METHOD OF PREPARING A RECONSTITUTED TOBACCO SHEET EMPLOYING A PECTIN ADHESIVE

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1. Claim

ABSTRACT OF THE DISCLOSURE

This disclosure relates to a process for producing a binder composition for use in the manufacture of reconstituted tobacco. The binder is made from tobacco plant parts and involves the use of the naturally occurring tobacco pectins, which are obtained by a process in which ammonium metaphosphate is employed to treat the tobacco plant parts. The treatment involves the destruction of the alkaline earth metal cross-links of the tobacco pectins, the release of the resulting tobacco pectins by a washing action and the depositing of the released tobacco pectins on the treated plant parts.

This application is a division of application Ser. No. 557,903, which was filed on June 16, 1966 now Patent No. 2,553,541, and which, in turn, is a continuation-in-part of application, Ser. No. 336,009, which was filed on Jan. 6, 1964, now abandoned and which, in turn, is a continuation-in-part of application, Ser. No. 240,130 filed Nov. 26, 1962 now forfeited and application, Ser. No. 169,995 filed Jan. 16, 1962, now abandoned.

This invention relates generally to a method for the production of an adhesive tobacco composition in which tobacco pectins within the tobacco itself serve as the binder.

During the processing and processing of tobacco products, including aging, blending, sheet forming, cutting, drying, cooling, screening, shaping and packaging, considerable amounts of tobacco fines and tobacco dusts are produced. It is known that such tobacco fines and dust can be combined with a binder to form a coherent sheet, which resembles leaf tobacco and which is commonly referred to as reconstituted tobacco. One method for making reconstituted tobacco of this general character is disclosed in United States Patent No. 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. The binder, in such compositions, ranges from about 5% to about 50% of the weight of the tobacco employed. United States Patent No. 2,708,175, describes a binder for reconstituted tobacco which consists of a plant gum, principally of galactomannan. United States Patent 2,592,554 to Frankenburg describes, as binders for reconstituted tobacco, various water-soluble polysaccharides, such as alginic and pectinic acids and their sodium and potassium salts, derived from plants other than tobacco; for example derived from citrus fruits. However, the addition of cellulosic binders further increases the amount of cellulosic material in the product and tends to create an acid and bitter smoke, when the product is used to make cigarettes. The natural hydrophilic cellulosic gums such as guar gum, locust bean gum, algin and other commonly used materials, such as Irish moss, have additional disadvantages. These materials contain proteins and other materials not found in tobacco which add distinctive flavors of their own to tobacco products during smoking. Thus, Frankenburg, in describing the use of various water-soluble polysaccharides derived from plants other than tobacco, teaches that care should be exercised that they must be in a state of refinement. Frankenburg teaches that these materials should be free of extraneous matter containing compounds of nitrogen, particularly proteins, and compounds of sulfur, phosphorus and the halogens; i.e., compounds giving undesirable products of combustion or dry distillation. Such refining is often a very tedious and difficult operation.

The present invention makes possible the production of improved reconstituted tobacco by a method which is simpler and more effective than the methods previously employed. The present method does not require refining of the binder and is, therefore, more easily and efficiently employed than other methods for making binders and for making reconstituted tobacco. The reconstituted tobacco which is obtained in accordance with the present invention need not contain any additional cellulose or proteinaceous material which is foreign to tobacco, since the binder which is employed may be derived solely from tobacco, and may be produced in such a manner that it contains no materials other than those which naturally occur in tobacco. Thus, reconstituted tobacco produced in accordance with the invention, can be so formulated as to be similar in physical properties and chemical composition to natural tobacco.

The term pectic substances 1 will mean those substances which are found in many plant products, and which consist essentially of partially methylated galacturonic acids joined in long chains.

The pectic substances found in tobacco plants contain acetyl groups and differ considerably from commercially available pectins found in other plants, including sugar beet pectins and citrus and fruit pectins. Tobacco protopicins are uniquely insoluble in hot water as compared with protopicins 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 crosslinks 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 above.

1 Note: Unless otherwise specified, the term "pectins" will, for convenience, hereinafter be employed interchangeably with the term "pectic substances."
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.

In accordance with the present invention, tobacco parts are bonded together by tobacco pectins which are especially prepared by a novel process which yields these pectins in a form in which they can be employed as binder materials. Our process for preparing tobacco pectins comprises forming tobacco parts, preferably in a form in which they present a large surface area, with an aqueous solution of a nontoxic reagent which is capable of reacting with and destroying the calcium and magnesium cross-links in the pecticaceous substances which naturally occur in tobacco. After the calcium and magnesium cross-links are destroyed, the tobacco pectins are liberated and made available for use as a binder. The tobacco pectins are then dissolved or dispersed in solution, or are at least sufficiently released from the interstices of the tobacco mass so that they form a coating on the surface thereof. Tobacco pectins which are dissolved or dispersed in the treating solutions, are thereafter precipitated or deposited from the solution, so that they become available for use as a binder material.

In this way the tobacco parts can be bonded together by a binder material which is made of ingredients that are closely related to the naturally occurring ingredients of tobacco. The bonding can be accomplished without the need for the purification of the tobacco pectins, inasmuch as any materials which are present are closely related to the materials which are normally present in tobacco and, thus, do not add any undesired qualities to the tobacco.

The tobacco parts which can be employed in the present invention including tobacco leaves, stems and stalks, or a mixture of these, whether in sheet, flake, particulate or other 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 pecticaceous materials but can also be employed.

In the first step of the process of our invention, tobacco pectins are liberated from pecticaceous materials in tobacco by reacting the pecticaceous materials with a reagent which, under the conditions of the reaction, 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. This reagent may, for convenience, be hereinafter referred to as a "cross-link destroying reagent."

The reaction may be generally represented by Equation 1, which illustrates the reaction of one type of tobacco proteose (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, in which case the product is a solubile pectate.
metal poly-metaphosphates such as tetra-metaphosphates, heptametaphosphates, octametaphosphates, pyrophos- 
phates and tripolyphosphates, such as sodium hexa-metaphosphate, 
tetrasodium pyrophosphate and pentasodium triphosphate. The mechanism which occurs when a 
sequestering agent is employed is the formation of a 
chelate; 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 reagents for calcium and/or magnesium ions. 
Representative examples include alanine, aspartic acid, 
glycine, glycyl glycine, glutamic acid, serine, tyrosine and 
diiodo-l-tyrosine. Amino acids that are effective as chelat-
izing sequestering agents include beta alanine, N,N-di-
acetic 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-aminoethylul-
finic acid, N,N-diacetic acid and ethylenediamine-tetra-
acetic acid. The pH of this reaction should, preferably, 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 cross-link destroying reagent may also function 
partially as a precipitating reagent, in accordance with the first 
step of this invention, and partially as a sequestering agent, in accordance with the second 
embodiment. Such a reagent, for example, is diammonium mono-
hydrogen orthophosphate (DAP), which is a particularly 
preferred material, in accordance with the invention.

In a third embodiment, the cross-link destroying re-
agent is an acid wash which forms a solubilized, free pectic acid and soluble calcium and magne-
sium salts. Generally the acid wash will comprise an 
organic acid, such as hydrochloric acid, phosphoric acid, 
sulfuric acid or a similar acid, which will form soluble 
calcium and magnesium salts under the following con-
titions. Hydrochloric acid and sulfuric acid are particularly 
preferred. 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 temper-
ature of from about −1° C. to about 50° 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 
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. The acid condi-
tions which are necessary for this embodiment of the 
invention may be achieved by the use of ion exchange 
resins which may be used, with suitable resins, to 
obtain the desired pH of the solution during treatment. The 
ion exchange resins may be used and regenerated in ac-
cordance with the usual practices for such resins.

Preferably, the mixture resulting from the acid treat-
ment is then washed with water. This water wash step is 
preferably conducted at a temperature of from about 15° C. 
and, preferably, distilled water is em-
ployed. 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, there should be 2 volumes of water per volume of the mixture resulting 
from the acid treatment. The wash water is separated 
from the tobacco may be used for any suitable means, for example, by con-
ducting the wash in a centrifuge, filter press, Buchner

funnel, or any other apparatus from which liquids can be 
substantially removed from solid materials.

In summary, in the first step of the first embodiment of 
this invention the treating agent Z-R attacks the calcium and/or magnesium cross-links of tobacco pectin and 
forms a precipitate which is a salt of calcium and/or magnesium, thus removing the calcium and/or magnesium from 
the pectin and from the solution. In the first 
step of the second embodiment, the treating agent Z-R 
is a sequestering agent which forms a chelate of the calcium and/or magnesium from the tobacco pectin and 
and makes the calcium and/or magnesium unavailable for 
recombining with the pectin. With cross-link destroying reagents, such as DAP, the first step of the present process may comprise a 
combination of the mechanisms of the first embodiment of 
this invention and the mechanism of the second em-
bodyment of this invention. In the first step of the third 
embodiment of this invention, the treating agent Z-R 
is an acid which attacks the calcium and/or magnesium 

cross-links of the tobacco pectin and forms the 
soluble calcium and/or magnesium salts, which are then 
crushed away from contact with the pectin.

In the first step of each of the first two embodiments of 
the invention, 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 is in condition for 
release from the tobacco cell structure.

The acid treated pectins are placed in condition for re-
lease by bringing the mixture resulting from the acid treat-
ment after the water wash step Z-R, above, to a pH of from about 5.0 to about 10.5 and, 
preferably, from about 6.3 to about 8.5, by the addition of 
an alkaline material. Suitable alkaline materials include 
ammonium hydroxide and alkali metal hydroxides, for 
example, sodium hydroxide, potassium hydroxide and 
lithium 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 comp-
pound containing a monovalent inorganic cation and cap-
able of producing hydroxide ions when dissolved in 
water. 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 a water-soluble compound having a concentration of from about 5 to about 50%

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 of, in certain instances, they will be 
merely deposited on the surface of the tobacco par-
cicles. This comprises the second step of the process of the 
present invention. In embodiments 1 and 2 of the inven-
tion, this release or second step may be accomplished 
concurrently with the first step by reacting with the solu-
tion 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 third step of our process, the 
liberated and separated tobacco pectins can be precipi-
tated or deposited in a relatively free form (as compared with the tobacco pectins as they were originally 
present in the tobacco), from the treating solution, for 
example, by being formed into the insoluble pectic acid 
or into an insoluble salt of pectic acid by or the action of a 
water-miscible solvent, such as acetic acid, 
causing a water-soluble salt of pectic acid to go out of so-
solution. In the case of tobacco pectins 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, if necessary. If any complex or precipitate formed in the first step of this process is present with the soluble pectates, the thixotropic properties of the mixture can also be adjusted by adjusting the pH to precipitate calcium and magnesium pectates.

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. If any complex or precipitate formed in the first step of this process is present, the soluble pectates, the thixotropic properties of the mixture can also be adjusted by adjusting the pH to precipitate calcium and magnesium pectates.

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As discussed above, a particularly preferred embodiment of the present invention involves the use of an ammonium or alkali metal orthophosphate, such as di-ammonium monohydrate orthophosphate (DAP), for the release of the tobacco pectins. The DAP will, generally, be added to the tobacco plant parts, which may, for example, be bright tobacco parts, burley tobacco parts, or a mixture of the same, in an aqueous solution. The concentration of the DAP in the aqueous solution is not critical, but generally, be in the range of 0.5 to 5.0% by weight. The DAP and water may be added separately to the tobacco. The amount of DAP should, preferably, comprise from about 0.01 to about 0.5 part, and, most preferably, from about 0.05 to 0.25 part (by weight) per part of tobacco being contacted. A humectant, such as glycerin or trichethylene glycol, may be present, if desired, at about 0.5 to 1 per part of DAP. The temperature during the DAP treatment of the tobacco may vary between room temperature and about 190° F. or higher, depending on the type of tobacco being treated. Under pressure, even higher temperatures may be employed.

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 dithran, such as dioxane. Water-immiscible solvents such as ether, for example, ethyl ether, may 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 can 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.

While the tobacco pectins can be separated and purified before use as a binder in reconstituted tobacco sheets, they are preferably employed just as they are produced in situ, i.e., in combination with the treated tobacco plant parts from which they were obtained, the entire combination comprising essentially the entire components of a reconstituted tobacco sheet. By using the entire mixture, no original tobacco flavors are lost, all of the tobacco is employed, and the expensive and time-consuming refining operations are required.

Although it is not necessary, the thixotropic properties of solutions containing soluble pectins can be adjusted in the preparation of a cured sheet by the addition of such materials as calcium, magnesium, or potassium salts, and if any complex or precipitate formed in the first step of this process is present with the soluble pectates, the thixotropic properties of the mixture can also be adjusted by adjusting the pH to precipitate calcium and magnesium pectates.

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for smoking. Sheet material of widely different properties may be formed by suitable variations in the manner of forming. One method and product comprises flowing the composite slurry onto a moving belt and applying a layer of dry ground or fragmented tobacco to the wet adhesive surface. If desired, there may be first applied to the belt a layer of tobacco followed by a layer of the binder, and then a top layer of the tobacco. Various additives may be included with the ground tobacco such as flavorants, plasticizers and aromatic substances. The web is ultimately dried and then suitably moistened and rolled up. Such methods of forming continuous sheets are known generally in the art and the details need not be further described. Representative of this procedure is the apparatus and method disclosed in U.S. Patent 2,734,513.

Another method of forming a reconstituted tobacco product, with the slurry of the isolated tobacco paecinct as a binder, comprises mixing ground tobacco thoroughly therewith into a mass of dough-like consistency and then casting the mass in sheet form onto a moving belt surface followed by drying and remoistening in accordance with the known procedures. Representative of this procedure is the apparatus and method disclosed in U.S. Patents 2,708,175 and 2,769,734. Obviously, the reconstituted tobacco may also be formed by molding or other suitable means.

A particularly preferred aspect of the present invention comprises employing, as a binder or directly, the mixture of tobacco and tobacco pectin which have been produced in situ, without any separation steps and without the necessity for any additional adhesive materials.

The following examples are illustrative:

**Example 1**

Tobacco stems (10 parts) were covered with cold water and leached for ½ hour. The water was then decanted and discarded. A treating solution, made from 1 part of sodium carbonate dissolved in 60 parts of water, was added to the leached parts. This mixture was heated at its boiling point for 30 minutes at atmospheric pressure and then for 20 minutes at 20 psi. In the course of this treatment, the tobacco pectin were dissolved from the tobacco parts. The entire wet mass (pulp mixture) was dried and ground in a Waring Blendor so that it would pass through a 50 mesh screen. The resultant material had gel-like properties and was thixotropic in nature.

To this material was added 2 parts of glycerin, to serve as a humectant. The pH of the resulting mixture was adjusted to 6 by the addition of a solution of 10% hydrochloric acid. One gram of sodium carboxymethyl cellulose (CMC) was added to the mixture, giving a proportion of about 1 part of CMC to 10 parts of total solids in the mixture. Since it was desired to use this mixture as a sprayed tobacco binder, the CMC was employed in order to adjust the spraying qualities. The mixture of (a) treated tobacco plant parts, including the liberated tobacco pectins, (b) the sodium carboxymethyl cellulose, and (c) the glycerin had a viscosity which was suitable for spray application of the mixture as a binding material for reconstituted tobacco. This material was sprayed on top of an undercoating of tobacco dust, of an 80 mesh size, which had been dusted on a wet belt. Another coat of the tobacco dust was laid on top of the binder. In general an apparatus similar to that described in U.S. Patent 2,734,051 was employed. As in said patent, the reconstituted sheet was dried and then humidified to the desired moisture content. The control in Table I was made in a conventional manner, using a relatively large amount of CMC in proportion to the pulped washed tobacco stems. The test data as observed are recorded in Table I.

**Example 2**

Fifty grams by weight of burley tobacco stems were thoroughly washed in about 5 liters of cold water for three hours. The washed tobacco stems were then mixed with 500 grams of water having dissolved therein 5 grams of sodium carbonate. The resultant mixture, containing about 8% solids, was steamed under atmospheric pressure for 30 minutes and under a pressure of 20 psi for an additional 20 minutes. At the end of this time, the mixture was allowed to cool and the liquid was separated from the solid materials. The solid materials were treated in a cinder press to recover as much as possible of the remaining liquid. The liquid was added to a previously prepared coagulant bath which consisted of ethanol and hydrochloric acid, in an amount to adjust the pH of the coagulant to about 1.0. The resulting mixture (which had a pH of about 3.0) was alternately stirred and allowed to settle for a period of two hours. At the end of this time, the mixture was strained through a cloth sieve and the filtrate was discarded leaving a solid, gel-like mass, consisting essentially of pectinaceous materials combined with approximately 10 parts of liquor. The yield of pectinaceous materials was 15%, based upon the dry weight of the starting tobacco plant parts. The mass was observed to be thixotropic, soluble in water at a pH of about 6 and soluble in a sodium carbonate solution.

The tobacco pectins thus isolated were quite impure and had a color characteristic of tobacco. The solid mass was then reprocessed in a sodium carbonate solution and the resultant solution was poured into an acidified ethanol bath similar to the coagulant bath used earlier. The re-coagulated solid was obtained by filtration and dried in an oven at 105° C. The dried tobacco pectins were then triturated into a powder of an opaque, somewhat, colorless sheet. When the sheet was pulverized, a white powder was obtained having a distinct and pleasant odor similar to vanillin.

Ten grams of the dried tobacco pectins prepared above were swelled in 100 ml of cold water. The mixture was then added to a slurry consisting of 8.5 grams of refined kraft pulp dispersed in 200 ml of water. The resultant mixture was homogenized in a Waring Blendor. Four grams of glycerin were then added to the mixture to serve as a humectant. The resulting mixture was cast into a binder film, using a Gardiner casting knife set to produce a sheet having a wet thickness of 50 mils. The physical properties of this sheet, after drying, were tested and were found comparable to the properties of conventional binder films. The physical test data are given in Table II. The control material was made by mixing pulp, which had
been refined with NaOH, with sodium carboxymethyl cellulose (CMC) and a humectant, as is shown in Table II.

<table>
<thead>
<tr>
<th>Binder material</th>
<th>(g)</th>
<th>Control binder film</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight, g/m²</td>
<td>8.6</td>
<td>8.4</td>
</tr>
<tr>
<td>Moisture, percent</td>
<td>14.8</td>
<td>14.0</td>
</tr>
<tr>
<td>Tensile coefficient</td>
<td>0.98</td>
<td>0.97</td>
</tr>
<tr>
<td>Intrinsic tensile, psi</td>
<td>6.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Elongation, percent</td>
<td>4.0</td>
<td>4.3</td>
</tr>
<tr>
<td>Work coefficient, gms/cm² in in.²</td>
<td>37.92</td>
<td>61.0</td>
</tr>
</tbody>
</table>

1. Dried tobacco pectins extracted from tobacco peteches.
2. CMC (sodium carboxymethyl cellulose) and pulp, as prepared by known methods and containing about 30% CMC.
3. Work coefficient is proportional to the product of the tensile strength and the elongation.

**Example 3**

One hundred grams of burley tobacco stems were covered with distilled water, leached for 30 minutes and then drained. The washed stems were then mixed with a solution containing 10 grams of diammonium monohydrogen orthophosphate in 600 mL of water. The resultant slurry was heated for 1 hour at a temperature of from 90 to 100°C. The pH of the reaction mixture, after completion of the reaction, was about 7. The entire reaction mixture was homogenized in a Waring Blender. The solids content was determined to be 5% by weight.

Two grams of glycerin, to serve as a humectant, were blended into the above reaction mixture. A film of 50 mL wet-thickness was cast from this mixture. The extruded film was found to have the property of being able to slide off a surface even when newly cast. After the film was partially dried, it was found that it could be peeled off a plate by hand, while still partially wet and then hung up to dry like wet cloth. This property provides definite advantages in the manufacture of tobacco products.

**Example 4-10**

**Example 11**

One hundred grams of burley tobacco stems were covered with distilled water, leached for 30 minutes and then drained. A solution of 10 grams of Versene (tetrasodium salt of ethylenediamine-tetraacetic acid) in 600 mL of water was added to the stems and the mixture was made basic with aqueous sodium hydroxide. The resulting mixture was then heated for 1 hour at room temperature. The entire mixture (a pulp) was homogenized in a Waring Blender and the solids content was determined to be 5% by weight. A 200 gram portion of the pulp, thus prepared, was combined with 2 grams of glycerin, as a humectant, and then cast into a film of 50 mL thickness by the use of a Gardner casting knife. The resultant sheet was found to have satisfactory physical properties and, upon burning, exhibited a very pleasing aroma.

**Example 12**

Green bright tobacco leaves were soaked in isopropanol to remove sugars and chlorophyll. The midrib was stripped out of the leaves leaving the web. One thousand grams of the web (82 grams on a solids basis) were placed in a porcelain bucket and boiled with boiling distilled water containing 9.3 grams of diammonium monohydrogen orthophosphate (DAP). The DAP was added on the basis of 10 grams of DAP per 100 grams of stems (which contained 12% moisture, by weight). The resulting mixture was boiled at low heat for one hour. The juice was then first expressed from the mixture by hand. Solids, for example cellulose and sand, were then further separated from the juice by centrifuging. The clear juice from both operations was then mixed with 70% ethanol to form a gel, which was then squeezed out in cheese cloth. The gel was transferred to a Buchner funnel where it was washed first with acetone and then with ethyl ether. Finally, the gel was placed in a vacuum desiccator and dried. The gel was suitable for use in the preparation of a reconstituted tobacco in accordance with the teachings of the present invention.

**Example 13**

Burley tobacco stalks were separated into cortical tissue, woody tissue, and pith. A sample of each was steam cooked with 10% sodium carbonate for 30 minutes at atmospheric pressure and for 20 minutes at 20 psig. After this cooking, the woody tissue was still hard and could not be pulped in a Waring Blender. The cortical tissue and pith were soft and pulbable. Each of these latter two preparations were suitable for use in the preparation of reconstituted tobacco.

**Example 14**

Coarse ground bright stem tobacco fines (30 grams) were washed thoroughly in cold water, and then placed in a boiling aqueous solution of 3 grams of diammonium monohydrogen orthophosphate and cooked for 5 minutes. The mixture was then placed in a Waring Blender,
After a very short period in the blender, the mixture was converted to a viscous, fine, impalpable slurry; wherein the tobacco stem particles had been completely separated to units of cellular size. This impalpable mass was suitable for use as a binder in reconstituted tobacco. When remixed with some of the cold water washings removed in the first step, the impalpable mass immediately became viscous and eventually jelled to a soft mass.

For further comparison, a similar sample of coarse ground bright stem fines (30 grams), was dispersed in boiling water and cooked for about 30 minutes with three grams of diammonium monohydrogen orthophosphate. The pH of this mixture was brought to a value of 7.1 by the addition to the mixture of 30% of aqueous ammonia. The granules of tobacco could then be refined to a pulp, similar to the soft mass produced in the experiment described in the first part of this example.

**Example 15**

Burley tobacco stems (½ pound) were covered with distilled water, allowed to stand several hours and the water decanted. This step was repeated several times and finally the stems were covered with distilled water containing 50 ml. of concentrated HCl and left overnight at 24°C. After standing overnight the acidic water was decanted and the stems washed repeatedly free of HCl until the wash water gave no precipitate when treated with silver nitrate solution. The stems were then covered with distilled water containing 15 grams of sodium carbonate and left overnight at 24°C. The pH of the sample, the following morning, was 8.8. The stems were swollen and soft and were easily disintegrated with the fingers and the mixture could be homogenized and employed, as a binder in reconstituted tobacco.

**Example 16**

The apparatus employed in this experiment was large scale equipment, comprising a 200 gallon conical bottom, open top, stainless steel tank, fitted with a Cowles high shear mixer.

One hundred and forty-eight gallons of water were placed in the tank and heated to a temperature of 207°F. One hundred and twenty-eight pounds of bright tobacco (milled to pass a 6 mesh per inch sieve) stems were added, while operating the Cowles mixer at a low speed. Almost immediately after the addition of the tobacco, nine and one-quarter pounds of diammonium monohydrogen orthophosphate (technical grade) were added to the mixture. Ammonia (assaying 28%, by weight NH₃) was added to adjust the pH to 7.1. The mixing speed was increased to 1700 r.p.m. After a period of 3 minutes the temperature of the mixture was 194°F. Most of the particles in the mixture were soft enough to be smeared by hand and the mixture had a jelly-like consistency. The mixing was continued for 1 hour to obtain the highest possible state of disintegration, although a 15 minute period appeared to be sufficient for this purpose.

The viscosity of the mixture was found to be 10,400 cps. and its solids content was found to be 8.05% by weight.

This mixture was then employed as a binder, being pumped through a filter to storage tanks and subsequently sprayed on tobacco by the method and equipment described in U.S. Patent 2,734,513. It was applied at the rate of 3 grams per square foot to form a reconstituted tobacco sheet having the following physical properties:

- **Basis weight, g/m² (1) **: 10.2
- **Moisture content (percent by weight) **: 13.0
- **Tensile, kg/in. **: 0.82
- **Fold test, kg/in. **: 0.82
- **Work-to-break, g/m² (2) **: 16.0

3 Weight of all the ingredients, including tobacco pulp, essentially free of moisture.  
2 Calculated by an integrator attached to the Instron Tensile Tester.

**Example 17**

Burley tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then dried and ground and used to make a binder as follows:

One hundred parts of water were brought to a temperature of 195°C, and to this were added:

- 7.00 parts by weight (dry basis) of the washed burley stems,
- 1.05 parts diammonium phosphate, and
- 0.70 part of glycerin, as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 7.1 but no higher than 9.0.

The mixture was then stirred for one hour and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.

**Example 18**

Burley tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then used directly in the wet condition to make a binder as follows:

One hundred parts of water were brought to a temperature of 195°C, and to this were added:

- 7.00 parts by weight (dry basis) of the washed burley stems,
- 1.05 parts diammonium phosphate, and
- 0.70 part of a glycerin, as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 7.1 but no higher than 9.0.

The mixture was then stirred for one hour and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.

**Example 19**

Burley tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then dried and ground and used to make a binder as follows:

One hundred parts of water were brought to a temperature of 195°C, and to this were added:

- 7.00 parts by weight (dry basis) of the washed burley stems,
- 1.05 parts diammonium phosphate, and
- 0.70 part of triethylene glycol (TEG), as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 7.1 but no higher than 9.0.

The mixture was then stirred for one hour and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.
Burley tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then used directly in the wet condition to make a binder as follows:

One hundred parts of water were brought to a temperature of 195° C, and to this were added:

7.00 parts by weight (dry basis) of the washed burley stems,
1.05 parts diammonium phosphate, and
0.70 part of triethylene glycol (TEG), as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 7.1 but no higher than 9.0.

The mixture was then stirred for one hour and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.

Example 21

Bright tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then dried and ground and used to make a binder as follows:

One hundred parts of water were brought to a temperature of 100° C, and to this were added:

7.00 parts by weight (dry basis) of the washed bright (flue cured) stems,
1.05 parts diammonium phosphate, and
0.70 part of glycerin, as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 8.0 but no higher than 8.5.

The mixture was then stirred for four hours and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.

Example 22

Bright tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then used directly in the wet condition to make a binder as follows:

One hundred parts of water were brought to a temperature of 100° C, and to this were added:

7.00 parts by weight (dry basis) of the washed bright (flue cured) stems,
1.05 parts diammonium phosphate, and
0.70 part of glycerin, as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 8.0 but no higher than 8.5.

The mixture was then stirred for four hours and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.

Example 23

Bright tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then dried and ground and used to make a binder as follows:

One hundred parts of water were brought to a temperature of 100° C, and to this were added:

7.00 parts by weight (dry basis) of the washed bright (flue cured) stems,
1.05 parts diammonium phosphate, and
0.70 part of triethylene glycol (TEG), as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 8.0 but no higher than 8.5.

The mixture was then stirred for four hours and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.

Example 24

Bright tobacco stems were washed in cold water whereby, from about 75 to 80% of the natural content of water-soluble substances were removed in the wash water. The stems were then used directly in the wet condition to make a binder as follows:

One hundred parts of water were brought to a temperature of 100° C, and to this were added:

7.00 parts by weight (dry basis) of the washed bright (flue cured) stems,
1.05 parts diammonium phosphate, and
0.70 part of triethylene glycol (TEG), as a humectant.

Concentrated aqueous ammonia was then added to bring the pH of the mixture to a value of at least 8.0 but no higher than 8.5.

The mixture was then stirred for four hours and subsequently refined in a disk type refiner until better than 99% of the pulp (in excess water) could be shaken through an 18 mesh sieve.

The resulting material was then employed as a binder for tobacco plant parts to form a reconstituted tobacco sheet in a manner similar to that described in Example 16.

Example 25

In the acid wash treatment of tobacco parts for removal of alkaline earth minerals of the tobacco pectin, it is necessary to use quite large volumes of water if it is desired to reduce the soluble anion content of the product to a very low level. In this case, the use of a cation exchange resin in a closed loop system with the tobacco parts can make it possible to conduct the process with limited amounts of water and acid.

The use of a resin (such as Dowex 50 W) in this way does not at all alter the principles of this form of treatment since the resin merely serves as a convenient reservoir of acidity, continuously reconditioning effluent from the stems for reuse in the extraction.

In the following example, the use of a cation exchange resin permits the treatment of stems with a small fraction of their natural nitrate ion content. Hydrochloric acid is used at intervals to regenerate the resin, but never directly contacts the tobacco.

The apparatus used for ion-exchange extraction of calcium from tobacco stems consisted of a 20 inch diameter washing column fitted with a 20 mesh screen to support the charge of stems and a 6 inch diameter Pyrex column filled with 15 pounds of Dowex 50 W-8 acid-form ion exchange resin beads. The valves and piping permitted a pump to be used either for recycling waters from the stem charge through the column or for sep-
arately regenerating the resin with hydrochloric acid solution.

In operation, fifty pounds of stems were placed in the washing column and rinsed with cold water until they were nearly free of water-soluble material. Then, the effluent waters were diverted through the ion exchange bed, returning by gravity to the top of stem charge. When the aqueous extract from one pound of burley stems was added to the recycling waters, a pH of between 1.5 and 2.0 was soon attained. During the treatment, the waters flowing from the resin column were monitored for their calcium content. (An appreciable precipitate from 50 ml. of resin effluent treated with ammonium oxalate and made basic with ammonia indicated that the resin was saturated with calcium and needed to be regenerated with hydrochloric acid.) After sixteen hours of operation, and one regeneration of the ion exchange resin, the treatment was considered complete. A subsequent analysis showed that the calcium content of the stem had been reduced to less than one-sixth of the starting value of 4.5% CaO. The stems were rinsed twice with cold distilled water, pressed lightly, and redried in a tobacco processing oven to a final moisture content of about 4%, and ground to pass a 40 mesh screen. When a small sample of the powder was stirred with a little cold ammonia, it dispersed immediately, forming a stiff paste.

The resulting material was then employed as a binder for tobacco plant products to form reconstituted tobacco sheet in a manner similar to that described in Example 16.

Example 26

Twenty grams of tobacco fines were washed in 1 liter of distilled water to get rid of the solubles. The fines were then admixed with 1 N hydrochloric acid until the mixture had a pH of 1.35. The pH was checked on a Beckman pH machine and the curves were also plotted against a titration of distilled water.

After titration, the acid was washed off the fines with three 400 ml. portions of distilled water. The fines were redispersed in 400 ml. of distilled water and sodium bicarbonate was added to bring the pH to 7. The slurry was cast at a thickness of 30-50 mils and dried to form a sheet and the resulting sheet was used as the adhesive binder in sandwich type reconstituted tobacco sheet.

Example 27

Twenty grams of tobacco fines were washed in 1 liter of distilled water to get rid of the tobacco solubles. The fines were then admixed with 1 N hydrochloric acid until the mixture had a pH of 1.35. The pH was checked on a Beckman pH machine and the curves were also plotted against a titration of distilled water.

After titration, the acid was washed off the fines with a 400 ml. portion of distilled water. The fines were redispersed in 400 ml. of distilled water and sodium bicarbonate was added to bring the pH to 7. The slurry was cast at a thickness of 30-50 mils and dried to form a sheet and the resulting sheet was used as the adhesive binder in sandwich type reconstituted tobacco sheet.

Examples 28-30

In each of these three examples, 20 gms. of tobacco fines were washed in 1 liter of distilled water to get rid of the tobacco solubles. The fines were then admixed with 1 N hydrochloric acid until the mixture had a pH of 1.35. The pH was checked on a Beckman pH machine and the curves were also plotted against the titration of distilled water.

After titration, the acid was washed off the fines with three 100 ml. portions of distilled water. The fines were redispersed in 400 ml. of distilled water and a neutralization agent was added as noted in Table VI. This was added bringing the pH to the value shown in Table V. The slurry in each case thickened to a viscous mass which is evidence that the pectin had been solubilized. The slurry was cast at a thickness of 30-50 mils and dried to form sheets. The binders formed in this way were tested to determine their physical properties. These properties are shown in Table V below. The binder was used as the adhesive in a sandwich type reconstituted tobacco sheet.
by the formation of a precipitate comprising an insoluble calcium or magnesium salt, and finally casting the tobacco and the in situ formed pectins to form a reconstituted sheet, the pectins serving as a binder for the treated tobacco parts in the final sheet.

References Cited

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