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METHOD OF MAKING A RECONSTITUTED TOBACCO SHEET

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This invention relates, generally to an improved method for the production of reconstituted tobacco composition comprising tobacco and tobacco derived pectins which serve as a binder for the tobacco.

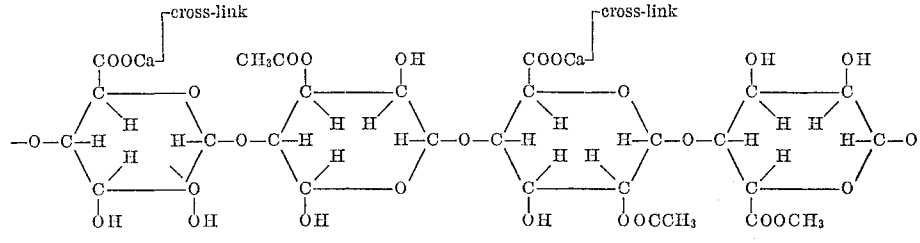
During the production and processing of tobacco products, including aging, blending, sheet forming, cutting, drying, cooling, screening, shaping and packaging, considerable amounts of tobacco fines and tobacco dust are produced. It is known that such tobacco fines and dust can be combined with a binder to form a 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 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 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. However, the addition of cellulosic binders further increases the amount of cellulosic material in the product and tends to create an acrid and bitter smoke when the product is used to make cigarettes. The natural hydrophilic colloid gums such as guar, locust bean, algin and other commonly used material, 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 invention set forth in copending application, Ser. No. 557,903 filed of even date herewith and now Patent 3,353,541 in the names of the present inventors and

entitled "Smoking Compositions and Method of Preparing Same," is a continuation-in-part of application, Ser. No. 336,009, filed on Jan. 6, 1964, now abandoned, and makes possible the production of improved reconstituted tobacco sheet by a method which is simpler and more effective than the methods previously employed. Such a 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 that invention need not contain any additional cellulose or protein foreign to tobacco, since the binder which is employed may be derived solely from tobacco, and contains no materials other than those which naturally occur in tobacco. Thus, reconstituted tobacco produced in accordance with that invention an be so formulated as to be similar in physical properties and chemical composition to natural tobacco.

The term pectic substances,[1] as used herein, 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 pectin 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 protopectins are uniquely insoluble in hot water 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 follows:



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 invention set forth in said Patent No. 3,353,541 tobacco parts are bonded together by tobacco pectins which are specially prepared by a process which yields these pectins in a form in which they can be employed as binder materials. The process for preparing tobacco pectins comprises first reacting tobacco parts, preferably in a form in which they present a large surface area, with an aqueous solution of a non-toxic reagent which is capable of reacting with and destroying the calcium and magnesium cross-links in the pectinaceous substances which naturally occur in tobacco. By destroying the calcium and magnesium cross-links, the tobacco

[1] NOTE.—Unless otherwise specified, the term "pectins" will, for convenience, hereinafter be employed interchangeably with the term "pectic substances."

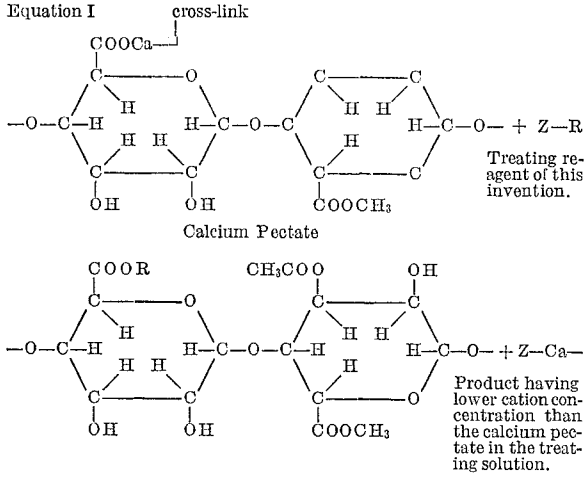
pectins are liberated and are available for use as a binder. The tobacco pectins are then dissolved or dispersed in solution, or are at least sufficiently released from the inerstices of the tobacco mass so that they form a coating on the surface thereof. Tobacco pectins which are dissolved or dispersed 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 without introducing any materials as binders which are foreign to the tobacco, and without the need for the purification of the tobacco pectins, inasmuch as any impurities present are normally present in tobacco and, thus, do not add any undesired qualities to the tobacco.

The tobacco parts which can be employed 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 set forth in said Patent 3,353,541, 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 [2] in the treating solution than the naturally occurring calcium (or magnesium) pectate.

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



A particularly preferred reagent for use in accordance with that invention, functions partially as a sequestering agent, and partially as a precipitating reagent. Such a reagent is DAP (diammonium monohydrogen orthophosphate).

Once the tobacco pectins have been liberated from the tobacco, by the removal of the calcium and magnesium cross-links, due to their chemical reaction with the DAP, the pectins 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. This release may be accomplished concurrently with the first step by reacting with the solution of the DAP treating reagent.

In accordance with the next step of the process, the liberated and separated tobacco pectins can next be precipitated from the treating solution.

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.

While the tobacco pectins can be separated and purified before use, they are preferably employed just as they are produced, i.e. in combination with the treated tobacco plant parts from which they were obtained. By using them in this state, no original tobacco flavors are lost and no expensive 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 chloride. 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.

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 a 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.

The tobacco pectins produced or liberated in situ or isolated by means of the invention set forth in said Patent No. 3,353,541 can be used as the sole binder material for reconstituted tobacco, i.e. no other materials need be added to make the sheet. They can be sprayed, extruded or cast, thus facilitating application onto a moving belt carrying tobacco dust. Under proper conditions of formulation and processing, reconstituted tobacco made with the tobacco pectins produced by the invention exhibit excellent physical and aromatic properties. The ultimate tensile and wet strengths of the reconstituted tobacco are good. While no other materials need be added to the pectinaceous binder other materials can be added, if desired. For example, organic acids and preservatives which may in themselves be of tobacco origin may be added. Plasticizers, such as glycols and polyglycols, and humectants, such as glycerin, may also be added, if desired. In addition, the gel strength of the tobacco pectins can be regulated by partial precipitation to control such rheological properties as viscosity, fluidity and elasticity. Other additives or dispersants may be added in small amounts to regulate slurrying qualities, provided, however, that such substances are not added in large enough quantities to adversely affect the flavor or aroma of the final product. Furthermore, the tobacco pectins can be combined with water-soluble gums or water-dispersible gums commonly used as binders for tobacco sheets such as methyl cellulose, sodium carboxymethyl cellulose, guar gum, locust bean gum, or alginates, although it is preferred to minimize or eliminate such additions in order to obtain a product which most closely resembles natural tobacco.

The product from treating the tobacco plant parts in accordance with the methods of the process of said

[2] By concentration is meant concentration or activity as set forth in Glasstone, "Textbook of Physical Chemistry," 2nd edition, page 954, D. V. Nostrand Company, Inc.

Patent No. 3,353,541 may be cast directly and dried and cut into particulate material similar in physical form to ordinary smoking tobacco and so used, preferably mixed with tobacco leaf cut or shreaded in the usual manner. The product may be cast in sheet form, in blocks or as threads or other shapes, as desired. An important use, however, of the prepared composite slurry or easily molded isolated pectinaceous mass is as a binder for ground tobacco and for the making of corresponding tobacco products suitable 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 the 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 pectins 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 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 comprises employing, as a binder or directly, the mixture of tobacco and tobacco pectins which have been produced in situ, without any separation steps and without the necessity for any aditional adhesive materials.

I have observed that, when reconstituted tobacco sheets are made using DAP under the conditions set forth in said Patent No. 3,353,541, the DAP which is employed can have varying effects on the resulting sheet. Thus, when more than about 5% by weight of DAP (based on the weight of tobacco) is used, under the circumstances set forth in said application, the resulting binder or cast sheet may have some qualities that are not completely satisfactory. For example, when more than about 5% by weight of DAP is employed the cast may be somewhat darker than might be desired or might burn less evenly than sheets produced using less than 5% of DAP.

I have discovered a means to improve the burning characteristics of reconstituted tobacco sheets and particularly those made employing more than 5% by weight of DAP and to greatly lower the viscosity of solution employed in making such sheets to the point where the resulting sheets are much more satisfactory from an engineering aspect.

Essentially, the present invention comprises a process by which an alkaline earth metal phosphate is added to the DAP treated slurry before it is cast directly on a belt.

The alkaline earth metal phosphate may be a calcium phosphate or a magnesium phosphate and may be a synthetic phosphate or a mixture of synthetic prosphates or may be in the form of a naturally-occurring phosphate. Examples of suitable phosphates include: dicalcium phosphate, calcium metaphosphate, monocalcium phosphate as salts of phosphoric acid, calcium pyrophosphate, tricalcium phosphate, monetite, brushite, martinite, isoclasite, fluorapatite, chloroapatite, podolite, dahllite, trancolite, tribasic or normal magnesium phosphate, magnesium acid phosphate, biphosphate, magnesium pyrophosphate, magnesium ammonium phosphate and the like. The types of phosphates and the states in which they may be employed are varied. For a detailed description of calcium and magnesium phosphates of the type which may be used, see J. R. Van Wazer, "Phosphorus and Its Compounds," vol. I, Interscience, New York, 1958, pages 523–542.

The best ash formation and subjective smoking qualities of tobacco products produced from such a process are obtained when the resulting sheet contains from about 13 to 20% of the alkaline earth metal phosphate (by weight) on a solids basis, although from 1 to 50% by weight on a solids basis, of the phosphate, based on the total weight of the reconstituted tobacco sheet, can be employed with good results.

The sheet in a preferred embodiment should be made using from 1 to 50% by weight (based on the total sheet) of DAP in combination with from 1 to 50% by weight alkaline earth metal phosphates. However, the alkaline earth metal phosphate may also be used to improve sheets made by any of the known methods for making reconstituted tobacco sheets, for example, those methods set forth in Patent No. 3,353,541.

The alkaline earth metal phospate may be added to the tobacco parts, while in slurry form, either with or without other ingredients, before the slurry is cast as a sheet.

I have found that such phosphates, as exemplified by calcium phosphate, contrary to what would be expected, lowered the viscosity of the slurries to which they were added. For example, calcium phosphate lowered the viscosity of a slurry of tobacco particles and DAP from about 17,000 centipoise to about 9,000 centipoise. The smoking composition made when the slurry was cast on the belt burned evenly yielding a firm gray ash and gave a subjectively acceptable smoke.

The following examples are illustrative:

Example 1

One hundred grams of whole bright stems were covered with 1500 milliliters of hot tap water. To the mixture was added 7.5 grams of diammonium monohydrogen orthophosphate. Sufficient ammonium hydroxide was added to bring the pH to 7.0. The resulting mixture was kept over a boiling water bath for three hours. A weighed sample was dried in a 100° C. Freas force draft oven to constant weight. The dry weight was divided by the original weight to determine percent solids. Total solids were found to be 6.61%. The slurry was filtered and proportional amounts of the filtrate and the filtered cake were then remixed for use as a binder base. Three hundred grams of the binder were mixed with 5.949 grams of calcium phosphate, NF (30% of the total solids). A like amount of the binder base to which no calcium phosphate was added was prepared for use as a control. After thorough mixing, the two sets of binder material were cast on metal plates in sheets 50 mils thick. The sheets were then steam dried. It was observed that the binder containing the calcium phosphate was much lighter in color than the control, a quality to be desired in a smoking composition. Two sets of the binders were shredded into cigarette filler, made into cigarettes, and smoked. The control which had no calcium phosphate burned unevenly and produced a hard, black ash. The experimental cigarettes with the calcium phosphate burned evenly, produced a gray ash which was slightly weak and gave a fairly mild smoke which was less hard than that of the control.

Example 2

One hundred grams of bright tobacco stems were treated as described in Example 1 and 300 grams of the slurry (total solids 6.61%) was used in preparing a mixture to which 3.966 grams of calcium phosphate were added (20% of total solids). The resulting material was mixed in a Waring blendor and cast on metal plates in a sheet 50 mils thick. A similar mixture without the addition of calcium phosphate was treated in the same manner for use as a control. The sheet containing the calcum phosphate was lighter in color than the control. The two sets of filler were shredded and made into cigarettes. When they were smoked, it was found that the cigarette

without the calcium phosphate burned unevenly and had a hard, black ash. The experimental cigarette with calcium phosphate burned evenly, had a strong gray ash and was milder in taste than the control.

Example 3

In a pilot plant run, a slurry having a viscosity of 16,800 centipoise (Brookfield, 20 r.p.m.) and a solids content of 12.05% was made from the following materials:

220 gallons water at 180° F.
242 pounds of scrap leaf and stem fines
18.1 pounds of DAP
17.0 pounds of concentrated aqueous ammonia

A portion of the slurry was sprayed into a stainless steel belt and the sheet was dried to form a sheet which weighed about 15 grams per square foot. The following data was obtained for the sheet.

	Run 1	Run 2	Run 3	Avg.
Sheet weight, at 23% moisture, g./ft.²	20.94	19.83	19.81	20.19
Dust, Loss/ft.²	0.09	0.10	0.10	0.10 (0.5%)
Moisture Check 23.1%, after 1 hr. in humidity cabinet				
Sheet wt. dry basis 15 grams				

Twenty-five pounds of calicum phosphate (NF) was added to a second portion of the slurry prepared from the ingredients given above. This amount of calcium phosphate corresponded to 0.20 part per part of leaf dust. This was sprayed on a stainless steel belt and dried to form a sheet which weighed about 10 grams per square foot.

The following data was obtained for the sheet:

	Run 1	Run 2	Run 3	Avg.
Sheet weight, at 25.4% Moisture, g./ft.²	13.36	13.45	13.27	13.36
Dust, loss/ft.²	0.00	0.08	0.05	0.04 (0.3%)
Moisture check 25.4%, after 1 hr. in humidity cabinet				
Sheet weight 9.97				

It was noted that the addition of the calcium phosphate actually caused a reduction of Brookfield viscosity from 17,000 centipoise to about 9,000 centipoise. The calcium phosphate addition also resulted in a lighter colored product.

Cigarettes made from filler prepared from the two types of sheets were smoked and the same advantages described in Examples 1 and 2 were observed.

I claim:

1. A method of making a reconstituted tobacco sheet which comprises reacting at a temperature of from room temperature to about 300° F. tobacco plant parts with an aqueous solution of diammonium acid phosphate, said phosphate comprising from 1 to 30 parts by weight per 100 parts of tobacco, the reaction being continued until a measurable amount of pectins are released from the tobacco, adding from 1 to 50 parts by weight per 100 parts of tobacco of an alkaline earth metal phosphate selected from the group consisting of calcium and magnesium phosphates, and casting the resulting material as a tobacco sheet.

2. The method of making a reconstituted tobacco as set forth in claim 1 wherein said alkaline earth metal phosphate is calcium phosphate.

3. The method of making a reconstituted tobacco as set forth in claim 1 wherein said alkaline earth metal phosphate is magnesium phosphate.

References Cited

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