

1

3,529,602

TOBACCO SUBSTITUTE SHEET MATERIAL

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No Drawing. Continuation of abandoned application Ser.
No. 557,878, June 16, 1966. This application Feb. 27,
1969, Ser. No. 804,380

Int. Cl. A24b 15/00, 3/14

U.S. Cl. 131-2

2 Claims 10

ABSTRACT OF THE DISCLOSURE

In accordance with the present disclosure a smoking
product, which is a substitute for tobacco, and which
contains substantially no tobacco, per se, which product
is prepared from ingredients which include: (1) a film-
forming ingredient comprising a pectinaceous material
derived from tobacco plant parts and having an acid
value in excess of 30 milligrams of KOH per gram and
(2) a mineral ingredient comprising an alkali metal salt,
an alkaline earth metal salt or a clay.

This application is a continuation of application Ser.
No. 557,878, filed June 16, 1966, now abandoned.

This invention relates to a tobacco substitute. More
particularly, the invention relates to a smoking material
which can be incorporated in cigarettes, pipe tobacco
and other smoking products, either as the sole smoking
ingredient or as a partial replacement for the tobacco
and to a method for making such a material.

However, the nature of smoking products is such that
the manufacture of a tobacco substitute is an extremely
difficult operation. The subtleties of smoking and of pro-
ducing a product which will be satisfactory to a smoker,
both from a taste and flavor aspect and from the aspect
of the other qualities of tobacco which are desired by
smokers, make synthesis of such a product difficult. Thus,
while many attempts have been made to prepare to-
bacco substitutes, including many attempts which were
made during wartime when tobacco was difficult to ob-
tain, none have resulted in the development of a satis-
factory tobacco substitute.

The biological requirements for the growth of a to-
bacco plant are very different from the chemical and
physical requirements for the generation of a smoke
which is desirable from a smoker's viewpoint. Thus, there
are often constituents in tobacco which result in a less
desirable smoke from a smoker's viewpoint and which
tend to adversely affect the character of smoke from
tobacco products. Thus, tobacco, being a natural prod-
uct, contains some constituents which would be better
omitted, were the user of the tobacco given his choice.
In addition, tobacco varies greatly from crop to crop,
and even from leaf to leaf, in both its chemical consti-
tution and its physical structure. It would clearly be most
advantageous if a smoking product could be designed
in such a manner that it has all of the desirable prop-
erties of tobacco and none of the undesirable properties
of tobacco. Such a synthetic product or tobacco substi-
tute would make it possible to omit from the formula-
tion those constituents which have an adverse affect, ei-
ther biologically or organoleptically, and permit the in-
corporation in the smoking product of those constituents

2

which have been demonstrated to be desirable in smoke.

Attempts have been made to prepare synthetic prod-
ucts that might serve as replacements for tobacco. How-
ever, prior to the present invention, no completely satis-
factory product has been found. In fact, no synthetic
product appears to have been produced which even re-
motely approaches the desirable qualities of a smoking
tobacco.

In accordance with the present invention, a tobacco
substitute has been developed which can provide the
satisfaction and smoking pleasure of natural tobacco
and which, at the same time, can be free of some of the
undesirable properties often encountered in natural to-
bacco. Furthermore, the present invention provides a
smoking product which is completely uniform and which
can be produced under controlled conditions. The pres-
ent invention also provides a novel method for manu-
facturing such a smoking product.

In accordance with the present invention a smoking
product, which is a substitute for tobacco, is prepared in
a novel manner from carefully selected ingredients.

The essential ingredients which are employed, in ac-
cordance with the present invention, include: (1) a film-
forming ingredient and (2) a mineral ingredient. These
two ingredients will be discussed in more detail below.

(1) *A film-forming ingredient.*—The film-forming in-
gredient is preferably a pectinaceous material, which will
be described in more detail below, but may also be an
alginic material or the like. The film-forming ingredient
may be an acid gum having an acid value in excess of
30 milligrams of KOH per gram of gum. One class of
substances, the calcium-magnesium-potassium-sodium
salts of the polyuronic acids, constitutes about one-third
of the structural carbohydrate of leaf tobacco, and pro-
vides, in combined form, the necessary mineral support
for the coal. Representatives of this class include acidic
pectins and pectates that are available from tobacco,
pectin from citrus fruits, alginic acid, polyuronic acids,
salts of these acids, synthetic esters of alginic acid, esters
of pectic acids, or any other pectins that will form films
are usable as the film former. Pectins of all degrees of
methylation can be used. Even blends of high and low
molecular weight pectic materials are usable in the in-
vention. Most preferably, a pectinic material is em-
ployed of a type which is derived from tobacco plant
parts containing pectins having alkaline earth metal cross-
links which comprises the steps of:

(1) Contacting said tobacco plant parts with a treat-
ing solution containing a reagent to destroy the alkaline
earth metal cross-links;

(2) At least partially releasing the resulting tobacco
pectins from the interstices of the treated tobacco plant
parts; and

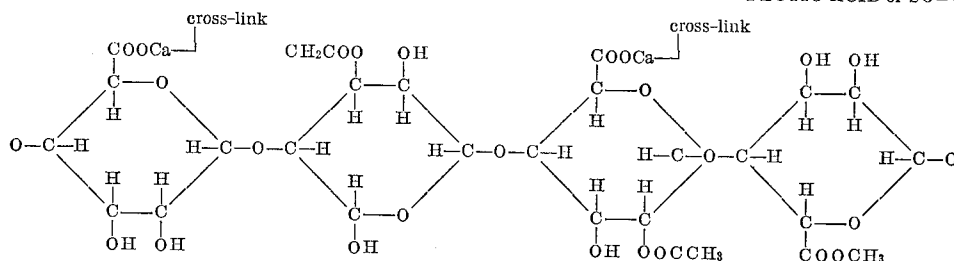
(3) Recovering said tobacco pectins.

Such a material provides a particularly desirable film-
forming ingredient. Some of the methods for producing
such tobacco pectins will be described below. In the de-
scription which follows, the term pectin substances (for
convenience, unless otherwise specified, the term "pectins"
will hereinafter be employed as meaning "pectic sub-
stances") will mean those substances which are found
in many plant products. They consist essentially of par-
tially methylated galacturonic acids joined in long chains.

The pectins found in tobacco plants contain acetyl
groups and differ from commercially available pectins

3

found in other plants, including sugar beet pectins and citrus and fruit pectins. Tobacco protopectins are uniquely insoluble in hot water and, in many instances, the pectic chains are particularly stable in alkaline solutions, as compared with protopectins from many other sources and comprise mainly water-insoluble pectins (protopectins) consisting of the calcium and magnesium salts of partially esterified and slightly acetylated polymers of galacturonic acid. The divalent calcium and/or magnesium atoms act as cross-links between acid chains, thus making the polymers water-insoluble. As an illustration, the structure of



the calcium salt of a polymer of galacturonic acid can be represented as shown above.

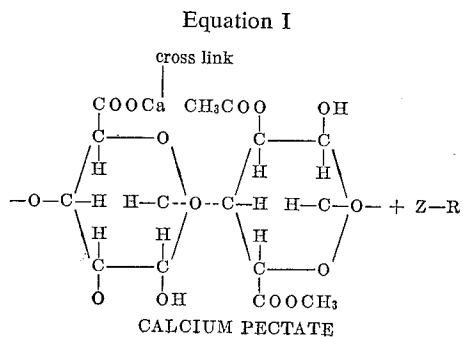
Although pectins have long been known as constituents of plant tissue, it has been found extremely difficult to separate pectins from the remainder of plant compositions and to obtain them as homogeneous compositions. The recovery of pectins from tobacco is even more difficult than the recovery of pectins from other plants.

The tobacco parts which can be employed in the present invention include tobacco leaves, stems and stalks, or a mixture of these, whether in sheet, flake or particulate form. Preferably, the parts are ground, cut or otherwise prepared in a form which presents a large surface area. The portions of the plant comprising the stems or midribs, and often referred to as tobacco petioles, are the preferred starting materials. Tobacco stalks contain lesser amounts of pectinaceous materials but can also be employed.

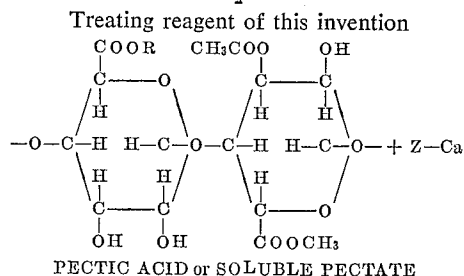
In the first step of the process, tobacco pectins are liberated from pectinaceous materials in tobacco by reacting the pectinaceous materials with a reagent which is reactive with the calcium (and/or magnesium) contained in them to form a compound or product having a lower calcium ion, and, in the case of magnesium, magnesium ion, concentration in the treating solution than the naturally occurring calcium (or magnesium) pectate. By concentration is meant mean concentration or activity as set forth in Glasstone, "Textbook of Physical Chemistry," 2nd edition, page 945, D. V. Nostrand Company, Inc.

The reaction may be generally represented by Equation I, which illustrates the reaction of one type of tobacco protopectin (a calcium salt of a polymer of galacturonic acid) wherein calcium cross-links are present with the reagent of the present invention. In the equation, R may be hydrogen, in which case the product is pectic acid, or R may be a monovalent inorganic cation, such as sodium, potassium or ammonium.

Equation I is as follows:



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Product having lower cation concentrations than the calcium pectate in the treating solution

In one embodiment of the process, the reagent, which can be, and preferably is, in aqueous solution, acts by forming a precipitate with the calcium or magnesium, in which case, it can be a water-soluble monovalent metal salt of the formula M_nX wherein M is a monovalent inorganic cation, n is an integer having a value of 1, 2 or 3, and X is an anion which may be monovalent or polyvalent, such that the calcium salt of the formula Ca_pX_q is essentially insoluble in the treating solution and p and q are integers corresponding to the functionality of X. Monovalent cations which are effective include the alkali metals such as sodium, potassium and lithium, and also include such monovalent cations as ammonium, and substituted ammonium ions $(NR_4)^+$, where R=aryl or alkyl. The anion portion of the molecule may be CO_3^- , PO_4^- , HPO_4^- , $H_2PO_4^-$, and the like. For example, the compound M_nX could be sodium carbonate, Na_2CO_3 , since sodium is a monovalent inorganic cation and calcium carbonate is essentially water insoluble. Additional representative examples of precipitating agents are the orthophosphates, metaphosphates, and carbonates of sodium, potassium, lithium and ammonium. In the case of the orthophosphates, the anion portion of the molecule may be either PO_4^- , HPO_4^- or $H_2PO_4^-$. Specifically, for example, when ammonium orthophosphate is used, the precipitate is calcium and/or magnesium ammonium phosphate. The pH of this reaction should be between about 5.8 and 10 and the temperature should preferably be between about 25° C. and about 135° C. for a period of from about 1 minute to about 24 hours. Specific examples of precipitating agents which may be employed include sodium carbonate, potassium carbonate, lithium carbonate, ammonium orthophosphate, ammonium acid phosphate, and sodium orthophosphate.

In a second embodiment of the process, the reagent acts by sequestering the calcium or magnesium, thereby removing the calcium or magnesium atoms by forming a soluble complex therewith. Suitable reagents of this type include any sequestering agent which will form a complex or chelate with the calcium or magnesium, thereby removing them and making them unavailable for recross-linking with the pectin. Illustrative of such sequestering agents are ethylenediamine-tetraacetic acid and similar amino acids, alkali metal polymetaphosphates such as tetra-metaphosphates, hexametaphosphates and trimetaphosphates, pyrophosphates and tripolyphosphates, such as sodium hexametaphosphate, tetrasodium pyrophosphate and pentasodium tripolyphosphate. The mechanism which occurs when a sequestering agent is employed, may either be the formation of a complex or the formation of a chelate; in either case calcium and magnesium ions are no longer available

to combine with the pectate ions in solution. Many naturally occurring amines and peptides are also effective as sequestering agents for calcium and/or magnesium. Representative examples include alanine, aspartic acid, glycine, glycylic acid, glutamic acid, serine, tyrosine and diiodo-1-tyrosine. Amino acids that are effective as chelating solubilizing agents include betaalanine, N,N-diacetic acid; amino barbituric acid, N,N-diacetic acid; 2-amino-benzoic acid, N,N-diacetic acid; beta-aminoethyl-phosphonic acid, N,N-diacetic acid; beta-aminoethylsulfonic acid, N,N-diacetic acid and ethylenediamine-tetraacetic acid. The pH of this reaction should be between about 4 and about 10 and the temperature should preferably be between about 0° C. and about 145° C. for a period of from about 1 minute to about 24 hours.

A reagent may also function partially as a precipitating reagent, in accordance with the first embodiment of this invention, and partially as a sequestering agent, in accordance with the second embodiment of this invention. Such a reagent, for example, is DAP (diammonium monohydrogen orthophosphate).

In a third embodiment of the process, the reagent is an acid which forms the released but insoluble free pectic acid and soluble calcium and magnesium salts. Suitable acids include inorganic acids, such as hydrochloric acid, phosphoric acid and sulfuric acid and similar acids which will form calcium and magnesium salts under the following conditions. The acid may be employed as 0.25 N to 5.0 N solutions, but is preferably employed as 0.5 N to 1.0 N solutions. The exact dilution and amount to be employed will vary with the particular acid which is used, it only being necessary that sufficient acid be present to convert the calcium and magnesium present in the tobacco being treated to the calcium and magnesium salts of the acid. The acid treatment is preferably conducted at a temperature of from about -1° C. to about 55° C. The acid treatment comprises reacting the tobacco parts with the acid until the resulting mixture has a pH of from about 1.0 to about 2.5. Preferably, the pH is brought to from about 1.0 to about 1.7, the most desirable pH being between 1.15 and 1.55. This treatment will generally be conducted from about 10 minutes to 24 hours, depending in part on the size of the tobacco particles.

Preferably, the resulting mixture is then washed with water. This water wash step is preferably conducted at a temperature of from about 15 to about 35° C. and, preferably, distilled water is employed. When this wash step is employed, sufficient water should be used to remove the calcium and magnesium salts of the acids, which salts are formed in the above-described treatment; thus, there should be at least 2 volumes of water per volume of the mixture resulting from the acid treatment. The wash water is separated from the tobacco by any suitable means, for example, by conducting the wash in a centrifuge, filter press, Buchner funnel, or any other apparatus from which liquids can be substantially removed from solid materials.

The mixture resulting from the acid treatment, and preferably after the water wash described above, is then brought to a pH of from about 2.7 to about 10.5, by the addition of an alkaline material. Suitable alkaline materials include alkali metal and ammonium hydroxide, and alkali metal salts, such as sodium bicarbonate, sodium carbonate, sodium phosphate and similar salts to convert the pectic acid to a soluble form. The alkaline material may be any water-soluble compound containing a monovalent inorganic cation and capable of producing hydroxide ions when dissolved in water. Additional examples of such a material include ammonium hydroxide, sodium hydroxide, potassium hydroxide and lithium hydroxide. Preferably, the alkaline treatment is conducted until the pH of the resulting mixture has a value of from about 4.5 to about 5.5. The temperature of this step may be from about -1° C. to about 45° C., but is preferably from about 15 to about 35° C. The alkaline material is preferably in the

form of solid particles or as solutions having concentrations of about 5 to about 50%.

In summary, in the first step of the first embodiment of the process, i.e., the first embodiment with respect to the removal of calcium and magnesium cross-links from the tobacco pectins, the treating agent Z-R attacks the calcium and/or magnesium cross-links of tobacco protopectin and forms a precipitate which is a salt of calcium and/or magnesium, thus removing the calcium and/or magnesium cross-links from the tobacco protopectin and from the solution. In the first step of the second embodiment, the treating agent X-R is a sequestering agent which forms a complex or chelate of the magnesium and/or calcium from the tobacco protopectin and makes the calcium and/or magnesium unavailable for recombining with the pectins. In the first step of the third embodiment, the treating agent Z-R is an acid which attacks the calcium and/or magnesium cross-links of the tobacco protopectin and forms the soluble calcium and/or magnesium salts, which are then washed away from contact with the pectins.

In the first step of each of the first two embodiments of the process, the pectin which results is in condition for release from the tobacco cell structure, R in Equation I being a monovalent inorganic cation, such as sodium. In the first step of the third embodiment, the insoluble pectic acid resulting from the acid treatment must be reacted with an alkaline material before it can be released from the tobacco cell structure.

Once the tobacco pectins have been liberated from the tobacco, by the removal of the calcium and magnesium cross-links, they should be released from the interstices of the tobacco. That is, they will be made available to the solution or suspension or, in certain instances, they will be merely deposited on the surface of the tobacco particles. In embodiments 1 and 2, this release may be accomplished concurrently with the first step by reacting with the solution of the treating reagent. In embodiment 3, however, as indicated above, the insoluble pectic acid resulting from the treatment should be reacted with an alkaline material before it can be released. In such event, the release may be concurrent with the addition of the alkaline material due to a washing action. In any case, additional treating liquid or water may be used to effect the release through a washing action of the treated tobacco particles.

In accordance with the next step of our process, the liberated and separated tobacco pectins can next be precipitated from the treating solution, for example by being formed into the insoluble pectic acid or into an insoluble salt of pectic acid or by action of a water-miscible solvent, such as acetone or ethyl alcohol to cause a water-soluble salt of pectic acid to go out of solution.

In the case of tobacco pectin solutions such as solutions of sodium and potassium pectinates and/or pectates, this can be accomplished by acidifying the solution until the pectins precipitate or by adding a gelation agent, such as an alcoholic solution, preferably having a pH of from about 1 to 9 and preferably from about 1 to 5. The pH of the alcoholic solution can be regulated by the addition of a mineral acid, such as HCl, to the alcohol. Although the preferred gelation agent is ethanol, any water-miscible organic solvent having up to about 10 carbon atoms may be employed, for example, a ketone, such as acetone, or a diether, such as dioxane. Water-immiscible solvents such as ether, for example, ethyl ether, can be used, if combined with a water-miscible solvent, such as acetone.

The tobacco pectins can be recovered by concentrating the solution or suspension in which they are present until they precipitate. This precipitate might also be characterized as an intractable mass, since the pectin solution, upon concentration, generally becomes progressively more viscous until it finally dries to leave a deposit in a glassy solid state.

A preferred preliminary step, in accordance with the present invention, comprises washing the tobacco plant parts, which are preferably ground or cut to a relatively small size, with cold water. This water wash serves to remove impurities which might otherwise hinder the subsequent treatments in accordance with the present invention. It is particularly desirable to employ such a cold water washing step when alkali metal carbonates are employed as the reagent in the first step. Generally, sufficient water should be used during such a water-wash operation to cover all of the tobacco plant parts present. The temperature of the water may be between -1° C. and 100° C., but is preferably about 20° C., and the water wash should generally continue for a period of from about $\frac{1}{2}$ to $2\frac{1}{2}$ hours. Agitation during the wash is desirable, but not necessary. After the water wash has been completed, the water can be removed from the tobacco parts by filtration, decantation or other suitable means.

The term "tobacco pectins" as used throughout this specification means "liberated tobacco pectins" and comprehends pectins which have been freed or liberated from tobacco and are, therefore, not bound into the tobacco structure, as differentiated from the insoluble, naturally-occurring protopectins which are bound into plant cell structure. The term includes the free pectinic or pectic acid, as well as soluble salts such as the sodium, potassium, ammonium, pectates and pectinates, and insoluble salts such as the calcium and magnesium pectates and pectinates, depending on what method is employed to liberate and obtain them from the naturally occurring insoluble protopectins.

(2) *A mineral ingredient.*—This ingredient, which is employed to provide the proper burning qualities and the proper ash to the smoking product, may comprise an alkali metal salt or an alkaline earth metal salt, for example, a calcium, sodium, potassium or magnesium salt, or a clay.

As can be seen from the preceding discussion of film-forming ingredients, many of the materials employed as film-forming ingredients contain combined sodium, potassium, calcium or magnesium and thus may contain sufficient "mineral ingredient" for the purposes of this invention. This combined mineral, for example, a mixture of calcium pectate and potassium pectate, can be made into a tobacco substitute having satisfactory burning qualities. However, in most cases, the film-forming component will be supplemented with other minerals. In many cases, it will be desirable and preferable to add water-insoluble minerals such as calcium and/or magnesium orthophosphates, pyrophosphate, polyphosphates and the like. A particularly advantageous mineral ingredient is precipitated tricalcium phosphate (NF grade), which has been calcined at 1000° C. for three hours. These phosphates have the particular advantage of being able to release the small amounts of calcium and magnesium ions which may be necessary to extrude the compositions at the correct texture which must be possessed by the formulation when it is cast on a steel belt for the like, as will be described later in this specification. This feature is especially important when the compositions do not contain fiber which ordinarily fulfills such a function. Examples of suitable alkali metal salts and alkaline earth metal salts for use in accordance with the present invention include the following: potassium chloride, potassium sulfate, potassium phosphate, potassium nitrate, sodium chloride, sodium sulfate, sodium phosphate, potassium nitrate, calcium chloride, calcium sulfate, calcium phosphate, calcium nitrate, magnesium chloride, magnesium sulfate, magnesium phosphate, magnesium nitrate, lithium chloride, lithium sulfate, lithium nitrate and the like. There are many clays which would be usable as mineral fillers. Clays are mixtures of hydrated silicates of aluminum, calcium, magnesium and

zinc usually with varying amounts of iron, manganese, cobalt or other heavy metals which often impart a heavy coloration. Common names of some useful clays are kaolin, montmorillonite, bentonite, atapulgitte, allophane, illite and the like. Usually it will be desirable to use a light colored or white clay, and it may sometimes be found advantageous to use fired and reground clays because such treatment renders the polyvalent cations less available (i.e. soluble) and hence less likely to interfere with the performance of the polyuronic acid constituent of our compositions.

A nicotine-donating ingredient is not essential, but is a preferred ingredient. The nicotine may be added in any of the known ways of incorporating nicotine in tobacco. For example, it may be added per se to the tobacco substitute or it may be added in the form of a material which releases nicotine upon burning of the tobacco substitute. The latter method is illustrated in U.S. Pat. 3,109,436, wherein the addition of a nicotine-ion exchange resin to tobacco is described. The nicotine may also be incorporated in other portions of the tobacco product, such as the filter or wrapper to accomplish the same result.

A non-essential, but very preferred ingredient is a plasticizer. The plasticizer is employed to provide the desired processing characteristics for the overall composition. Suitable plasticizers include certain tobacco extracts, obtained by leaching tobacco parts with water; or mixtures of solvents such as acetone, methanol isopropanol with water; or by leaching of tobacco parts in non-aqueous solvents, such as hexane, tetrachloroethylene, ethyl ether, and the like. Other plasticizing agents include the monobasic, dibasic and tribasic acids, for example: lactic, malic, tartaric, citric. Additional plasticizers include glycerine, triethylene, glycol, sorbitol, invert sugar, sucrose, oligosaccharides, triglyceride fats and oils, long chain fatty alcohols, linear paraffins, normal paraffins, paraffin waxes, beeswax, candlelilla wax, carnauba wax, sugar cane wax, maleates, citrates and corn syrup. Particularly desirable plasticizers are sodium citrate and potassium citrate. When one of these materials is employed, or a combination of these materials is employed, it has been found that the subjective evaluation of the taste and aroma of the smoke resulting from products incorporating the same have been favorable.

Other materials which may be included in the tobacco substitute include nicotine-containing extracts from tobacco leaf and other flavorants which had characteristics to make a desirable smoke. Such flavorants include, for example: licorice, deer tongue, principal oils of rum, chocolate, fruit essence and the like.

The amounts of the essential ingredients of the formulation of the present invention are dictated by the types of materials used as the mineral substrate and as the plasticizer. For example, the polyuronic acid content can be varied from about 20–70% of the total weight of the mixture. When a hygroscopic organic salt is used as the plasticizer, the preferred amount of polyuronic acid is about 50%. In general, the film-forming ingredient should comprise from 5 to 90% by weight of the composition.

The minerals in tobacco leaf which provide the total ash in the pyrolyzed product are in the range of 18–23% of the total weight. These are primarily calcium-magnesium-potassium salts in which the calcium magnesium predominates in various molar ratios in which a representative molar average is 1 mole of calcium and magnesium to 1 mole of potassium. Calcium to potassium ratios as high as 2.5:1 and as low as 0.7:1 and even 0.45:1 by weight, have been reported for some leaves and stems. There are no rigid limits within the general range given below for the Mg:Ca:K ratio which is desirable since the composition may vary just as there is a wide variety in natural tobacco compositions. However, in general, the mineral ingredient should comprise from 5 to 90%, and

preferably from about 15 to 30% by weight of the compositions.

The preferred range of the plasticizer is around 25% by weight, although plasticization is effective at a 15-40% range. However, as pointed out above, a plasticizer is merely a very preferred ingredient and can be omitted from the composition.

Nicotine, which is also a preferred ingredient, when employed can comprise from about 0.3 to about 3% by weight of the composition.

The order in which the ingredients are added is important, in that calcium salts, when employed, should be added to the film-forming ingredient at a time when the pH of the mixture is at least 5.0 in order to prevent the calcium salts from being solubilized prematurely. The pH of the mixture should be maintained above about 5.0, because at a lower pH the calcium is very soluble and causes gelling. A preferred pH range is 5.6-8.0.

When the mixture is to be cast, it can be made into a binder material having a solids content of 5.0-25.0%. In this regard, a preferred solids content is in the range of 9-15%. If the mixture is to be extruded, a much higher solids content can be used, as high as 80%. For economic reasons, it is desirable to keep the solids content high to prevent having to evaporate great amounts of water per pound of product.

A film may be cast on a steel belt or the like from the composition of the present invention by a conventional casting technique to form a material that can be shredded for filler in a cigarette. The compositions of the present invention may, alternatively, be extruded into a variety of shapes of may be converted by hot roll extrusion to film form.

The use of a cast film as the base for the present composition provides the more preferred mode of operation in accordance with the present invention, since the film can be more readily processed and thus more readily converted into a product which closely resembles the natural tobacco leaf product. However, the present tobacco substitute may be made by other methods, including extrusion in fibrous or sheet form or in other shapes, all of which can be cut into pieces of the desired size or incorporation in a tobacco substitute.

The filler made by variations of the range given above and cast at 9-15% solids content on a steel belt processed well on a cigarette-making machine. Its filling power resembled that of natural leaf. Its burning qualities and ash strength were good. Subjective evaluation of cigarettes made from the present filler showed that it produced a desirable, non-irritating smoke, which closely resembled that of leaf tobacco.

The tobacco substitute of the present invention may be employed alone for incorporation in a smoking product, such as a cigarette, cigar, cigarillo, smoking tobacco or the like, or may be combined in any proportion with tobacco, either natural leaf tobacco or reconstituted tobacco. The tobacco substitute, however, is particularly adapted for use without the addition of any tobacco, since it can be made in such a manner that it provides many of the desirable properties of tobacco while it eliminates many of the undesirable properties of tobacco.

The invention may be illustrated by the following examples:

EXAMPLE 1

Pectin was extracted from the midribs of burley tobacco by treating them with diammonium phosphate (DAP)—20%, based upon the dry weight of the midribs. The pH was adjusted to 7 at the beginning of the treatment and the mixture was heated at 90° C. for one hour. At the end of that time, the juice was pressed from the mixture and poured into acidified acetone to obtain the gel. The gel was filtered on cheese cloth, pressed, dried and weighed. This process gave a pectin yield of about

15%. The material was granular and had the properties of a pectic acid.

The extracted pectin (9.1 g.) was used as a film former in combination with 0.3 g. potassium hydroxide, 0.5 g. ammonia in solution to bring the pH to 5.0, and 1.4 g. calcium pyrophosphate. The calcium and potassium were used to provide good burning qualities to the film. The calcium salt was added last to prevent the pectin from gelling before the film could be formed. The mixture was extruded on to an endless belt and the resulting film was steam dried. The film was about 5 mils thick, was opaque, and showed a good plasticity. When ignited, the film burned well, held fire well, and formed a compact white ash. The film was shredded to make cigarette filler, which was incorporated into cigarettes. The cigarettes were smoked and their burning characteristics were observed. The burning qualities were good, and the smoke had a very mild taste.

EXAMPLE 2

Potassium hydroxide (197.5 g.) and magnesium hydroxide (193.5 g.) were added to 18.6 kilograms of water and dispersed in a Cowles Dissolver.

Alginic acid (1135.0 g. of Kelacid, made by Kelco Company) was added to the dispersion and the mixture was further agitated. Additional water (18.6 kilograms) and the following ingredients were then put into the Dissolver, 454.0 g. triethylene glycol (TEG) 45.0 g. nicotine 57.0 g. bright tobacco extract (ethylene dichloride solutions) with hexane as the carrier

The pH of the mixture was 4.7. The solids content was 6.35%.

The material was extruded onto an endless belt, partially dried with infrared heat, and then removed from the belt. Strips 8"-10" long were cut from the film and laid out to complete the drying process. The strips were then cut into cigarette filler. The material processed well on a cigarette-making machine.

EXAMPLE 3

A series of formulations were prepared to determine the ratios of magnesium or calcium to potassium that would give the most effective burning characteristics to a film designed to substitute for tobacco filler in a cigarette. The binder made from each of the formulations was prepared by dispersing pectic acid and the calcium or magnesium hydroxides in hot tap water, then adding potassium hydroxide to a pH of 5.6. The mixture was heated on a steam bath, and an equilibrium pH of 6.5 was reached.

The material was cast by conventional casting procedures and either steam or air dried. The resulting film was shredded into cigarette filler, and made into cigarettes. The formulations and burning characteristics are given below:

(A)

	G.
Pectic acid	51.5
Potassium hydroxide	7.1
Magnesium hydroxide	3.7

The film that was formed held fire well, the coal and ash did not intumesce (puff up), and a compact white ash was formed.

(B)

When 4.7 g. of calcium hydroxide was substituted for the magnesium hydroxide in the formula above, the same burning characteristics were observed.

(C)

	G.
Pectic acid	51.5
Magnesium hydroxide	5.54
Potassium hydroxide	3.16

The film prepared from this formula did not hold fire.

11
(D)

Pectic acid -----	G.	51.5
Calcium hydroxide -----		3.13
Potassium hydroxide -----		9.52

The film from this formulation held fire well, the coal and ash intumesced (puffed up), and formed a dark ash.

(E)

When 2.45 g. of magnesium hydroxide was substituted for the calcium hydroxide in formula (D) above, the same burning characteristics were observed.

EXAMPLE 4

Malic acid (268 g.) was dispersed in 20 liters of tap water in a Cowles dissolver. The dispersion was neutralized with 272 g. of ammonium hydroxide solution. One thousand grams of sodium polypectate (Product 6024, Sunkist Growers) was added in the Cowles dissolver and the mixture was agitated thoroughly. Twenty grams of nicotine, 50 g. of tobacco extract (ethylene dichloride extractables from bright tobacco leaf), and 208 g. of tricalcium phosphate were added in the order named. Coloring material was added to simulate the color of cured tobacco leaf. The colors used were F, D and C dyes—No. 1 blue, No. 6 yellow, No. 2 red and No. 5 yellow. The resulting binder material had an equilibrium pH of 6.8. The binder was extruded onto an endless belt in a layer approximately 60 mils thick, dried with infrared heat, and then stripped from the belt with a doctor knife. The film, which was leathery and flexible with a wrinkled surface, was quite similar in feel and appearance to tobacco leaf.

The film was cut into 8" x 12" sheets and allowed to equilibrate to 12% moisture. The sheets were then shredded into cigarette filler by making 25 cuts/inch. The filler was made into non-filter cigarettes on a Hauni cigarette maker. The filler processed well as compared with regular cigarette filler from tobacco.

The cigarettes were tested for resistance-to-draw (RTD). 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 1050 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. A commercial cigarette was found, for comparison, to be about 25% lower than that of the cigarette made from tobacco but was not so low that the cigarette did not perform sufficiently well.

The test cigarettes were weighed on an analytical balance in groups of forty cigarettes and the weights of the individual cigarettes were calculated and compared with the weight of the control. The test cigarette was slightly lower in weight than the control.

The test and control cigarettes were smoked on a constant volume smoking machine which takes a 35 ml. puff of two seconds duration once in 60 seconds. The smoke was trapped on a Cambridge filter pad which retains particles larger than 0.3 micron. The filter assembly was weighed before and after smoking four of each of the types of cigarettes to determine the amount of total particulate matter (TPM) collected. The TPM from the test cigarette was 12.5 mg./cigt., about half that from the control.

To determine the total alkaloid content of the test and control cigarettes, the filler was steam distilled to remove the steam-volatile alkaloids. The distillate was then used in a spectrophotometric determination. The ultraviolet absorption spectrum of the distillate was compared with appropriate standards and, with this comparison as the basis, a quantitative estimate of the total alkaloids was made. The total alkaloid content of the test cigarette compared favorably with that of the control.

12

The puff count for the test and control cigarette was determined by smoking four cigarettes, counting the number of puffs it took for the char line to reach the 30 mm. mark on the cigarettes, and then by taking the average of the number of puffs as the count for the individual cigarette. The puff count for the test cigarette was 13.2 and for the control, 8.0.

Forty test cigarettes were smoked on a smoking machine as described above and the particulate phase was collected on Cambridge filter pads. The pads were then extracted with methanol and the material was used to estimate the amount of benzo(a)pyrene in the smoke as compared with that from an all-bright tobacco cigarette which was run as a control.

The methanol-extract was evaporated on a steam bath to 3-4 ml. and enough silica gel (3-4 g.) to absorb the solution was added. The silica gel was freed of methanol in a stream of nitrogen and was added to the top of a previously prepared 25 x 600 mm. column containing 40 g. of silica gel packed as a slurry in hexane. The whole column was first eluted with 400 ml. of hexane to remove waxes. It was then eluted with benzene and the first 130 ml. of eluate after the benzene front reached the bottom of the column was collected.

The benzene eluate was evaporated to dryness and the residue, taken up in a few drops of benzene, was applied to acetylated paper in a one-inch streak. The paper was developed ascending for 16 hours with methyl Cellosolve. After development, the benzo(a)pyrene zone appeared under illumination with an ultraviolet lamp as a purple fluorescent spot against a bluish-white background R_f —0.3. The spot was excised and cut into small pieces, which were placed in a small vial and covered with 5.0 ml. of benzene-methanol (4:1). After one hour the solvent was decanted and its fluorescence emission spectrum was measured on an Aminco-Keirs Spectrophosphorimeter, using an excitation wave length of 385 $m\mu$. The amount of benzo(a)pyrene was determined by comparing the height of the 405 $m\mu$ emission band with a calibration curve obtained from standard benzo(a)pyrene solutions. The delivery of benzo(a)pyrene from the cigarette of all-bright tobacco was 0.8 part/million. The delivery from the test cigarette was 0.45 part/million, a reduction of almost half.

The cigarette was smoked by a smoking panel and rated in comparison with commercially available standard cigarettes. The panel found that the smoke from the test cigarette was remarkably free of harsh notes. It was deemed better than acceptable since many panel members preferred it over the control—a standard cigarette.

EXAMPLE 5

Seven hundred and fifty grams of sodium polypectate fortified with 250 g. of polygalacturonic acid (Sunkist product) were dispersed in five gallons of tap water by agitating the mixture in a Cowles Dissolver. The materials listed below were added to this dispersion.

	G.	
Calcium pyrophosphate -----		111.0
Nicotine -----		21.00
Tobacco extract (ethylene dichloride solubles) ..		53.00
Triethylene glycol (TEG) -----		200.00
Concentrated ammonia -----		43.00

The materials were added in a specific order. The calcium pyrophosphate was added first and then the tobacco extract which had been put in the TEG. Nicotine was added to the mixture at pH 3.5-4.0. Finally, the concentrated ammonia raised the pH to 5.0-5.5. This order of addition produced a binder-type product with a solids content of 6.3%. Coloring material was added to simulate the color of tobacco, in the same manner as in Example 4.

The material was extruded onto an endless belt in a layer approximately 60 mils thick. The film was partially dried with infrared heat, removed from the belt and laid out in

the air to complete drying. The dried film was about 6 mils thick, was pliable, and had a dull surface. The film was cut into sheets and allowed to equilibrate to 12% moisture. The sheets were then shredded into cigarette filler. They shredded well without forming undesirable quantities of dust. Cigarettes were made on the Hauni cigarette maker.

When the cigarettes were tested for RTD and weighed, as described in Example 1, it was found that the RTD was 0.7-0.9 inch of water and that their average weight was 1.10 grams.

The test cigarettes and a commercially available cigarette used as a control were smoked on a constant volume smoking machine, the smoke was trapped, and the TPM determined as described in Example 1. The TPM from the test cigarette was about 50% of that from the control.

The puff count for the test cigarette and control was determined as described in Example 1. The count was slightly higher than that for the control.

The benzo(a)pyrene content of the smoke from the test cigarette was determined as described in Example 1 and compared with that from a control cigarette made from all-bright tobacco.

The test cigarette had a benzo(a)pyrene content greatly reduced over that of the control.

The members of a smoking panel judged the cigarette subjectively and found the smoke mild and desirable.

EXAMPLE 6

Seven hundred grams of sodium polypectate was dispersed as described in Example 1. The ingredients listed below were added as described in Example 2.

- 350.0 g. sucrose
 - 157.5 g. calcium pyrophosphate
 - 210.0 g. triethylene glycol
 - 14.0 g. nicotine
 - 35.0 g. tobacco extract (ethylene dichloride solubles)
 - 14 liters tap water
- The equilibrium pH was 68.

This mixture was cast on an endless belt and partially dried with infrared heat. The film was removed from the belt with a doctor knife and dried further by air drying. The film was then cut into sheets and allowed to equilibrate to 12% moisture.

They were shredded into cigarette filter and used to prepare cigarettes.

The RTD of the cigarettes, determined as described in Example 1, was 0.9-1.0 inch of water. Their weight was about 75% that of standard cigarettes used as a control.

The TPM, determined as described in Example 1, was 31.1 mg./cigt. This was higher than the control which had a TPM of 21.8 mg./cigt.

The puff count, for the test cigarette, obtained as described in Example 1, was 11.3. The control had a puff count of 8.

The benzo(a)pyrene delivery of the test and control cigarettes (an all-bright tobacco cigarette), as determined chromatographically by the procedure given in Example 1, was 0.35 part/million and 0.8 part/million, respectively.

The test and control cigarettes were smoked by a test panel. The smoke from the test cigarette was judged mild and pleasing. It had a slightly sweet taste and an aroma reminiscent of caramelized sugar.

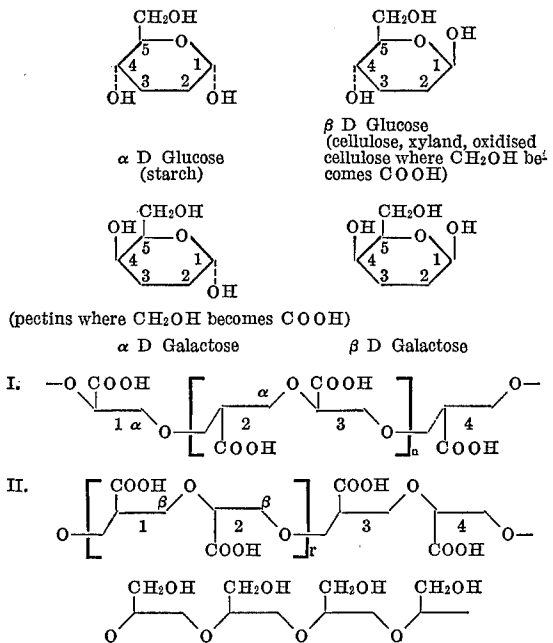
While we do not wish to be bound by any particular theory, we believe that the sheet-forming material employed in accordance with the present invention results in a desirable product because of the unique chemical and stereo-chemical properties of the natural pectic substances, algin and the like.

The pectins and algin are acids by virtue of the carboxyl groups attached at the 5th carbon position of their monomer units, whereas cellulose or hemicellulose con-

tain primary alcohol groupings, or methyl groups or hydrogen at this point. The carboxy group is more readily attacked during low temperature pyrolysis than the corresponding groups of cellulose and hemicellulose; it also offers the possibility of combining ash producing cations and carbohydrate material into a single molecule.

The usual synthetic oxy-celluloses carry a partial complement of carboxyl groups at C₅, but retain some unchanged cellulose units, and other cellulose units in various states of oxidation and randomly esterified by nitrogen oxides. Thus, pectins are constitutionally different from competitive smoke producing carbohydrate materials. They are also unique and different with respect to some specific stereochemical configurations which are known to produce large differences in response to pyrolysis. The pectins (in common with starch) possess alpha structure at the C₁ carbon, while cellulose, hemicellulose, or oxycellulose have a beta structure at the C₁ carbon. That this difference is a very large one with respect to pyrolysis may be seen by comparing the different responses of starch and cellulose to pyrolysis. Starch forms low-temperature pyrolysis intermediates; i.e., thermal starch dextrins, with which a large area of starch technology is concerned; whereas cellulose decomposes at much higher temperatures without forming any similar materials.

The pectins are also different from starch or celluloses by reason of the different configurational arrangement at the C₄ carbon which gives the pectin polymer "trans" rather than the "cis" configuration which is found in starch. Thus, while alpha configuration leads uniquely to a "cis" starch polymer, the same configuration leads to "trans" polymer structure in the case of pectins. Other relationships are evident from the following formulas which show the structural relationships of pertinent monomer units and polymers:



where I is pectic acid (poly galacturonic) (alpha configuration, galactose)

where II is poly glucuronic; xylan COOH=H (beta configuration glucose)

where III is starch (alpha configuration, glucose)

It will be seen that the algin has beta configurations at C₁, but because of the configurations of the mannuronic and glucuronic units, they have "trans" polymer structure.

What is claimed is:

1. A burnable sheet which may be used as a tobacco substitute, said sheet containing substantially no tobacco and comprising from 5 to 95% by weight of a film-form-

15

ing ingredient comprising a pectinaceous material derived from tobacco plant parts and having an acid value in excess of 30 milligrams of KOH per gram and from 5 to 90% by weight of a mineral ingredient comprising an alkali metal salt, an alkaline earth metal salt or a clay.

2. The burnable sheet of claim 1, wherein the mineral ingredient is tricalcium phosphate or magnesium phosphate and is present in an amount of about 25-75% by weight.

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16

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MELVIN D. REIN, Primary Examiner

10

U.S. Cl. X.R.

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15