coated with the tobacco slurry and the sheet was dried. It had good strength, and when shredded and blended with tobacco in equal parts, it gave a satisfactory mild smoke.

Example 10

A pentaerythrityl phosphoric acid ester of cellulose was prepared following essentially the method set forth in U.S. Patent 2,592,544.

Into a 500 ml. beaker was added 20 grams of urea, and while stirring with a glass rod, 19.3 g. of 85% orthophosphoric acid. The mixture was heated on a hot plate until a uniform solution was formed. Water, 5 ml., and pentaerythritol, 5 grams, was added with a pipette. The beaker was put into an oven at 150° C. and kept there for 90 min. The product was left to cool and was collected in a jar. To a solution of 15 grams of the product in 35 ml. of water was added 15 grams of urea and let dissolve. Steripad gauze, 10 pads weighing a total of 25.0 grams was dipped into the solution, squeezed, air-dried and cured for 15 minutes at 140° C. The cured gauze was washed in water and air-dried. It weighed 27.5 g. The gauze did not burn when lighted with a match. It has become flame resistant. Chemical analysis showed it to contain 1.4% total nitrogen and 0.5% total phosphorus. The gauze was coated on one side with a slurry of Cellulase 3.5—modified tobacco dust (50% leaf 50% midrib) in the way described before. The ratio flameproof gauze to tobacco was 1 to 2. The reinforced tobacco was shredded and made into cigarettes. The cigarettes burned very well and had a pleasant smoking aroma.

Example 11

Filter cigarettes of the following different compositions but with identical resistance-to-draw, filter, and make-up were prepared and submitted to a panel of 5 expert smokers.

(A) A uniform blend of 25% shredded untreated Steripad cotton gauze and 75% shreds of a thinly cast sheet obtained by treating —50 mesh tobacco dust composed of equal parts of tobacco leaf and tobacco leaf midrib with Rohm and Haas Cellulase 35, water, citric acid and glycerine as described before.

(B) A uniform blend of shreds of 40% of the above gauze and shreds of 60% of the above cast sheet.

(C) A 100% blend of Steripad gauze coated with the same tobacco slurry which was used to cast the sheets of cigarettes A and B. The ratio gauze to tobacco was 1 to 3.

(D) A 100% blend of phytic acid-treated cheese cloth coated with the same tobacco slurry which was used to make cigarettes A, B and C. The cheese cloth matrix contained 25% of phytic acid, the ratio of phytic acid-treated cloth to tobacco was 1 to 2.4 (42% treated cloth, 58% tobacco).

(E) A 100% blend of Steripad cotton gauze made flameproof with diammonium phosphate-urea and coated with the same tobacco slurry which was used for making cigarettes A to D. The treated Steripad matrix contained 22% of $(\text{NH}_4)_2\text{HPO}_4$ -urea and 78% of cellulose. The ratio of flameproof gauze to tobacco was 1 to 2.

The panel results were as follows:

- A—very harsh to tongue and throat, cannot be inhaled.
- B—harsher and hotter than A.
- C—milder than A or B; better flavor.
- D—sweet aromatic; milder than A or B; in general preferred to A, B or C.

E—milder than A or B; delivers less smoke; slight metallic note.

This example indicates that the smoke from a cigarette in which the cellulosic matrix is intimately mixed with tobacco is much milder than the smoke from a cigarette in which the cellulosic material is blended with tobacco. It also indicates that a cigarette containing a matrix of non-combustible cellulose is preferred over a cigarette containing a blend of cellulose and tobacco.

Example 12

"Curity" No. 10 cheese cloth (Kendall Co., 20 x 12 webs/sq. in.), 29 grams, was added to 600 ml. water in a 2 liter beaker. A mixture of 7.2 ml. 80% THPC (Tetrakis (hydroxymethyl) phosphonium chloride) and 2.4 ml. triethanolamine was added. The gauze was stirred for 15 minutes. NH_4Cl , 5 grams, was added; the pH was 4.1. A total of 25 grams of anhydrous sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) dissolved in 500 ml. of water was added slowly to bring the pH up to 7.5. The mixture was heated to 88° C. NH_4OH conc., 6 ml., was added. After cooling, the treated gauze was washed with water, dried and cured at 138° C. for 5 minutes. The material was washed again and dried. The material did not burn when lighted with a match. An analysis of this flameproof material revealed a total ash content of 1.4%, an insoluble phosphorous content of 0.12% and an insoluble nitrogen content of 0.25%. Equal amounts, 10 g. each, of THPC-treated and THPC-untreated material were heated in an oven for 105 minutes at 390° C. in the presence of air. The residue ("char") of the treated material weighed 3.3 g. while the residue of the control weighed 0.3 g. THPC treatment has increased the char formation and this is a clue that pyrolysis of cotton treated with THPC occurs differently than pyrolysis of untreated cotton.

In a related experiment 30 grams of "Curity" No. 10 cheese cloth was immersed in an aqueous solution of diammonium phosphate. The gauze was squeezed to remove excess solution and dried. The dry material weighing 34.5 grams was pyrolyzed at 390° C. in the presence of air. The residue ("char") weighed 10.0 g. of which not more than 4.5 g. can be inorganic matter. A control sample of 30 grams "Curity" No. 10 cheese cloth pyrolyzed together with the treated sample yielded a residue of only 2.3 g.

Example 13

A double layer of "Steripad" cotton gauze of total weight 50 g. was coated with one layer of enzyme-treated tobacco dust in the manner described in Example 11.

The dry, trimmed, reinforced material was composed of 43.5 g. original cotton gauze and 130.5 g. tobacco material. Tobacco solubles had fully penetrated the cotton gauze. Filter cigarettes were made from 100% of the reinforced material. They contained 0.8 g. filler each and had an RTD of 5.0–6.0 with the filter. The cigarettes delivered 9.5–10.9 g. benzo(a)pyrene per cigarette. In a control experiment cigarettes were prepared containing the same ratio of gauze (25%) to tobacco material (75%). However, the enzyme-treated tobacco dust was cast separately into sheets. Shreds of the cast tobacco sheet were blended with shreds of the cotton gauze. The cigarettes contained 1.1 g. filler and had an RTD of 5.0–6.0 with the filter. The cigarettes delivered 18.10⁻⁹ g. benzo(a)pyrene per cigarette, thus twice as much as the cigarettes from reinforced reconstituted tobacco.

Example 14

Oxidized cellulose gauze (Eastman Co., 16–22% carboxyl) 21 g. was covered with one layer of enzyme-treated tobacco dust from 100% leaves in a manner identical to the one described in Example 11.

The dry reinforced reconstituted tobacco contained 18 g. of the original gauze and 53 g. of tobacco material. The sheet was shredded and made into non-filter ciga-

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rettes of RTD 3.4-4.0 and filler weight 1 g. The cigarette yielded 8 puffs per cigarette on a smoking machine and had a static burning rate of 4 mm./min. The phenols delivery was 22.10^{-6} g./cigarette and the nicotine delivery was $0.39-10^{-3}$ g./cigarette. In a similar experiment Steripad cotton gauze was used with the same enzyme-treated tobacco slurry. The dry reinforced reconstituted tobacco contained also 18 g. of the original gauze and 53 g. of tobacco material. The sheet was shredded and made into non-filter cigarettes of RTD 3.0-4.2 and 1.0 g. filler weight. The cigarette yielded 8 puffs per cigarette and had a static burning rate of 4 mm./min. The phenols delivery was 33.10^{-6} g./cigarette and the nicotine delivery was $0.44.10^{-3}$ g./cigarette.

American non-filter cigarettes of the same length presently on the market have a static burning rate of 4 to 5 mm./min. and deliver 150 to 180.10^{-6} g. phenols per cigarette and deliver 1.3 to $2.0.10^{-3}$ g. nicotine per cigarette.

This experiment demonstrates that both a material which bursts into flame when lighted (cotton gauze cellulose) and a material which does not burn at all (oxidized cellulose gauze), when coated with tobacco material and made into a cigarette, burn like an ordinary cigarette and yield low amounts of phenols and of nicotine.

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What is claimed is:

1. A reinforced reconstituted tobacco sheet comprising a web woven of treated cellulose having a weight of from 14 to 45 grams per square yard and having 15 to 50 threads per inch, said woven web having adhered thereto from 1 to 20 parts by weight of particulate tobacco per part of said treated cellulose, said reinforced reconstituted tobacco sheet being such that when it is incorporated with a cigarette, said cigarette has a static burning rate of not less than 2 millimeters per minute and not more than 5 millimeters per minute, said treated cellulose comprising oxidized cellulose.

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MELVIN D. REIN, Primary Examiner

U.S. Cl. X.R.

131-2, 14, 140, 142

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,459,195

Dated August 5, 1969

Inventor(s) Henri C. Silberman

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

- Col. 6, line 68, "an" should read --and--.
- Col. 8, line 29, "was" should read --were--; line 49, "homog-
cnized" should read --homogenized--; line 57, "benzo(a)-
pyrene" should read --benz(a)pyrene--; and line 73,
"Benzo(a)pyrene" should read --Benz(a)pyrene--.
- Col. 9, lines 4 and 6, "benze(a)pyrene" should read --benz(a)-
pyrene--; line 11, "Benzo(a)pyrene" should read
-- Benz(a)pyrene-- 10^{-9} g./cig.
- Col. 10, line 65, "Burn" should read --Burnt--.
- Col. 11, line 15, "pentaerythrityl" should read --pentaerythrito
and line 22, "was" should read --were--.
- Col. 12, line 16, "cholride" should read --chloride--; line 38,
"was" should read --were--; and line 64, " $18 \cdot 10^{-9}$ " shou
read -- 18×10^{-9} --.
- Col. 13, line 4, " $22 \cdot 10^{-6}$ " should read -- 22×10^{-6} --; line 5,
" $0.39 \cdot 10^{-3}$ " should read -- 0.39×10^{-3} --; line 13, " $33 \cdot 10^{-3}$ "
should read -- 33×10^{-3} --; line 14, " $0.44 \cdot 10^{-3}$ " should
read -- 0.44×10^{-3} --; line 17, " $180 \cdot 10^{-6}$ " should read
-- 180×10^{-6} --; and line 18, " $2.0 \cdot 10^{-3}$ " should read
-- 2.0×10^{-3} --.

SIGNED AND
SEALED

MAY 12 1970

(SEAL)

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