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3,616,801

PROCESS FOR THE TREATMENT OF TOBACCO TO EFFECT ION REMOVAL

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U.S. Cl. 131-143

1 Claim

ABSTRACT OF THE DISCLOSURE

This disclosure relates to a process for the treatment of tobacco. More particularly, the disclosure relates to a process for improving the burning properties of the tobacco, the flavor of the tobacco smoke and the quality of the tobacco ash, by controlling the ion content of the tobacco. The process involves the steps of (1) contacting tobacco plant parts with water to obtain an aqueous tobacco extract, (2) treating said extract to adjust its content of certain metallic ions, without removing desirable tobacco constituents and (3) recombining the treated aqueous tobacco extract with the extracted tobacco parts. The adjustment of the ion content of the aqueous tobacco extract may be accomplished by contacting the extract with an ion-exchange resin. If desired, other ions may be added to the treated tobacco plant parts to further improve the final tobacco product.

The burning properties of tobacco and the flavor and the make-up of smoke from tobacco are dependent to a very significant degree on the water-soluble, ionizable materials occurring in the tobacco. These materials have been found to mainly comprise salts of metals. The metallic ions which are present in tobacco have been found to control the burning rate and character of the burning of the tobacco. The nature of the ash is at least partially dependent on the metallic ions and their proportions, and this in turn affects the combustion. Thus, the formation of a porous ash results in steady burning, whereas the presence of a low-melting metal salt in excess can cause premature quenching of the burning coal, with attendant formation of acrid and irritating smoke components and of a non-porous coal which obstructs the transmission of air through the tobacco.

The most prevalent source of premature quenching of tobacco coals has been found to be the presence in the tobacco of a high proportion of low-melting mineral salts, i.e. salts which melt in the 600° to 850° F. temperature range. This premature quenching produces unburned carbon so that the ash is dark or black.

It has been found that if the proportion of low-melting mineral salts in the ash is less than the capacity of other ash constituents, such as calcium carbonate, magnesium carbonate or calcium phosphate, to absorb them, a satisfactory, substantially complete combustion of the tobacco can be realized.

In the best grades of leaf tobacco, the low-melting salts are present in amounts that provide excellent combustion and, thus, excellent subjective performance in smoking of the tobacco product can be provided, naturally, by the tobacco. However, in many grades of poorer-burning tobacco, and in stems and other lower grades of tobacco products, the proportion of low-melting salts is so high that a clear porous coal structure is not formed. When such lower grades of tobaccos burn, the structural carbohydrates and other principal constituents of the combustible organic material are alternately extinguished and reignited in the fitfully burning mass, producing acrid smoke.

In the past, metallic ion proportions have been adjusted

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in tobacco by the addition of metal salts to the tobacco leaf. While this technique provides for an increase in the concentration of one or more ions, it does not provide for the partial or complete replacement of a specific metallic ion or even a decrease in the concentration of a specific ion, both situations often being desirable.

Water washing of tobacco will remove some soluble salts, primarily potassium salts, from the tobacco. However, it is not possible to avoid removing desirable water-soluble constituents by this method.

Treatment of the water used in the extraction of ground tobacco by acid ion-exchange resins for the purpose of solubilizing pectins and removing them from the tobacco has been disclosed in United States Pat. 3,385,303 to myself and G. H. Burnett. This treatment involves the removal of ions from the insoluble pectin-carbohydrate structure and accomplishes the removal of some ions, which may later be replaced. However, the treatment also solubilizes the pectins, so that they are removed or at least relocated in the tobacco. In contrast, the process of the present invention involves the removal of water-soluble ions, exclusively, and, for the purposes of the present invention, it is desirable to leave the pectins undisturbed during the ion adjustment step, since such pectins are structural agents in the tobacco, serving as a "glue" to bind other constituents.

Certain polyvalent metallic ions have been removed from tobacco by treatment of slurried ground tobacco with desired salts or acids so that the ions, such as calcium or magnesium, are converted to insoluble salts and are replaced by a monovalent metallic ion or by a hydrogen ion in the treating agent. Such treatment has also been found to solubilize the tobacco pectins and to remove them from, or at least relocate them in, the tobacco structure. As discussed earlier in this specification, it is desirable to leave the pectins undisturbed in the process of ion adjustment, since such pectins are structural agents in the tobacco, serving as a "glue" to bind other constituents.

The present invention involves a method whereby metallic ions may be removed from tobacco parts with selectivity and without concurrent solubilization of the tobacco pectins. The ions may then be replaced with other ions, or may be retained in acid form, as desired. In accordance with the present invention, a process is provided for improving the burning properties of tobacco, the flavor of the tobacco smoke and the quality of the tobacco ash, by controlling the ion content of the tobacco. The process involves the steps of (1) contacting tobacco plant parts with water to obtain an aqueous tobacco extract, (2) treating said extract to adjust its content of certain metallic ions, without removing desirable tobacco constituents and (3) recombining the treated aqueous tobacco extract with the extracted tobacco parts. The adjustment of the ion content of the aqueous tobacco extract may be accomplished by contacting the extract with an ion-exchange resin. If desired, other ions may be added to the treated tobacco plant parts to further improve the final tobacco product.

In one embodiment of the present invention, tobacco plant parts are extracted with water and the aqueous extract is then treated with an ion-exchange resin to reduce the amount or eliminate the presence of certain ions from the aqueous tobacco solution. The extract is then combined, if desired, with a solution which contains controlled amounts of other ions; and the resulting mixture is recombined with the extracted tobacco parts.

The aqueous extract may be subjected, as an alternative to an ion-exchange treatment, to treatment by membrane electrodialysis, in order to remove all or part of certain ions from the solution.

I have found that it is desirable to remove from the tobacco as much as 90% and up to 95% of the metallic

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ions which are present in the tobacco as water-soluble, low-melting salts, i.e. salts which melt at temperatures of from about 600° F. to about 850° F. and to replace such ions with ammonium, hydrogen, calcium or magnesium ions. It is particularly desirable to remove potassium ions and replace the potassium ions in the tobacco with ammonium, hydrogen, calcium or magnesium ions. Such replacement of ions has been found to result in an improved and strengthened ash when the thus-treated tobacco is smoked. I have found it desirable to remove at least 20% of the potassium or similar ions and to replace them with ammonium, hydrogen, calcium or magnesium ions.

There are many results which can be obtained by control of the ion content of tobacco. The potassium ion content of tobacco may be cut down to a low level to eliminate the undesirable burning qualities which result from salts of low melting point. Nitrate ion may be removed to give a slower-burning product and to do away with flare-up, or under certain conditions may be increased to provide a faster-burning tobacco. Ammonium ion is preferably introduced to tobacco to provide a smooth flavor. Phosphate or chloride ion may be added to the tobacco to retard burning. Removal of chloride ion may be accomplished to increase the burning rate of the tobacco. The ion content may be altered in such a way that the tobacco has an acid, neutral, or alkaline pH when wet. The ions may be exchanged with little or no net effect on the nicotine content, though this is not always possible. The product resulting from the proper adjustment of ion content is improved over the original tobacco or a product made from it without adjustment of ion content, in that the burning rate, combustion products, ash-forming quality, appearance and other characteristics of the tobacco can be controlled to a desired extent.

The present invention provides a method for effectively accomplishing this result. Tobacco treated in this manner has been found to possess improved and controlled burning rate, more desirable combustion products, ash quality and ash appearance.

One means for accomplishing the selective ion control of this invention after extracting the tobacco parts, which may, for example be tobacco leaves, stems, or dust, and which preferably have been ground or pulverized, with water, is to treat the extract with an ion-exchange resin or with more than one such resin in serial treatments. The treated extract may then be titrated or otherwise combined with desired additives and recombined with the extracted parts. If the combination is a slurry or paste, it may be formed into a web of reconstituted tobacco by any of the methods which are known in the art, for example it may be formed by casting, roll coating, or paper-making techniques.

The aqueous extract is contacted with sufficient ion-exchange resin to remove from about 20 to about 95% by weight of the metallic ions, particularly the potassium ions, which are present in the tobacco as low-melting salts (as defined earlier in this specification). The contacting may be done at room temperature or at higher or lower temperatures and will generally be conducted for a period of from several minutes to several hours, although shorter or longer times may be employed, depending on the specific form and type of resin employed, the amount of ions to be removed and similar factors.

Conventional means can be employed to calculate the amount of resin required in the contacting operation. For example, it may be desirable to remove one half of a molecular equivalent of potassium ions and one tenth of a molecular equivalent of calcium ions from ten liters of an aqueous tobacco extract. This would require at least the amount of acid-form ion-exchange resin to correspond to one half plus one tenth or six tenths molecular equivalents of hydrogen ion. If, for example, a resin having a capacity of four milliequivalents per gram is em-

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ployed, it would be employed in an amount corresponding to at least 150 grams ($6/10 \times 1000/4 = 150$). Thus the 10 liters of extract would be contacted with 150 grams or more of the resin for a period of perhaps 10 minutes to 2 hours, depending upon the temperature, bead size of the resin, degree of cross-linking in the resin and other factors which determine the diffusional characteristics of the resin.

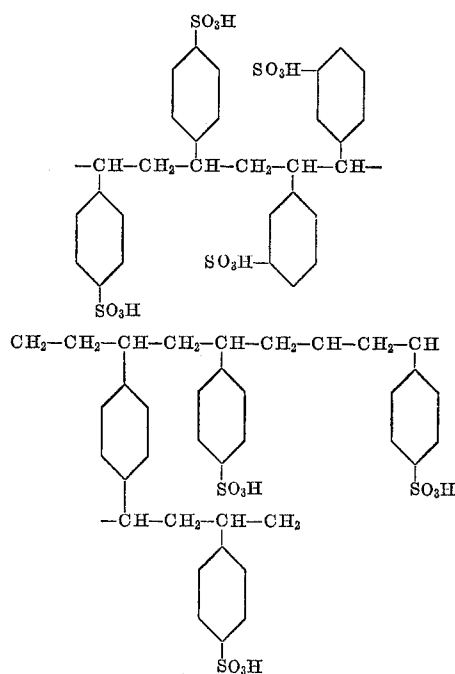
Any technique by which the desired removal of ions will be effected will be satisfactory and conditions of time, temperature and the like may be selected by those skilled in the art to best effectuate the particular purpose involved in a particular contacting operation. The ion-exchange resin may be employed in a batch operation or may be a continuous or a semi-continuous operation.

Semi-continuous operation in a column can be effected by placing pretreated resin in a column of suitable size and passing the reactants through the column continuously.

Preferably, the contacting is conducted under continuous conditions. This can be done by packing a column with the ion-exchange resin in particulate form, for example bead form, and passing the aqueous extract through the column. The technique employed can be the same as is used in chromatographic columns.

Cation-exchange resins which may be employed in accordance with the present invention may be strong cation type resins, intermediate cation type resins or weak cation type resins and can, for example, be any of the commercially available cation-exchange resins.

Satisfactory strong cation-exchange resins include the sulfonic acid types, such as resins formed by cross-linking polystyrene with divinylbenzene and sulfonating the cross-linked product. Such resins are illustrated by the structural formula:

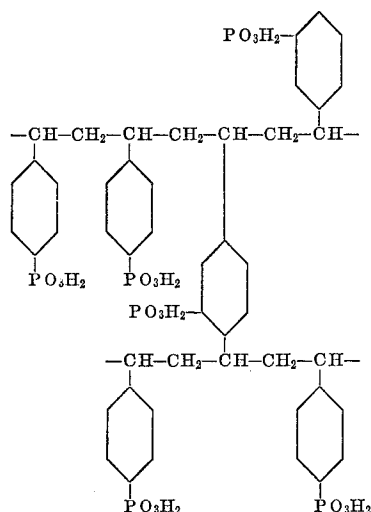


There are numerous commercial cation-exchange resins of this type, including Amberlite IR 112-H+, Amberlite IR 120-H+ (both are manufactured by Rohm and Haas Co.), Dowex 50 W-X8 (manufactured by the Dow Chemical Co.) and the like.

Satisfactory intermediate cation-exchange resins include phosphonic acid types, such as resins formed by cross-linking polystyrene with divinylbenzene and reacting the cross-linked product with phosphoric acid to incorporate a phosphonic acid difunctional group on the styrene-

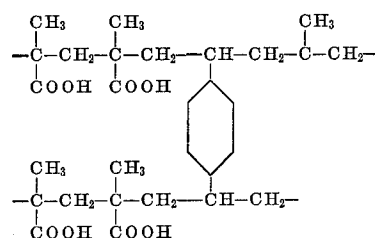
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divinylbenzene lattice. Such resins are illustrated by the structural formula:



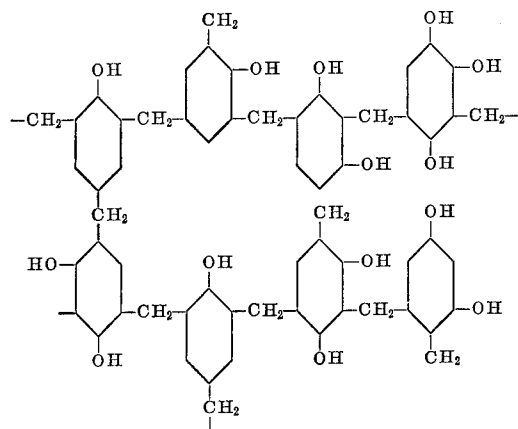
Illustrative of a commercially available resin of this type is Bio-Rex 63 (manufactured by Bio-Rad Laboratories).

Satisfactory weak cation-exchange resins include carboxylic acid types, such as resins formed by copolymerizing methacrylic acid with a cross-linking agent, for example divinyl benzene. Such resins are illustrated by the structural formula:



Illustrative of a commercially available resin of this type is Amberlite CG 50-type 1 (manufactured by Rohm and Haas Co.), which is described as a synthetic weakly acidic cation-exchange resin; carboxylic acid type; hydrogen form.

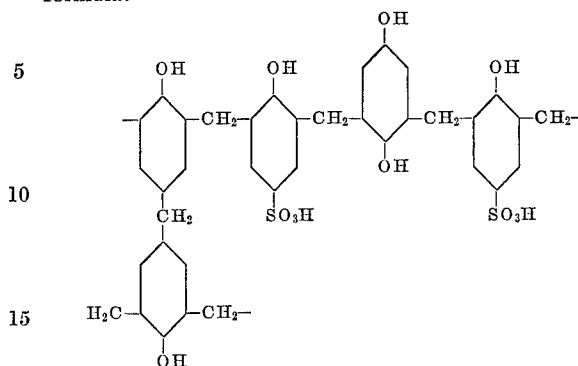
Another type of weak cation-exchange resin comprehends resins having an $-\text{OH}$ group as the ion functional group and formed by reacting polyhydric phenols with formaldehyde. Such resins are illustrated by the structural formula:



Such resins may be further modified by the addition of one or more additional functional groups. For example, the above-shown phenol-formaldehyde resin may be sulfonated to introduce sulfonic groups, giving a resin having

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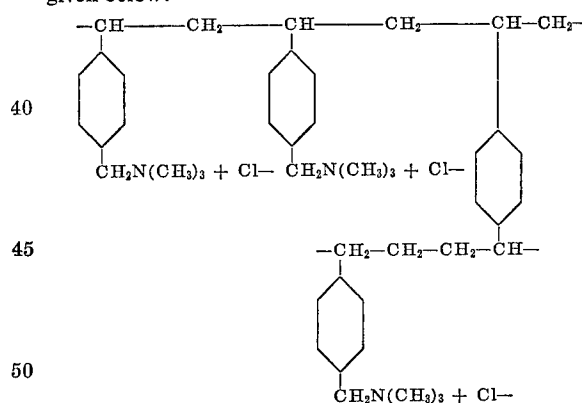
both SO_3H and OH groups, as illustrated in the structural formula:



Other variations of the cationic exchange resins may also be employed. For example, suitable resins include carbonaceous cation-exchange resins of the sulfonated coal-type. Such resins are commercially obtainable as, for example Zeo-Karb resins. Another type of resin which is suitable is the Zeolite type, either natural or synthetic. These resins are hydrated alkali-aluminum silicates.

Cation-exchange resins which may be employed in accordance with this invention may be strong, weak or intermediate cation-exchange resins of the same types as have been described above.

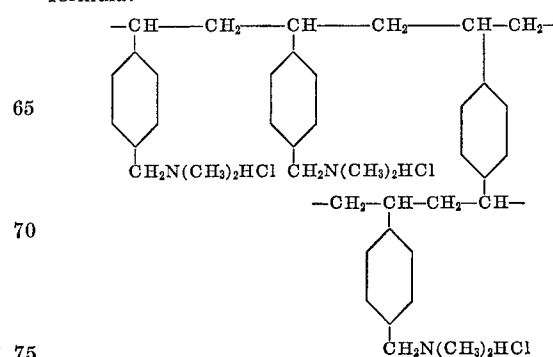
Anion-exchange resins which may be employed in accordance with this invention may be strongly basic resins such as the polystyrene quaternary ammonium resins. Satisfactory commercial resins of this type are Amberlite IRA 400, Amberlite IRA 401, Amberlite IRA 410, Dowex 1 and Dowex 2 and can be illustrated by the formula given below:



Representing strongly basic anion-exchange resins.

Satisfactory weakly basic anion-exchange resins include the primary, secondary, and tertiary amines and are illustrated by such commercially available tertiary amines as Amberlite IR 45, Dowex 3, Amberlite IR 4B, Duolite A2, Duolite A4, Duolite A6 and Duolite A7.

Duolite A114, which is representative of the weakly basic anion-exchange resins can be represented by the formula:



Another means for adjusting the ions in tobacco is membrane electrodialysis. The aqueous extract of tobacco is subjected to an electrodialyzing potential in a series of cells separated from alternating water cells by means of permeable and semi-permeable membranes. The tobacco extract is separated from the water on the side toward the anode by a neutral membrane, and on the side toward the cathode by a cation-permeable membrane. The latter, because it will not transmit anions, will not become clogged by the large anions such as those of the polypeptides or the polyphenolics which are found in the extract. Since there are essentially no bulky cations present, similar blockage by cations does not occur.

The respective anions and cations are often present in the water cells, and are removed as the water is replaced by fresh water and carried away as waste. Alternatively, the water may be recirculated. The extract is also replaced by constant flow, but is preferably recirculated to permit more thorough deionization. The removal of ions may approach 90%, or it may be stopped before that amount has been removed by limiting the time of treatment.

The treated extract may be combined with water-soluble additives including those which contain ions required or desired to be supplemented in the tobacco product. It is then recombined with the extracted insoluble portion

for preparation of a reconstituted product by any of the known ways.

By this method the ion content of tobacco can be controlled and adjusted to give a predetermined combustion characteristic, smoke flavor and ash color.

A preferred apparatus for electrodialysis of tobacco extract has a stack with six operating solution compartments that are 0.063 inch thick, two compartments for isolating the electrode solutions from the tobacco extract solution, and two electrode solution compartments. The width and length of the solution compartments are three inches and twenty-two inches, respectively. The cation-selective membranes are Ionac MC-3142 (Ionac Chemical Company, Birmingham, N.J.), and the neutral membranes are A. H. Thomas & Company, 4465-A2-4.9 cellulose dialyzer film.

Five cation-selective membranes and four neutral membranes are arranged alternately forming ten solution compartments between two graphite electrodes. Electrolyte

solutions (a solution of NaCl altered in pH with NaOH for the anode and with HCl for the cathode) are fed through the compartments adjacent to each electrode to neutralize the acids and bases produced at the electrodes. To insure that pH effects of the electrode streams do not influence the pH of the tobacco extract, water or dilute saline solution is passed through the isolating compartments adjacent to either electrode compartment. Tap water is recycled through three of the center solution compartments and tobacco extract is recycled through the other three center compartments. When voltage is applied to the electrodes, the ions in the tobacco extract are transferred through the membranes to the tap water stream.

The tobacco extract is fed continuously through alternate compartments in the stack, through a conductivity cell (to show the ionic concentration of the solution), a flowmeter and to a reservoir. A pump recycles the tobacco extract through a filter and back to the stack. The tobacco extract is recycled through the stack until the desired

amount of demineralization has been achieved. Likewise, the waste solution (originally tap water) is pumped through the adjacent compartments in the stack, receiving the inorganic salts removed from the tobacco extract.

The following examples are illustrative:

EXAMPLE 1

A 100 g. lot of powdered bright tobacco stems was leached with cold water. Four hundred thirty milliliters of this extract, at 5% total solids content, was treated for 1½ hours with strong anion (+) resin which had a total exchange capacity of 130.0 milliequivalents. The resulting solution had a volume of 500 ml. with a total solids content of 2.9% and was then contacted with 140.0 milliequivalents of strong cation (—) exchange resin for 1½ hours. The 550 ml. of liquor recovered as product from the overall serial contact with both resins had a total solids content of 1.5%. Thus, 32½% of the extract solids had been retained by the anion resin, 19% of the extract solids had been retained by the cation resin, and 48½% of the extract solids was recovered as a deionized product.

The untreated and deionized materials were analyzed and shown to have the following (dry basis) compositions:

TABLE I
Composition, as Percent of Total Solids

	Ca++	K+	Mg++	Cl-	Phosphorus	SO ₄ -	Nicotine	Ash
Untreated-----	2.09	13.97	0.83	3.96	0.52	2.40	0.75	31.3
Deionized-----	0.05	1.66	0.01	2.90	0.81	-----	0.10	4.2

The serial deionization drastically reduced all components but the chloride and phosphate. (In this instance, the high chloride content probably indicates that the cation resin regenerant (HCl) was not completely washed out of the resin.) The large loss of material to the anion resin is characteristic since a substantial fraction of the organic solids of stem extract consists of mono- and polyfunctional carboxylic acids.

EXAMPLE 2

Cold water leachings from bright tobacco stems were treated serially with weakly basic and weakly acidic ion exchange resins (IR-4B and IRC-50-CP, respectively, from Rohm and Haas Co.) using the procedure outlined in Example 1 above. In this case, 13.5% of the total dissolved solids was retained by the anion resin, 10% was retained by the cation resin, and 76.5% was obtained as product. The following solution analyses show that little removal of inorganic ions was achieved.

TABLE II
Composition, Percent of Extract Solids

	Ca++	K+	Mg++	Phosphorus	Cl-	SO ₄ -	Nicotine	Ash
Untreated-----	0.34	2.96	0.14	0.06	0.84	0.52	0.2	6.5
Treated-----	0.30	2.40	0.11	0.02	0.77	0.52	0.08	5.2

A portion of this solution was added to a proportionate amount of pulp from the leached stems and cooked for 25 minutes at 18 lb. pressure. The slurry was refined in a Waring blender and cast into sheets weighing approximately 10 g. per sq. ft. The sheets were shredded and converted to cigarettes.

These cigarettes were smoked by a panel of experts who found them not to be substantially different from cigarettes made similarly from untreated bright tobacco stems.

EXAMPLE 3

The cold water leachings from 100 grams of bright stems were treated in 290 milliequivalents of strongly acidic cation exchange resin, "Dowex" 50 W-X8 from Dow Chemical Company. The composition of the soluble effluent from the resin (dry basis) was: K, 0.3%; Ca, 0.15%; total ash, 7.47%; this indicates very complete removal of the most abundant cations. Part of this ef-

fluent was combined with washed bright stem pulp from a proportionate weight of stems, and cooked for 25 minutes at 18 lb. pressure. The slurry was refined in a Waring blender and cast into sheets weighing approximately 10 g. per sq. ft., which were shredded and converted to cigarettes.

These cigarettes were smoked by a small panel of experts who judged them to be different in taste and much milder than cigarettes made similarly from untreated bright tobacco stems.

EXAMPLE 4

Cigarettes were made from deionized liquor as described in Example 3 but with the difference that the deionized slurry was adjusted to pH 5.5 with ammonia prior to formation of the reconstituted sheets. These cigarettes were preferred over the test (acidic) cigarettes described in Example 3.

EXAMPLE 5

Separate cold water leachings from several 100 g. portions of bright stems were treated with 290 milliequivalents of acid cation-exchange resin, "Dowex" W-X8 from Dow Chemical Company. The treated solutions were recombined with the bright stem pulp, and cooked for 25 minutes at 18 lb. pressure. The slurries were refined by Waring blender and treated as follows:

(A) The acidic slurry was brought to pH 5.5 with ammonia as in Example 4.

(B) The acidic slurry was brought to pH 5.5 using a mixture of 3.3 pts. KOH and 1.2 pts. CaO.

(C) The acidic slurry was brought to a pH of 5.5 using CaO.

(D) Slurry was prepared directly from bright stems with no deionization.

Sheets were cast from the four slurries and the dried sheets were shredded and converted into cigarettes. These cigarettes were smoked by a small panel with the following result:

Cigarette A (containing ammonium ions) was considered to produce the best tasting and mildest smoke.

Cigarette C (mostly calcium) produced a fairly mild smoke but had a somewhat unusual taste.

Cigarette B (calcium plus potassium) was most similar to the control, producing a harsh smoke with a characteristic "stemmy" taste.

Since all the cigarettes were made from the same starting material, and had similar compositions except for differences in kind and amounts of cations present, it may be inferred that both the taste and harshness of cigarettes can be varied almost as will be adjusting their cationic composition.

EXAMPLE 6

Tobacco extract was prepared by soaking 20 lb. of bright stems overnight in 50 lb. of water and expressing approximately 25 lb. of the extract from the soaked stems. One gallon of the extract was introduced into the tobacco extract reservoir of a membrane electrodialysis apparatus. Tap water was introduced into the waste reservoir. The water and extract were circulated through the compartment. The voltage applied to the electrodes was adjusted to give a current flow of about

8.5 amp, or a current density of 20 millamp/sq. cm. of membrane. The two solutions were circulated through the stack for approximately five hours, so that about 85% of the ions was removed, according to conductivity measurement. Analysis of the stem extract before and after demineralization is compared in Table III.

TABLE III.—PARTIAL ANALYSIS OF BRIGHT STEM EXTRACT AFTER ELECTROMEMBRANE DIALYSIS

	Original extract	Demineral- ized extract	Percent removal
Soluble solids.....	15.3	8.4	45
pH.....	4.8	4.8	-----
Specific gravity.....	1.070	1.025	-----
	Mg./ml.	Mg./ml.	
Na.....	1.68	.98	42
K.....	9.25	4.34	53
Cl.....	7.0	.61	91
Ca.....	2.32	1.08	53
NO ₃ -N.....	.22	.10	55
Mg.....	1.63	.48	71
Total alkaloids.....	1.4	.64	54
Reduced sugars.....	53.0	38.4	28
Total N.....	2.64	1.66	37
Ash.....	45.2	10.2	77
P.....	.82	.32	61
S.....	1.3	.2	85

Part of the demineralized extract was combined with washed bright stem pulp from a proportionate weight of stems and subjected to cooking at 18 lb. pressure for 25 minutes. The slurry was then refined in a Waring blender, cast into sheets, and dried over a steam bath. The sheets weighing approximately 10 g. per sq. ft. were shredded and made into cigarettes.

These cigarettes were smoked by a small panel of experts who judged them to be different in taste from, and much milder than, cigarettes similarly made from untreated bright stems.

Unless otherwise indicated, all percentages and proportions set forth in this specification are on a weight basis.

I claim:

1. A method for treating tobacco which comprises the steps of:

- (1) extracting tobacco plant parts with water to produce an aqueous tobacco extract and an insoluble tobacco portion;
- (2) removing from about 20 to about 95% by weight of alkali and alkaline earth metallic ions whose salts in the tobacco have melting points of from about 600° to about 850° F. from the tobacco extract by treating said extract with an ion exchange resin; and
- (3) recombining the deionized product of step (2) with the insoluble tobacco portion of step (1).

References Cited

UNITED STATES PATENTS

802,487	10/1905	Wimmer	131—143
3,390,685	7/1968	Von Bethmann et al. ..	131—143
3,385,303	5/1968	Hind et al.	131—140 X

MELVIN D. REIN, Primary Examiner

U.S. Cl. X.R.

131—17; 204—180, 302

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,616,801 Dated November 2, 1971
Inventor(s) John D. Hind

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

Col. 7, line 70. Change "though" to --through--

Col. 8, Table I. Change " SO_4^- " to $--\text{SO}_4^{--}$

Col. 8, Table II. Change " SO_4^- " to $--\text{SO}_4^{--}$

Col. 8, line 70. Change "in" to --with--

Col. 9, line 51. Change "as" to --at--

Change "be" second instance to --by--

Signed and sealed this 21st day of November 1972.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents