

1

3,280,823

## ADDITIVE-RELEASING FILTER FOR RELEASING ADDITIVES INTO TOBACCO SMOKE

Abraham Bavley, Bon Air, and Ernest W. Robb II, Richmond, Va., assignors to Philip Morris Incorporated, New York, N.Y., a corporation of Virginia

No Drawing. Filed Oct. 1, 1963, Ser. No. 312,879

1 Claim. (Cl. 131-10)

This invention relates to an additive-releasing filter for tobacco smoke for releasing additives into tobacco smoke. More particularly, the present invention relates to an additive-releasing filter for tobacco smoke for releasing additives into tobacco smoke, which additives can be maintained and preserved during storage of the tobacco products containing them and which additives are released in controlled amounts when tobacco smoke passes through said filter.

One of the additives which can be released into tobacco smoke in accordance with the present invention is nicotine. It has long been known in the tobacco industry that in order to provide a satisfying smoke, it is desirable to maintain the nicotine content of tobacco products at a uniform level. 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 an 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.

In copending application Serial No. 149,540 filed November 2, 1961, now Patent 3,109,436, a solution to this

2

problem has been provided by the incorporation of nicotine-ion exchange resins in the tobacco. The present invention provides even greater improvements than those attained in accordance with that invention, in that there are no ion-exchange breakdown products introduced into the smoke.

The present invention provides a solution to this longstanding 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. In addition, the present method does not introduce any ion-exchange breakdown products into the smoke.

Another type of additives which can be released into tobacco smoke in accordance with this invention is a flavorant. Often flavor or flavors which are incorporated in tobacco are lost or altered during subsequent manufacturing steps or during storage. Furthermore, it is difficult to control the amount of flavor released during the smoking of a tobacco product to insure uniformity of tobacco flavor during the entire smoking process.

While many efforts have been made to introduce flavors into tobacco smoke, no completely satisfactory method has been found. For example flavoring acids have been incorporated into the tobacco in the form of stable esters which break down into the acids upon pyrolysis. Such a method, however, is only useful for certain types of flavorants and also results in the incorporation into the smoke of the other breakdown products of the pyrolysis of the esters.

The present invention overcomes the above-mentioned disadvantages. This invention permits the release into tobacco smoke, in controlled amounts, of desirable flavorants, as well as the release, in controlled amounts and when desired, of nicotine into tobacco smoke.

In accordance with this invention, the desired additive is incorporated in a tobacco-containing article in a manner such that it will not be released prior to the time the tobacco product is smoked. By the term "tobacco" as used in this specification is meant any composition intended for human consumption by smoking whether composed of tobacco plant parts or substitute materials or both.

The present invention comprises incorporating into a filter for tobacco smoke a material which can be characterized as an additive-ion exchange resin. This additive-ion exchange resin may be a flavor-ion exchange resin or a nicotine-ion exchange resin.

In the case of nicotine, the additive-ion exchange resin can be 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 filter for cigarettes, pipes, 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 or the filter. However, when the tobacco is smoked and the smoke passes through the filter, 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 filter.

The nicotine-cation exchange resin, which will hereinafter also be referred to as the nicotine-resin, can be pre-

3

pared 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.

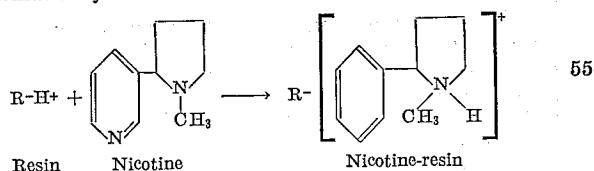
Preferably, the contacting is conducted under continuous conditions. This can be done by packing a column with the ion exchange resin in particulate form, for example bead form, and passing an aqueous solution of nicotine through the column. The technique employed can be the same as is used in chromatographic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



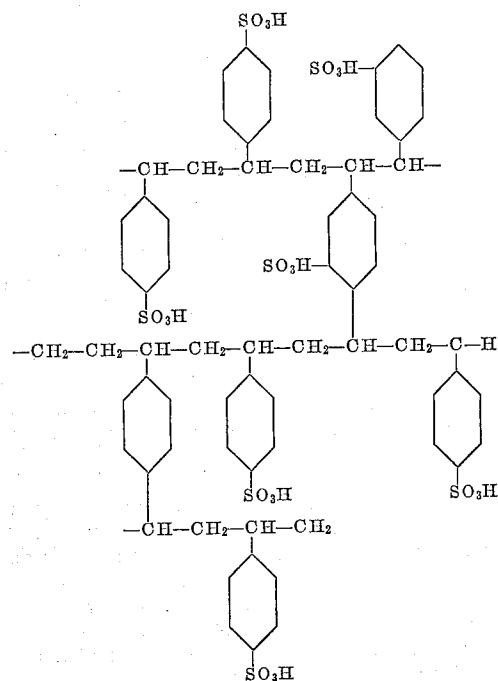
The above equation represents the reaction when the cation exchange resin is in the hydrogen ion form, as will be described below. A similar reaction could occur with a cation exchange reaction in which the hydrogen ion were replaced with another ion such as sodium ion, potassium ion or other ions. However, 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-link-

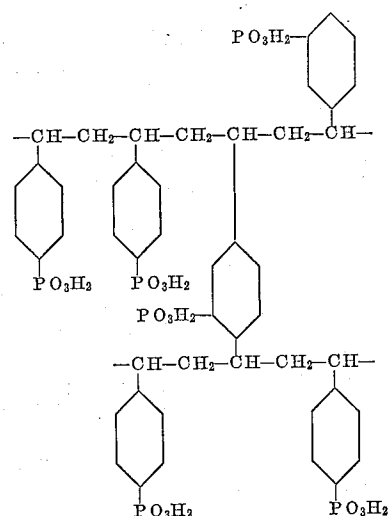
4

ing 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<sup>+</sup>, Amberlite IR 120-H<sup>+</sup> (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:

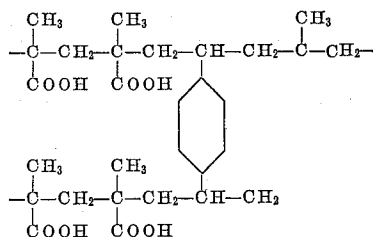


Illustrative of a commercially available resin of this type is Bio-Rex 63 (manufactured by Bio-Rad Laboratories).

Satisfactory weak cation exchange resins include carboxylic acid types, such as resins formed by copolymerizing methacrylic acid with a cross-linking agent, for ex-

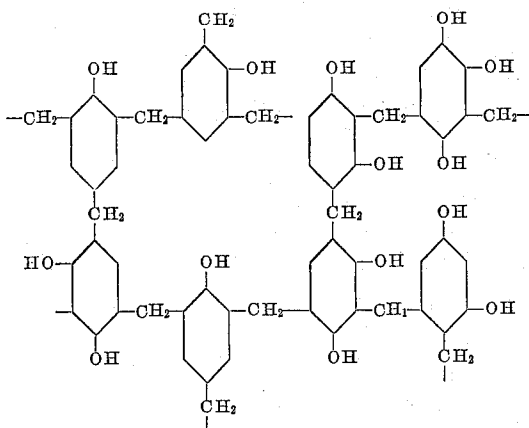
5

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

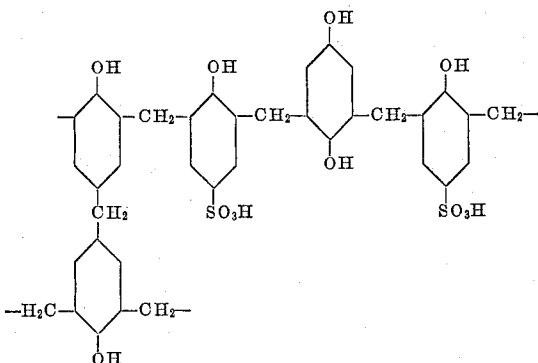


Illustrative of a commercially available resin of this type is Amberlite CG 50-type 1 (manufactured by Rohm and Haas Co.), which is described as a synthetic weakly acidic cation exchange resin; carboxylic acid type; hydrogen form.

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 having both  $\text{SO}_3\text{H}$  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, 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 the filter in many different ways. For example, it can be used directly as it is taken from the reaction vessel after its preparation,

6

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 the components of the filter or otherwise applied to the filter.

The amount of nicotine-resin that is added to the filter 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 filter 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 filter 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 0.1  $\mu$  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  $\text{H}_2\text{SO}_4$  has previously been added. Dilute the distillate exactly to mark with distilled water, mix well, and examine spectrophotometrically between 230 and 300  $\text{m}\mu$ . Correct the absorbance of the unknown solution at approximately 260  $\text{m}\mu$  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 wave length 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.

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

In the case of a flavorant, the additive-ion exchange resin can be a flavorant-anion exchange resin, a flavorant-intermediate ion exchange resin or a flavorant-cation exchange resin.

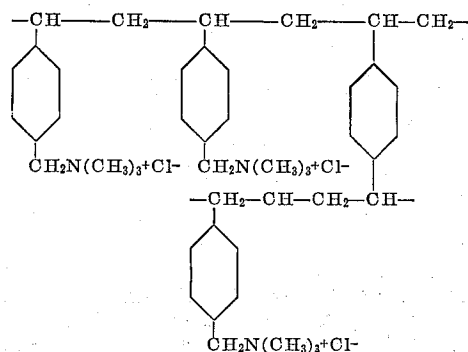
Flavorants which can be used in accordance with this invention include both acidic and basic flavor materials which will volatilize and be released from the ion-exchange resin to be carried in the smoke when the tobacco containing the flavorant-ion exchange resin is burned. Basic flavor materials which can be employed include flavorful alkaloids, amines, myosmine, or quinine derivatives. For example, the basic flavorants can be: alkaloids, such as nornicotine, cotinine, myosmine, nicotine, nicotyrine, anabasine, anatabine, and metanin; hetero-cyclic bases, such as pyridine, pyrrolidine,

2,3<sup>1</sup>-dipyridyl, 2-picoline, 3-picoline, 4-picoline, alpha-collidine, beta-collidine, gamma-collidine, 2,4-lutidine, 3, 4-lutidine, 2,6-lutidine; 3-pyridyl ethyl ketone, 3-pyridyl methyl ketone, methyl nicotinate, methyl isonicotinate, 6-methylquinoline, and 6-isopropylquinoline; aliphatic amines such as ammonia, triethylamine benzylamine, octylamine; aromatic amines such as 3-phenyl-2-propen-1-yl anthranilate, methyl 2-methylaminobenzoate, ethyl o-aminobenzoate, methyl anthranilate (methyl o-aminobenzoate) and phenylethyl o-aminobenzoate; Schiff bases such as methyl N-3,7-dimethyl-7-hydroxyoctylidene-anthranilate and methyl N-(p-tert-butyl-alpha-methylhydrocinnamylidene)anthranilate; and amino acids, such as glycine, alanine, glutamine, lysine, valine, leucine, isoleucine, proline, ornithine, arginine, and serine. The preferred basic flavorants are: nornicotine, myosmine, 3-pyridyl methyl ketone, methyl nicotinate, ethyl o-aminobenzoate, methyl anthranilate (methyl o-aminobenzoate), glycine, and alanine. Acidic flavorant materials which can be employed include organic carboxylic acids having from 3 to 8 carbon atoms, inclusive. Representative acids are the saturated aliphatic fatty acids, for example propionic acid, n-butyric, and isobutyric acid, 4-methyl valeric acid, 3-methyl valeric acid, 2,2-dimethyl butyric acid, 2-methyl isovaleric acid, straight or branched chain caprylic acids; the unsaturated fatty acids, such as acrylic acid, crotonic acid, vinylacetic acid, 4-methyl-4-heneoic acid, and 5-methylsorbic acid; the cycloalkane or cycloalkene aliphatic acids, such as cyclopentanecarboxylic acid, cyclohexanecarboxylic acid, cyclopentaneacetic acid or cyclohexaneacetic acid or the corresponding unsaturated cycloalkenes; the aromatic carboxylic acids, such as benzoic or toluic acids; and phenylacetic acid. In addition the volatile derivatives of the above acids, for example hydroxy acids or keto acids may be employed. It is preferred that that flavoring acid be an aliphatic or alicyclic saturated monocarboxylic acid of the fatty acid series having 4, 5, or 6 carbon atoms.

Although many of the materials mentioned above either are odorless or have a disagreeable odor per se when they are smelled in certain concentrations, they increase the flavor of tobacco smoke when used in low concentrations by altering the acid-base ratio in the smoke. The acids also tend to produce a mildness effect.

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

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 I and Dowex 2 and can be illustrated by the formula given below:



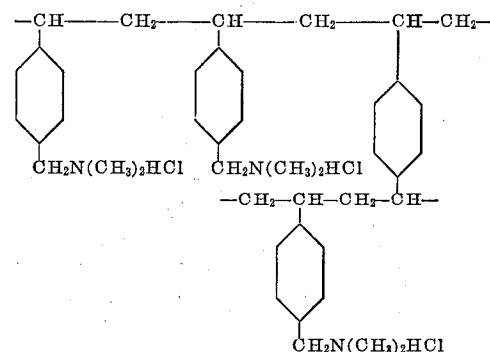
Resin obtained by treatment with trimethylamine.

Representing strongly basic anion exchange resins.

Satisfactory weakly basic anion exchange resins include the primary, secondary, and tertiary amines and are illus-

trated by such commercially available tertiary amines as Amberlite IR 45, Dowex 3, Amberlite IR 4B, Duolite A2, Duolite A4, Duolite A6 and Duolite A7.

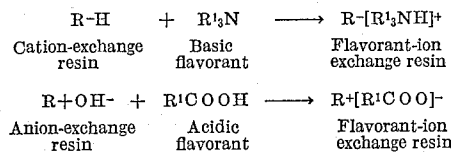
Duolite A114, which is representative of the weakly basic anion exchange resins can be represented by the formula:



Resin obtained by treatment with dimethylamine.

The flavorant-ion exchange resin, i.e. the resinate, can be prepared by contacting the resin with the flavor-producing material under either continuous or batch conditions. The amount of materials, the temperature, and the time of operation will depend upon the reactants involved. In general, however, the time will be between about 1 second and about 30 minutes and the temperature will be between about 50° and about 130° F. Ion exchange particles in the 20-40 mesh size are preferred. At the end of the reaction period, the solution can be decanted and the suspended resinate removed by filtration. The resinate can then be rinsed and air-dried.

Representative equations for the reactions involved in the preparation of the flavorant-ion exchange resin are schematically shown below:



The filter base can comprise any filter material which is an adsorbent and/or absorbent material, including the commercially available filter materials. For example, it can be paper, cellulose acetate, cellulose paper or synthetic polymers, such as polyethylene. The filter can also contain additives, such as carbon, molecular sieves, crystalline cellulose, alumina, fuller's earth, rice starch, cellulose powder and diatomaceous earth.

The additive-ion exchange resin (resinate) can be added to the filter base in a variety of ways. For example, the resinate can be placed between the two sections of a dual cellulose acetate filter; a finely divided resinate can be dispersed in a solvent and sprayed on cellulose acetate tow which is then dried and made into a filter; the resinate can be ground and added as dust to the cellulose acetate after which the cellulose acetate is made into a filter; or the resinsates can be made in situ in ion exchange paper or in certain celluloses having ion exchange activity, and the materials are then processed as filters.

The range of levels for application of the resinsates is approximately 0.01-50 mg./cigt. for all of the additive ion exchange resins on the filter base. The preferred range is one which will produce 0.10-0.50 mg./cigt. of the flavorant in the smoke.

The flavorant-ion exchange resin will not decompose under ordinary storage conditions and does not impart undesirable odors to the tobacco product.

When fibers containing the flavorant-ion exchange resin are attached to a filter rod and smoked, the flavorant transfers well into the smoke.

The invention may be illustrated by the following examples;

## Example 1

A sulfonated polystyrene cation exchange resin (Rohm and Haas Amberlite IR 112) was converted to the H<sup>+</sup> form and mixed with an aqueous solution of nicotine. After the rapid absorption of the nicotine was complete, the resin was filtered off and dried in air. Analysis of the dried resin showed that it contained 33%, by weight, of nicotine. It had no detectable odor of nicotine. The percent of nicotine in the resin did not change significantly after storing for one year.

The resin was ground to 60–80 mesh size and incorporated into the filter of dual filter-type cigarettes by placing it between the carbon filter and the cellulose acetate filter. The amount applied was 20 mg. of the resin per cigarette. A smoking panel, which evaluated the cigarettes subjectively, reported that these cigarettes had the characteristic effect of nicotine; i.e., they increased throat impact and increased overall flavor and "smoke sensation" as compared with control cigarettes of the same type but containing no resin. Determination of nicotine in smoke by the procedure described earlier in this specification<sup>1</sup> showed that the cigarettes containing the resin in the filter delivered 0.98 mg. per cigarette compared with 0.83 for the control cigarettes.

## Example 2

A cation exchange resin of the phosphonic acid type (Bio-Rex 63) in the H<sup>+</sup> form was treated with nicotine as in Example 1. The resin, after drying contained 30% by weight nicotine. It had no odor of nicotine. The resin was incorporated into the filter of dual filter cigarettes by the procedure used in Example 1. The increased nicotine effect in the smoke as compared with that of the control was observed substantially. The analyses were: resin cigarette 0.96 mg. per cigarette, control 0.83 mg. per cigarette nicotine in smoke.

## Example 3

The IR 112 resin containing 33% nicotine (Example 1) was ground to pass 200 mesh and then dispersed in ethanol. The ethanol suspension of the resin was sprayed onto cellulose acetate filter tow. The tow, after spraying was manufactured into filter rods, which were cut into 15 mm. lengths and attached to 57 mm. sections of tobacco filler to form cigarettes. The amount of resin incorporated into the filter was 18 mg. per cigarette. These cigarettes, when smoked, had a noticeable "nicotine effect" when compared with control filter cigarettes made the same way but containing no resin.

## Example 4

A strongly basic quaternary ammonium type anion exchange resin (Rohm & Haas IRA 400) was converted to the OH<sup>-</sup> form and stirred with an aqueous solution of glycolic acid. After absorption of the acid was complete, the resin was air-dried and ground to 60–80 mesh. The resin was analyzed by displacing the adsorbed glycolic acid in solution with tetramethylammonium hydroxide and determining the displaced glycolic acid by gas chromatography. This analysis showed that the resin contained 0.183 g. glycolic acid per g. of resin.

The resin containing glycolic acid was incorporated into

<sup>1</sup> Journal of the Association of Official Agricultural Chemists (vol. 42) (Nov. 2, 1959) on pages 424–429.

dual filter type cigarettes as in Example 1. Fifty mg. per cigarette of the resin were applied. These cigarettes were smoked mechanically and the total particulate material, collected on FTC filters, was analyzed for glycolic acid by a gas chromatographic procedure. The results were:

Cigarettes with glycolic acid resin in filter: 376 µg. of glycolic acid per cigarette glycolic acid.

Control cigarettes with no resin in filter: glycolic acid, less than the detectable limit of 100 µg. per cigarette.

## Example 5

A weakly basic tertiary amine type anion exchange resin (Rohm & Haas IRC 45) was converted to the OH<sup>-</sup> form and was treated with an aqueous solution of acetic acid. After absorption of the acid by the resin was complete, the resin was dried and ground to 60–80 mesh. Analysis of the resin by the same method used in Example 4 showed that this resin contained 16.4% acetic acid by weight.

This resin was incorporated into dual filter cigarettes by the method used in Example 1, at a level of 50 mg. per cigarette. The pH of the mainstream smoke from these cigarettes was 5.4; while the pH of control cigarettes, not containing the resin in the filter gave a mainstream smoke pH of 5.9. Analysis of the acetic acid in smoke of these cigarettes gave the following results:

Cigarettes containing acetic acid-resin in filter: 720 µg. acetic acid per cigarette.

Control cigarettes without resin: 460 µg. acetic acid per cigarette.

We claim:

A tobacco product comprising a tobacco section and a filter section, said filter section including, prior to ignition of said tobacco section, a nicotine-ion exchange resin as an integral part thereof, said nicotine-ion exchange resin being adapted to release nicotine upon contact with tobacco smoke subsequent to ignition of said tobacco section, said tobacco section, prior to the ignition of said tobacco section, being substantially free of said nicotine-ion exchange resin and having a nicotine content which is below that of a conventional tobacco product, whereby smoke produced by ignition of said tobacco section passing from said tobacco section through said filter section and emerging from said filter section, will have a nicotine content approximating that of a conventional tobacco product.

## References Cited by the Examiner

## UNITED STATES PATENTS

2,293,954	8/1942	Tiger	131—208
2,739,598	5/1956	Eirich	131—10
2,754,829	7/1956	Hess	131—208
2,839,065	6/1958	Milton	131—10
3,047,431	7/1962	Bavley et al.	131—17
3,109,436	11/1963	Bavley	131—17

## FOREIGN PATENTS

173,262 12/1952 Austria.

## OTHER REFERENCES

Linde: Chemical-Loaded Molecular Sieves, Form F-1311, published by Linde Co., Division of Union Carbide Corp., Aug. 3, 1959.

SAMUEL KOREN, *Primary Examiner*.

M. D. REIN, *Examiner*.