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TOBACCO PRODUCTS

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18 Claims. (Cl. 131—17)

This invention relates to tobacco products and more particularly relates to tobacco compositions which will release a controlled amount of nicotine upon pyrolysis.

It has long been known in the tobacco industry that it is desirable to maintain the nicotine content of tobacco products at a uniform level, in order to provide a satisfying smoke. However, it is difficult to accomplish this result, since the nicotine content of tobacco varies widely, depending on the type of tobacco and the conditions under which the tobacco is grown.

Among the factors affecting the nicotine content of any variety of tobacco are the conditions which exist during the growth of the tobacco, for example, the moisture conditions, the type of soil, the fertilizers that are employed, the number of tobacco plants per acre and the care which is given to the plants during their growth. The nicotine content also varies widely, depending on the variety of tobacco. Many of the newer varieties of tobacco plants yield tobacco which is low in nicotine. Furthermore, methods of preparing tobacco products frequently remove some or all of the nicotine that is naturally present in the tobacco. In addition, modern technology has made it possible to utilize portions of the tobacco plant other than the leaves for smoking and some of these portions, such as the petioles, are low in nicotine content.

Maintaining the nicotine content at a sufficiently high level to provide the desired physiological activity, taste, and odor which this material imparts to the smoke, without raising the nicotine content to an undesirably high level, can thus be seen to be a significant problem in the tobacco art.

The addition of nicotine to tobacco in such a way that it remains inert and stable in the tobacco product and yet is released in a controlled amount into the smoke aerosol when the tobacco is pyrolyzed is a result which is greatly desired.

Previous efforts to adjust the amount of nicotine in tobacco have not been successful. It has not been feasible to add nicotine per se to tobacco products. Since it can be absorbed through intact skin, nicotine is difficult and hazardous to handle in processing operations. In addition, free nicotine is unstable material and has been found to decompose readily at room conditions. Thus, if nicotine were simply added as the free material to tobacco, it would be likely to decompose during storage of the tobacco product, thereby resulting in the formation of undesirable decomposition products and resulting in a decrease in nicotine. Even though the nicotine content of tobacco products could, by the addition of nicotine under conditions involving considerable effort, be made initially uniform, the decomposition attending storage of the product would not provide a smoke containing a uniform amount of nicotine.

The present invention provides a solution to this long-standing problem and results in accurate control of the amount of nicotine which is released in tobacco smoke. By employing the methods and compositions of the present invention, it is possible to eliminate the hazards of handling nicotine and to incorporate exact amounts of nicotine in a tobacco composition which will remain constant over extended periods of time and which will ultimately yield a smoke containing a controlled amount of nicotine.

The present invention comprises incorporating into a tobacco product a material which can be characterized as a nicotine-cation ion exchange resin (referred to hereinafter for convenience as a nicotine-cation exchange resin). The resulting composition is inert and stable and can be employed in a cigarette filler, in pipe tobaccos, in cigars or in other tobacco products. The nicotine-cation exchange resin will not decompose under ordinary storage conditions and does not impart undesirable odors to the tobacco. However, when the tobacco is smoked, nicotine is released from the nicotine-cation exchange resin and goes into the smoke. The amount of nicotine which is desired in the smoke can be adjusted within desired limits by the proper control of the amount of nicotine-cation exchange resin which is initially incorporated in the tobacco.

The nicotine-cation exchange resin, which will hereinafter also be referred to as the nicotine-resin, can be prepared by contacting a cation exchange resin with nicotine under either continuous or batch conditions. When the contacting is done in the batch state, the reactants are agitated in a reaction flask with a volume of resin, which can, for example, comprise from 20 to 30% by weight of the reactant. The amount of materials the temperature and the time of operation will depend upon the reactants involved. The mixture is agitated by shaking or stirring. The use of a fine mesh resin will minimize any physical deterioration of the resin which might be caused by a stirrer. Particles in the range of 100–200 mesh are preferred. At the end of the reaction period, the solution can be decanted and the suspended resin recovered by filtration. The resin can then be rinsed and air-dried and it is then ready for use. The solvent is preferably water, although the other inert liquids in which the nicotine is soluble can also be employed.

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 an aqueous solution of nicotine through the column. The technique employed can be the same as is used in chromatographic columns. As in the the case of the batch contacting, other inert liquids may be employed in place of water.

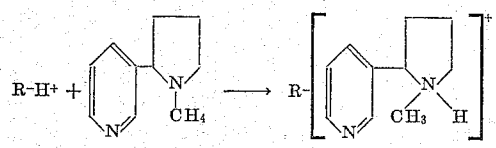
In either the batch or continuous method, after the desired amount of nicotine has been taken up by the resin, the resin can be removed from the contacting vessel directly employed in accordance with the present invention.

The exact amount of nicotine which is incorporated in the resin can be determined by methods well known in the art. For example the method set forth by R. B. Griffith in "Tobacco Science," volume 1 (1957), on pages 130–137 may be employed. Another method is that described in the "Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists," Fourth Edition, 1935.

The proportion of nicotine in the resin is not critical,

so long as the amount of nicotine is known. However, it is advantageous to utilize a nicotine-resin in which a considerable amount of nicotine is reacted, since the amount of nicotine-resin required to incorporate any particular amount of nicotine which is desired in a tobacco composition obviously decreases with increasing proportions of nicotine to resin.

A representative equation for the reaction involved in the preparation of the nicotine-cation exchange resin is schematically shown below:

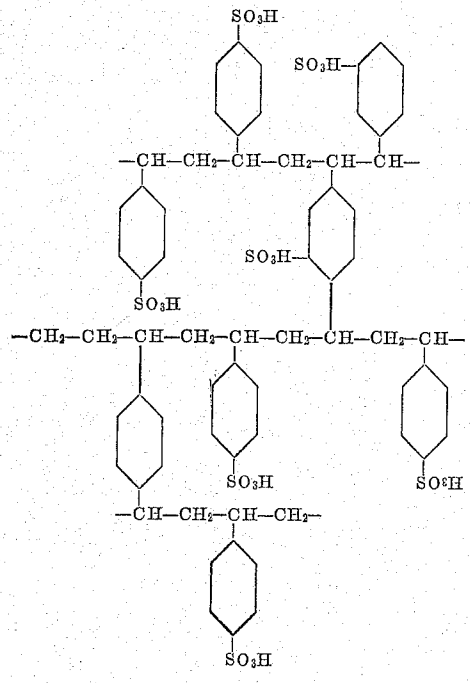


Resin Nicotine Nicotine-resin

The above equation represents the reaction when the cation exchange resin is in the hydrogen ion form, as will be described below. A similar reaction could occur with a cation exchange reaction in which the hydrogen ion were replaced with another ion such as sodium ion, potassium ion or other ions. However, the hydrogen ion type is preferred, because it is more easily replaced by nicotine and more readily takes up the nicotine upon contact.

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.

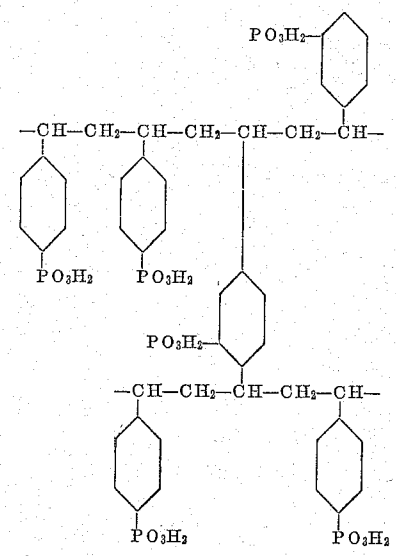
Satisfactory strong cation exchange resins include the sulfonic acid types, such as resins formed by cross-linking polystyrene with divinylbenzene and sulfonating the cross-linked product. Such resins are illustrated by the structural formula:



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.

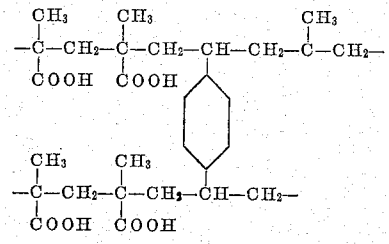
Satisfactory intermediate cation exchange resins include phosphonic acid types, such as resins formed by cross-linking polystyrene with divinylbenzene and reacting the cross-linked product with phosphonic acid to incorporate a phosphonic acid difunctional group on the styrene-

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



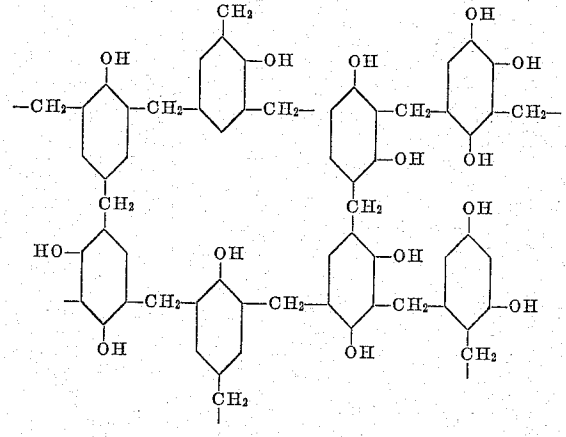
Illustrative of a commercially available resin of this type is Bio-Rex 63 (manufactured by Bio-Rad Laboratories).

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



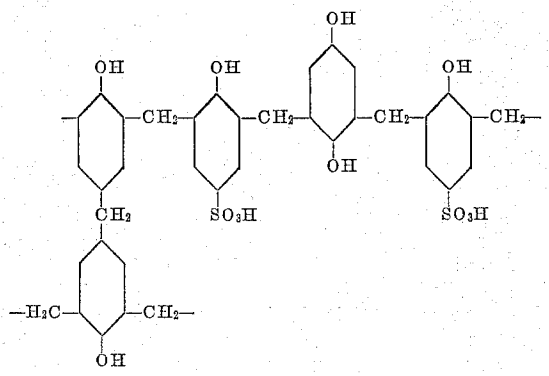
Illustrative of a commercially available resin of this type is Amberlite CG 50-type 1 (manufactured by Rohm and Haas Co.) which is described as a synthetic weakly acidic cation exchange resin; carboxylic acid type; hydrogen form.

Another type of weak cation exchange resin comprehends resins having an —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 phenol-formaldehyde resin may be sulfonated to introduce sulfonic groups, giving a resin hav-

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



Other variations of cationic exchange resins may also be employed. For example, suitable resins include carbonaceous cation exchange resins of the sulfonated coal-type, in either the hydrogen or sodium condition, i.e. in which the ion which is replaced by the nicotine is either hydrogen or sodium. 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.

The nicotine-resin can be applied to tobacco in many different ways. For example, it can be used directly as it is taken from the reaction vessel after its preparation, or it can first be ground to form smaller particles. The resin particle size can vary widely. The nicotine-resin particles can be admixed with a sticker, such as a corn syrup solution, honey, molasses or other similar material, and can then be sprayed on, admixed with or otherwise applied to the tobacco.

The nicotine-resin can be employed with tobacco products of all kinds, including cigarette filler, cigar filler, pipe tobacco and the like.

The amount of nicotine-resin that is added to the tobacco will vary depending upon the nicotine content originally present in the tobacco and upon the nicotine content desired in the tobacco. Generally, the nicotine content of the tobacco is brought to a level whereby there are 0.1–3.0 mg. of nicotine in the smoke per cigarette.

One method of determining how much of a particular nicotine resin to add to a particular tobacco is to analyze the smoke for nicotine, which can be done by conventional methods, such as is described in the Journal of the Association of Official Agricultural Chemists (vol. 42) (Nov. 2, 1959) on pages 424–429. In accordance with this method an aqueous solution of smoke particulate phase is steam distilled under appropriate conditions; this is followed by spectrophotometric examination of the resulting distillate in the ultraviolet spectral region.

The directions for the details of this procedure include the following:

Collect the smoke particulate phase from 10 successive cigarettes, using a standard robot smoking procedure (35 ml. puff volume taken over a 2 second interval, once per minute) upon a glass wool plug or an equivalent collection medium suitable for the separation of 0.1μ particles and larger from a gas particulate phase mixture. Strip the nicotine alkaloids from the collection medium with four 10 ml. portions of 0.05 N HCl. Combine the separate eluates and dilute to exactly 50 ml. with 0.05 N HCl. Transfer a 10 ml. aliquot of this solution to the port of the distillation unit. Distill approximately 100 ml., and discard. Make the sample in the unit alkaline by adding a size 00 capsule of NaCl and a size 00 capsule of NaOH, in that order. Repeat the distillation and collect a second 100 ml. portion, as follows: distill approximately 98 ml. into a 100 ml. volumetric flask to which 5 ml. 3 N H_2SO_4 has previously been added. Dilute the distillate exactly to mark with distilled water, mix well, and examine spectrophotometrically between 230 and 300 mμ. Correct the absorbance of the unknown solution at approximately 260 mμ by a baseline selected on the basis of the curve. Draw a line from the lowest point on both sides of the maximum absorbance. The difference between the baseline and peak at the wavelength of the peak is taken as the absorbance of the sample. Compare this corrected absorbance to the absorbance of the standard nicotine solution corrected in the same manner, and calculate the nicotine content of the sample directly from this comparison, using standard spectrophotometric technique.

Mg. nicotine alkaloid=$(A/A')\times$(mg. known per ml.$\times$dilution factor/no. cigarettes in sample); where A is corrected absorbance of unkown, and A' is corrected absorbance of known. The nicotine-resin content for the tobacco can then be adjusted to bring the nicotine in the smoke to within the range which is desired.

The following examples are illustrative:

Example I

Twenty-five grams of synthetic weakly acidic cation exchange resin of the carboxylic acid type, hydrogen form, having the trade name Amberlite CG–50, type 1 (Rohm and Haas Co.) was placed in a 250 ml. beaker. Twenty milliliters of nicotine and 100 ml. of distilled water were added to the beaker containing the resin. The resulting slurry was added to a 1-inch diameter chromatographic column, which was 36 inches long, and the slurry was eluted. Since it contained a large quantity of nicotine, the first 50 ml. of eluate was collected in a beaker and added to the column. The column was washed until the eluate was free of nicotine. This was determined by a spot test (a Konig reaction as described in J. Prakt. Chem. N.F. 69, pages 1–39 and 105–137 (1904). The nicotine-resin, when removed from the column and dried, was ready for use as an additive to tobacco.

Example II

Nicotine was incorporated into a weak cation exchange resin of the type, and in the manner, described in Example I.

Regular cigarette filler was divided into two portions. One portion was then set aside as a control and a second portion was employed to prepare experimental cigarettes, with the nicotine content increased by the addition of the nicotine-resin. The nicotine-resin was slurried in a Waring Blendor with an aqueous solution of corn syrup to give it the proper consistency for spraying and was then sprayed on the second portion of filler. The control portion was sprayed with an aqueous solution of corn syrup alone. A standard nicotine analysis showed that the nicotine content of the experimental cigarette was approximately double that of the control. In the case of the control, the nicotine content was about 14 milligrams per cigarette, whereas in the cigarette containing the nicotine-resin compound, the nicotine content was about 27 milligrams per cigarette.

The experimental cigarettes were smoked on a standard constant volume smoking machine. The puffs were of two-second duration and had a volume of 35 ml. The cigarettes were smoked to a 25 mm. length and the smoke was collected on a Cambridge-type filter pad which trapped paritcles greater than 0.1 micron in size. All of the nicotine was trapped on this pad. The pads were removed. The nicotine alkaloids were stripped from the pads with four 10 ml. portions of 0.05 N HCl. The separate eluates were combined and diluted to exactly 50 ml. with 0.05 and HCl. A 10 ml. aliquot of this solution was transferred to a distillation unit. Approximately 100 ml. were distilled and discarded. The sample remaining in the distillation unit was made alkaline by adding a size 00 capsule of NaCl and a size 00 capsule of NaOH, in

that order. The distillation was repeated and a second 100 ml. portion was collected as follows:

Approximately 98 ml. was diluted into a 100 ml. volumetric flask to which 5 ml. 3 N H_2SO_4 has previously been added. The distillate was diluted exactly to mark with distilled water, mixed and was examined in a Cary spectrophotometer for its nicotine content. Analysis of the smoke from these cigarettes showed that the nicotine content of the smoke from the experimental cigarettes was increased 0.4 mg./cigt., or approximately 33% over that of the control. The smoke data obtained are given below:

	Control (mg. nicotine/cigt.)	Experimental (mg. nicotine/cigt.)
(1)	1.2	1.5
(2)	1.3	1.7
(3)	1.1	1.4
(4)	1.1	1.6
(5)	1.3	1.7
Average	1.2	1.6

tine present in the tobacco filler prior to the addition of the resin was 14 mg./cigt., or 1.27%.

Cigarettes were also prepared using nicotine incorporated in Bio-Rex 63 resin (manufactured by Bio-Rad Laboratories), a phosphonic acid cation exchange resin containing a phosphonic acid difunctional group on a styrene-divinylbenzene lattice. This material was used in the acid form and had a particle size of 20–50 mesh. This resin was used in Examples VI and VII. The figures for these examples were obtained in a similar manner as in the case of Examples I–V.

In the table, after certain examples, the figures are given for a control in which the identical filler was employed, without the addition of nicotine-resin.

The details and results of Examples III, IV, V, VI and VII are presented in the following table. Ranges of addition of resin to tobacco filler and the resulting increase in the nicotine content of the smoke due to the incorporation of the nicotine-resin can be seen from the table. It can be seen from the table that the nicotine content of the smoke has been increased in a range of from 0.1 to 0.8 mg. per cigarette over the controls.

Cigt. type	Nicotine in cigt. filler prior to the addition of resin, mg./cigt.	Theoretical amt. of resin added, mg./cigt.	Actual amt. of resin added, mg./cigt.	Total nicotine content of cigt. filler, mg./cigt.	Nicotine in filler from resin, mg./cigt.	Total amt. of nicotine in smoke, mg./cigt.	Nicotine increase in the smoke due to the resin, mg./cigt.
Example III	14.0	50	47.6	27.0	13.0	1.6	0.4
Control	14.0	0	0	14.0	0	1.2	0
Example IV	18.5	10	10.5	20.9	2.4	1.3	0.1
Control[1]	18.5	0	0	18.5	0	1.2	0
Example V	18.5	20	19.6	25.4	6.9	1.4	0.2
Example VI	2.5	5	4.7	3.7	1.2	0.4	0.1
Control	2.5	0	0	2.5	0	0.3	0
Example VII	1.6	35	35	10.5	8.9	1.0	0.8
Control	1.6	0	0	1.6	0	0.2	0

[1] NOTE.—same control for Examples IV and V.

Examples III, IV, V, VI and VII

Cigarettes were prepared using nicotine incorporated into Dowex 50W–X8 resin, a strong cation exchange resin of the sulfonic acid type. This resin was used in Example IV. They were prepared to give a theoretical yield of 10 mg. of resin per cigarete (22.8% of the treated resin was nicotine). The theoretical amount of nicotine would have been 2.3 mg./cigt. Chemical analysis of the tobacco filler showed that the actual nicotine content was 2.4 mg./cigt., corresponding to 10.5 mg. of the resin. The amount of nicotine present in the tobacco filler prior to the addition of the resin was 18.5 mg./cigt., or 1.67%.

Cigarettes were also prepared using nicotine incorporated into Amberlite IR 112, a strong cation exchange resin of the sulfonic acid type. This resin was used in Example V. The cigarettes were prepared to give a theoretical yield of 20 mg. of resin per cigarette (35.3% of the resin was nicotine). The theoretical amount of nicotine would have been 7.1 mg./cigt. Chemical analysis of the tobacco filler showed that the actual nicotine content was 6.9 mg./cigt. corresponding to 19.6 mg. of the resin. The amount of nicotine present in the tobacco filler prior to the addition of the resin was 18.5 mg./cigt., or 1.67%.

Cigarettes were also prepared using nicotine incorporated in Amberlite CG–50, type 1 (IR–50), a weakly acidic cation exchange resin of the carboxylic type, hydrogen form. This resin was used in Example III. Cigarettes were prepared to give a theoretical yield of 50 mg. of resin per cigarette (27.3% of the resin was nicotine). The theoretical amount of nicotine would have been 13.6 mg./cigt. Chemical analyses of the tobacco filler showed that the actual nicotine content was 13.0 mg./cigt. corresponding to 47.6 mg. of the resin. The amount of nico-

We claim:

1. A tobacco composition comprising tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco.

2. A tobacco composition comprising tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco of the sulphonic acid type.

3. A tobacco composition comprising tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco of the phosphonic acid type.

4. A tobacco composition comprising tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco of the carboxylic acid type.

5. A tobacco composition comprising tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco of the phenol-formaldehyde type.

6. A tobacco composition comprising tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco of the sulfonated coal-type.

7. A process for incorporating a controlled amount of nicotine in tobacco comprising incorporating in the tobacco a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco.

8. A process for incorporating a controlled amount of nicotine in tobacco comprising incorporating in the tobacco a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco, of the sulfonic acid type.

9. A process for incorporating a controlled amount of nicotine in tobacco comprising incorporating in the tobacco a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco, of the phosphonic acid type.

10. A process for incorporating a controlled amount of nicotine in tobacco comprising incorporating in the tobacco a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco, of the carboxylic acid type.

11. A process for incorporating a controlled amount of nicotine in tobacco comprising incorporating in the tobacco a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco, of the phenol-formaldehyde type.

12. A process for incorporating a controlled amount of nicotine in tobacco comprising incorporating in the tobacco a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco, of the sulfonated coal-type.

13. A tobacco composition comprising smoking tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco which, upon smoking of the tobacco, releases nicotine into the smoke resulting from the smoking.

14. A tobacco composition comprising smoking tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco which, upon smoking of the tobacco, releases nicotine into the smoke resulting from the smoking, said cation ion exchange resin being of the sulfonic acid type.

15. A tobacco composition comprising smoking tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco which, upon smoking of the tobacco, releases nicotine into the smoke resulting from the smoking, said cation ion exchange resin being of the phosphonic acid type.

16. A tobacco composition comprising smoking tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco which, upon smoking of the tobacco, releases nicotine into the smoke resulting from the smoking, said cation ion exchange resin being of the carboxylic acid type.

17. A tobacco composition comprising smoking tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco which, upon smoking of the tobacco, releases nicotine into the smoke resulting from the smoking, said cation ion exchange resin being of the sulfonated coal-type.

18. A tobacco composition comprising smoking tobacco and a nicotine-cation ion exchange resin in an amount sufficient to release nicotine upon pyrolysis of said tobacco which, upon smoking of the tobacco, releases nicotine into the smoke resulting from the smoking, said cation ion exchange resin being of the phenol-formaldehyde type.

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UNITED STATES PATENT OFFICE

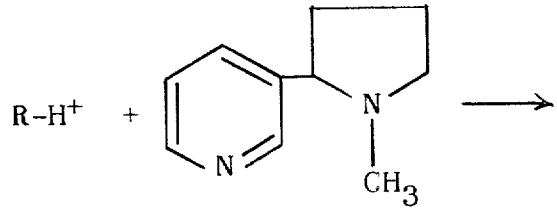
CERTIFICATE OF CORRECTION

Patent No. 3,109,436 November 5, 1963

Abraham Bavley et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

In the grant, lines 1 and 2, for "Abraham Bavley, of Bon Air, Virginia, and Frank E. Resnik, of Richmond, Virginia," read -- Abraham Bavley, of Bon Air, Virginia, and Frank E. Resnik, of Richmond, Virginia, assignors to Philip Morris Incorporated, of New York, N. Y., a corporation of Virginia, --; line 11, for "Abraham Bavley and Frank E. Resnik, their heirs" read -- Philip Morris Incorporated, its successors --; in the heading to the printed specification, lines 3 to 5, for "Abraham Bavley, 9817 Oldfield Drive, Bon Air 35, Va., and Frank E. Resnik, 10024 Hobby Hill Road, Richmond, Va." read -- Abraham Bavley, Bon Air, Va., and Frank E. Resnik, Richmond, Va., assignors to Philip Morris Incorporated, New York, N. Y., a corporation of Virginia --; column 3, lines 11 to 18, the left-hand portion of the formula should appear as shown below instead of as in the patent:



Signed and sealed this 12th day of May 1964.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents