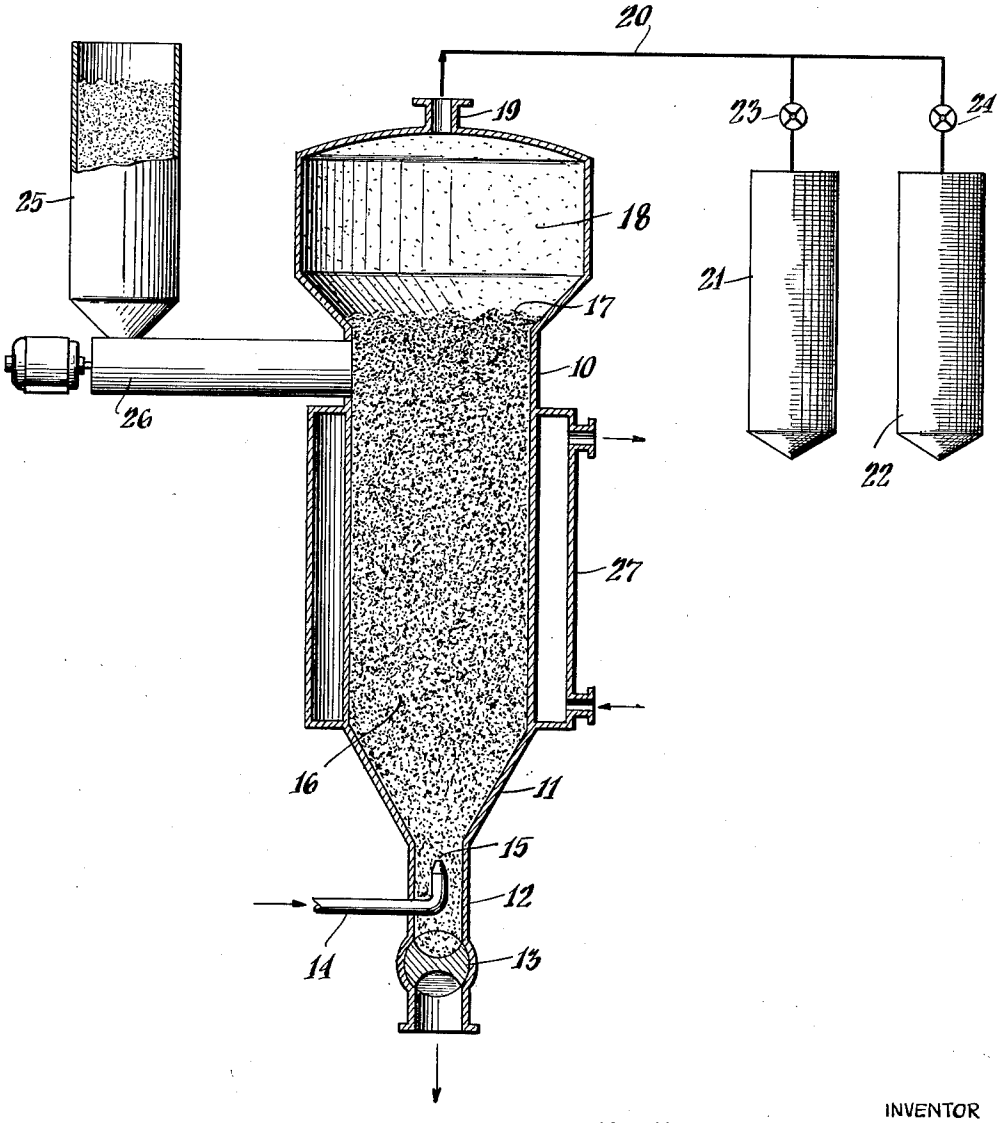
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NICOTINIC ACID PRODUCTION

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NICOTINIC ACID PRODUCTION

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This invention relates to the production of nicotinic acid and, more particularly, to the conversion of nicotine in tobacco to nicotinic acid.

Nicotinic acid or niacin has received very considerable attention because of its prominence in the vitamin field. The production of this chemical compound has been the subject of intensive research which has led to the development of several chemical processes centering chiefly around the oxidation of nicotine, quinoline or beta-picoline by strong chemical oxidants like sulfuric and nitric acids. The current large-scale production of nicotinic acid in this country relies principally on quinoline and beta-picoline derived from coal tar because of price advantage over nicotine which is laboriously extracted from tobacco.

A principal object of this invention is to provide an economical process for converting the nictoine in tobacco to nicotinic acid.

Another important object is to convert the nicotine in tobacco to nicotinic acid without recourse to expensive chemical oxidants.

A further object is to open a commercial outlet for tobacco waste, dust and trimmings and tobacco not suitable for smoking purposes, which classes of tobacco are commonly considered to be a total loss, by converting the nicotine content of such tobacco directly to valuable nicotinic acid.

Additional objects and advantages of my invention will be evident from the description which follows.

I have discovered that nicotine in tobacco can be converted to nicotinic acid in situ, thus eliminating the costly preliminary step of extracting nicotine from tobacco. The significance of this discovery is more fully appreciated when it is remembered that prior processes for producing nicotinic acid from nicotine have in essence involved two tedious extractions: one for separating nicotine from tobacco and the other for separating nicotinic acid from the complex reaction mass resulting from the oxidation of nicotine by chemical oxidants. The invention makes it possible to derive nicotinic acid from tobacco with a single extraction.

An important aspect of my discovery is the conversion or oxidation of nicotine in tobacco to nicotinic acid essentially by means of ordinary air or gas containing free oxygen. The expense of powerful chemical oxidants, conventionally used in the oxidation of extracted nicotine, is thus circumvented. I have also found that chemical agents can be added to the tobacco to facilitate or hasten the oxidation of its nicotine by free oxygen but these chemical agents are employed in limited quantities since they appear to function as catalysts. Furthermore, such catalyst-like agents are often recoverable from the treated tobacco and may be reused in the treatment of additional tobacco by the process of my invention to produce more nicotinic acid. It is thus seen that little or no expenditure is made for chemicals in oxidizing nicotine in tobacco to nicotinic acid as taught herein.

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More specifically, I take harvested tobacco, the term, tobacco, being herein intended to embrace any plant material containing nicotine, and expose it to an oxygen-containing atmosphere under conditions favoring fermentation. It is in the course of fermentation that the nicotine in the tobacco is converted to nicotinic acid. It is advantageous to comminute the tobacco so as to expose a larger surface area to the reaction; accordingly, shredding or, better still, grinding of the tobacco as with a hammer-type pulverizer to form a powder, say passing through a 40-mesh screen, is carried out in most cases. The tobacco used in my process has usually been cured, i. e., it has been hung to dry until it has turned brown. When tobacco scraps or trimmings resulting from the manufacture of cigars and other smoking products are utilized in my process, such tobacco will have been also sweated and fermented (resweated) in accordance with common practices in the tobacco industry. Fermented tobacco is frequently referred to as resweated tobacco because the preliminary sweating is a mild, slow form of fermentation.

As previously stated, the conversion of the nicotine in tobacco to nicotinic acid pursuant to my invention involves exposing tobacco, preferably in comminuted form, to an oxygen-containing atmosphere under conditions inducing fermentation. As known to tobacco experts, fermentation is promoted by moisture which may be added directly as water to the tobacco, for instance, by spraying water on the tobacco, or indirectly by humidifying the oxygen-containing atmosphere in which the desired reaction in the tobacco is to be effected. While conventional fermentation is aimed at making tobacco acceptable by smoking standards such as mellowness and aroma and is therefore carefully controlled to develop the desired qualities in the tobacco because prolonged or strong fermentation will destroy the same qualities which are sought, I favor strong and continued fermentation to the end that the nicotine content of the tobacco may be substantially completely converted to nicotinic

acid. In short, for the purposes of my invention, the tobacco is fermented to an extent where it is no longer suited for smoking products.

Deep fermentation can be achieved by methods well known in the tobacco industry but it is advisable to take steps which shorten the reaction time. One of the accelerating steps has previously been mentioned, namely, comminution of the tobacco. Another is to conduct the fermenting reaction at elevated temperatures above those prevailing when tobacco is fermented preparatory to its use in cigars, cigarettes and the like. A reaction temperature above about 130° F. is desirable, preferably in the range of about 150° to 220° F. Excessive temperatures leading to spontaneous combustion of the reaction mass are obviously to be avoided.

Moisture is an important factor in tobacco fermentation and is most readily controlled by the humidity of the oxygen-containing atmosphere in which fermentation proceeds. It is usually advisable to maintain a relative humidity of at least about 60%; humidities of at least about 80% are frequently advantageous.

In addition, I have found that there are chemical substances which when added in minor proportions to the reacting or fermenting tobacco function like catalysts to accelerate and/or drive closer to completion the oxidation of the nicotine in the tobacco to nicotinic acid. Water-soluble compounds of elements of Series 4 of the Mendeleeff periodic table having atomic numbers 25 to 28 (Mn, Fe, Co and Ni), inclusive, are effective catalysts. These catalysts are usually applied to the tobacco before fermentation in the form of an aqueous solution either by spraying the solution or by dipping the tobacco in the solution. It is advisable to select compounds, generally metal salts, which are stable under the reaction conditions. Manganese and iron catalysts are preferred. Catalysts comprising two metals either as physical mixtures of two metal compounds or as single complex compounds containing the desired metals are often used to advantage. Such salts of the catalytic metals as the nitrates, sulfates, acetates, citrates and tartrates represent suitable catalysts for the process of my invention. The proportion of catalysts added is generally not more than 1% by weight of the dry tobacco, and frequently not more than 0.5%, the foregoing percentages being based on the molecular weight of the catalytic element or metal in the catalyst compound. In my copending application Serial No. 783,626, filed November 1, 1947, the use of the foregoing catalysts in the fermenting or resweating of tobacco to yield smoking grade tobacco is fully disclosed; said copending application contains generic claims to the use of fermentation catalysts.

Another factor which permits promotion and regulation of the conversion of nicotine in tobacco to nicotinic acid is pH. The maintenance of a pH in the acid range, especially a pH of about 3 to 6.5, is beneficial. For this purpose, a suffer system such as a mixture of disodium phosphate and citric acid may advantageously be introduced by addition to water which is sprayed on the tobacco. In many cases, however, the addition of a buffer solution is unnecessary because the tobacco contains a natural buffer system which keeps its pH in the acid range.

Further refinements of the process which I have developed include pressure changes and wetting agents. By subjecting tobacco to a reduced pressure, say below 50 mm. Hg absolute, and immersing the thus vacuumized tobacco in water or an aqueous catalyst solution, the liquid infiltrates more thoroughly and quickly into the tobacco because the plant cells are at least partially evacuated of gas which tends to obstruct the pentration of liquid. Wetting agents added to the water or aqueous catalyst solution also function to drive the liquid into the tobacco and thus aid in the fermentation process. Less than 0.05% by weight of wetting agents like sulfonated alcohols or sulfonated alkyl-benzenes dissolved in water materially improves the penetration of the liquid into the tobacco.

While my process of fermenting tobacco to produce nicotinic acid may be carried out by disposing the tobacco in bins, cases, trays or reticular containers and exposing the thus arranged tobacco to air, moisture and other desired conditions of fermentation, I prefer to agitate the tobacco so that fermentation or oxidation of nicotine proceeds uniformly and rapidly therethrough. Tumbling drums or other rotary reaction vessels are convenient devices in which my process may be performed.

For further elucidation of my invention, reference is now made to the drawing accompanying this specification and forming a part thereof. The drawing is a schematic elevation, partly in section, of a fluidizing vessel or reactor in which a preferred embodiment of my invention may be carried out.

An elongate cylindrical vessel 10 is provided at its lower end with a conical section 11 to which is connected pipe 12 having rotary bucket-type valve 13 for withdrawing comminuted tobacco from vessel 10. An inlet pipe 14 terminating in a discharge nozzle 15 in the bottom of conical section 11 serves to introduce the gaseous stream required for the treatment of the tobacco in accordance with my invention. Vessel 10 holds a charge or bed of comminuted tobacco, say tobacco ground to pass through a 40-mesh screen, maintained in a fluidized state by the gasous stream discharging from nozzle 15. The fluidized tobacco bed 16 has a pseudo-liquid level 17 which is the region where the gases rising through bed 16 disengage themselves from the bulb of the tobacco particles. The gases ascend through settling space 18 which is of larger diameter than the portion of vessel 10 holding the fluidized bed 16; because of the enlarged cross-section of space 18, the gases move therethrough at a decreased velocity and this minimizes the entrainment of tobacco particles by the gases leaving vessel 10 through outlet pipe 19. The gaseous effluent is conducted by pipe 20 to cloth bag filters 21 and 22 which recover the fine tobacco particles usually inevitably carried out of vessel 10 by the gaseous effluent. Valves 23 and 24 serve to cut off the gaseous stream from filters 21 and 22, respectively, so that one filter may be emptied of recovered tobacco powder while the other filter is on stream for the separation of additional quantities of tobacco powder from the gases passing therethrough. Other devices such as cyclone separators and electrical precipitators may be substituted for the bag filters 21 and 22.

The comminuted tobacco is conveniently supplied to vessel 10 from hopper 25 by means of screw conveyor 26. When desired, the fluidized mass 16 may be heated to any required temperature by passing steam or other heating medium through jacket 27 surrounding the lower portion of vessel 10.

The equipment shown in the drawing may be

operated batchwise or continuously. Batchwise operation involves charging into vessel 10 a quantity of tobacco powder which when fluidized by a stream of air from nozzle 15 forms the fluidized bed 16. Moisture to assist the reaction may be introduced by mixing steam with the air passing through vessel 10. The mixed gases are supplied at a rate such that the mass of tobacco powder in vessel 10 assumes a turbulence resembling that of a boiling liquid and is, therefore, said to be fluidized. The fluidizing technique is best known for its application to the catalytic cracking of petroleum hydrocarbons and is widely described in the technical literature, e. g., Chemical and Metallurgical Engineering, June 1944, pages 94 et seq.

As known, the gas velocity necessary to give good fluidizing results will vary in each case with such factors as particle size, shape and density, and gas density and viscosity. However, with tobacco in comminuted form, a gas velocity of not more than about 1 foot per second is generally satisfactory; a velocity in the range of about 0.1 to 0.5 foot per second is usually preferred.

Fluidization of the tobacco powder at a suitable reaction temperature, say 200° F., is continued until a sample of tobacco withdrawn periodically from vessel 10 shows that the conversion of the nicotine in the tobacco to nicotinic acid has proceeded to the desired extent. The temperature in vessel 10 may be maintained by preheating the gases passing therethrough and/or by flowing steam through jacket 27. Having reached the desired extent of conversion, the tobacco powder is withdrawn from vessel 10 by opening valve 13 in outlet pipe 12. The discharged powder may be made to fall directly into a tank containing the liquid used to extract the nicotinic acid from the tobacco.

To operate on a continuous basis, comminuted tobacco is fed to the fluidized bed 16 at regular intervals or continuously by means of conveyor 26 and a corresponding amount of treated tobacco is withdrawn also at regular intervals or continuously by way of valve 13. In such case, the vessel 10 must be made large enough to give the tobacco particles an average residence time in vessel 10 adequate for a substantial conversion of their nicotine content to nicotinic acid. Where conditions for vigorous fermentation or reaction are maintained, a residence time of approximately 20 hours is generally satisfactory. It is well to note at this point that if the conversion of nicotine to nicotinic acid has gone to completion, no significant harm is done in continuing the exposure of the tobacco to the oxygen-containing gas and other conditions of reaction since nicotinic acid is a relatively stable compound. Over-exposure of the tobacco powder is, of course, to be avoided because it decreases the productive throughput or capacity of the equipment.

With either batchwise or continuous operation, the moist air passing through the fluidized bed 16 flows through line 20 to bag filters 21 and 22 which catch any tobacco powder carried in suspension by the gaseous stream. The recovered tobacco, if its nicotine has not been sufficiently oxidized to nicotinic acid, may be returned to vessel 10 for further treatment. Otherwise, it may be added to reacted tobacco which is ready for the separation of nicotinic acid therefrom.

The recovery of nicotinic acid from the reacted tobacco can be effected by diverse methods. One method involves a conventional extraction, for instance, with gasoline in the presence of lime to remove residual alkaloids from the tobacco, neutralization of the lime in the tobacco and another

extraction with a solvent for nicotinic acid. In another method, the reacted tobacco is acidified by wetting it with a solution of phosphoric or sulfuric acid and the acidified tobacco is extracted with a nicotinic acid solvent such as methyl or ethyl alcohol, ethyl ether or chloroform. It will be understood that the extract containing the nicotinic acid will usually contain other substances, e. g., citric and malic acids. Mixtures of nicotinic, citric and malic acids find valuable uses in pharmacy and nutrition. Another alternative method is to extract the reacted tobacco with water, to precipitate any alkaloids in the liquid extract through the addition of phosphotungstic or silicotungstic acid, and to decant the liquid containing in solution nicotinic acid and other substances, several of which have nutritional value.

Several procedures for separating nicotinic acid from complex mixtures have been developed and are well known in the art. A common procedure is to bring the mixture to dryness, to dissolve from the resulting solids the nicotinic acid with hot water or alcohol, to filter off the solids, to cool the filtrate so as to crystallize the nicotinic acid, and to separate the crystals by filtration. The crystals may be washed with cold water but, where further purification of the nicotinic acid is indicated, the crystals may be redissolved in hot water or alcohol, a decolorizing carbon suspended in the hot solution, the suspension filtered, and the filtrate cooled to recover crystallized nicotinic acid. Other procedures for isolating nicotinic acid involve its precipitation from solution as an insoluble metal salt, for instance, as copper or zinc nicotinate. The insoluble salt is separated from the original solution, is suspended in a strong aqueous solution of sodium hydroxide so the nicotinate is converted to the soluble sodium salt while the metal is precipitated as the oxide, the insoluble metal oxide is removed by filtration, the alkaline filtrate is acidified to a pH of about 2, e. g., sulfuric acid, and allowed to stand until the nicotinic acid has crystallized. The crystals are separated from the acid solution and washed with cold water. If desired, further purification may be effected by redissolving and recrystallizing the nicotinic acid. Still another way to isolate the nicotinic acid in mixtures with other tobacco constituents is to bring such mixtures to dryness, to powder the solid residues, and to subject these residues to vacuum sublimation; the nicotinic acid will sublime and condense in solid form on cooled surfaces, in a condition of high purity.

A specific example of the process of my invention will be given in terms of the equipment shown in the drawing. Leaves of cured (dried) tobacco containing 3.8% by weight of nicotine are dipped in an aqueous solution containing manganese sodium citrate (manganese citrate soluble N. F. VII) and iron ammonium citrate in the relative proportions of 1.0 molecular weight of manganese to 1.5 molecular weight of iron. The leaves are dried and show that 0.2% by weight of manganese and 0.3% by weight of iron were added to the tobacco by the dipping operation. The leaves are then ground in a hammer mill to a powder passing through a 40-mesh screen. The tobacco powder is placed in hopper 25 and thence fed regularly by screw conveyor 26 into vessel 10. A stream of air which has been admixed with steam is supplied to vessel 10 by way of pipe 14 and nozzle 15. The gaseous stream of about 95% relative humidity rises

through vessel 10 at a velocity of about 0.25 foot per second and maintains the tobacco powder therein in a well fluidized state. The fluidized reaction mass 16 is maintained at a temperature of 205° F. Tobacco powder collected in filters 21 and 22 from the gaseous effluent of vessel 10 is returned to hopper 25 for reintroduction into vessel 10. Tobacco powder in amount commensurate to that fed to vessel 10 by conveyor 26 is regularly withdrawn through outlet pipe 12 and valve 13. The tobacco powder has an average residence time of 22 hours in vessel 10 and in this period its nicotine content is practically completely oxidized to nicotinic acid.

The reacted tobacco is then extracted with water or other suitable solvent for nicotinic acid, like alcohol, and the nicotinic acid isolated from the liquid extract, for instance, by one of the procedures outlined hereinbefore.

Since the nicotine in the tobacco is converted to nicotinic acid by my process, the reacted tobacco, particularly after any residual alkaloids have been eliminated, say by extraction or by steaming, is per se a valuable product which may be incorporated in cattle feed to enrich its vitamin content. Another direct use of reacted tobacco containing nicotinic acid is as a high grade plant food. Accordingly, in some cases, the nicotine in tobacco may be oxidized to nicotinic acid and utilized without performing any costly extractions. Where the fermented or reacted tobacco is to be used directly in a cattle feed or plant nutrient, the addition of catalysts for the fermentation must be made judiciously or avoided completely as circumstances may dictate.

The surprisingly facile oxidation of nicotine in tobacco to nicotinic acid by free oxygen in accordance with my invention appears attributable to natural agents, perhaps catalysts, present in the tobacco. This theory seems to be corroborated by the fact that refined nicotine is not converted to nicotinic acid by air and moisture under the conditions set forth in this specification but rather requires the use of strong chemical oxidants like nitric acid to effect the conversion. Regardless of the exact nature of the reaction occurring in my process, it is sufficient that nicotinic acid is produced by following the teachings of this specification. The term, fermentation, has herein been used in the same general sense commonly understood in the tobacco industry; that is to say, the term does not imply that any process similar to the process of alcoholic fermentation occurs in tobacco and does not mean that microorganisms are necessarily involved.

Those skilled in the art know that tobacco usually contains several nicotine-type alkaloids, i. e., alkaloids like nicotine composed of the pyridine ring with another heterocyclic ring attached to its beta- or 3-position carbon, which are also oxidizable to nicotinic acid. Such oxidizable nicotine-type alkaloids, notably nornicotine and myosmine, can be converted to nicotinic acid by the process of my invention.

The foregoing description and examples are intended to be illustrative only. The many possible variations and modifications of my invention conforming to its spirit are to be considered within the scope of the appended claims.

What I claim is:

1. In the conversion of tobacco nicotine to nicotinic acid, the improvement which comprises reacting said nicotine while still in the tobacco with an oxygen-containing gas and moisture at a temperature effecting simultaneously fermentation of said tobacco, continuing the reaction and simultaneous fermentation until said nicotine has been substantially completely consumed and the smoking qualities of said tobacco have been destroyed, and thereafter recovering the resultant nicotinic acid from the thus fermented tobacco.

2. The process of claim 1 wherein the tobacco is in comminuted form.

3. The process of claim 1 wherein the tobacco has been cured and comminuted.

4. The process for the production of nicotinic acid which comprises adding to tobacco containing nicotine a water-soluble fermentation catalyst containing an element selected from Series 4 of the Mendeleeff periodic table and having an atomic number between 25 and 28, inclusive, fermenting said tobacco containing said catalyst with an oxygen-containing gas and moisture and continuing the fermentation until said nicotine has been substantially completely consumed and the smoking qualities of said tobacco have been destroyed, whereby nicotinic acid is produced, and thereafter separating the resulting nicotinic acid from the thus fermented tobacco.

5. The process of claim 4 wherein the tobacco has been cured and comminuted.

6. The process of claim 4 wherein the catalyst comprises a water-soluble manganese compound.

7. The process of claim 4 wherein the catalyst comprises a water-soluble iron compound.

8. The fluidized process for the production of nicotinic acid which comprises fluidizing a mass of comminuted tobacco containing nicotine with an oxygen-containing gas in the presence of moisture, the fluidized mass having a turbulence resembling that of a boiling liquid, effecting fermentation of said tobacco and simultaneous conversion of said nicotine to nicotinic acid within said fluidized mass until said nicotine has substantially completely disappeared, and thereafter separating product nicotinic acid from the thus treated tobacco.

9. The process of claim 8 wherein said fermentation and simultaneous conversion are effected at a temperature in the range of about 150° to 220° F.

10. The process of claim 8 wherein the product nicotinic acid is separated from the thus treated tobacco by extraction with water.

11. The process of claim 8 wherein the product nicotinic acid is separated from the thus treated tobacco by extraction with alcohol.

12. The process for the production of nicotinic acid, which comprises adding to tobacco containing nicotine a water-soluble fermentation catalyst containing an element selected from Series 4 of the Mendeleeff periodic table and having an atomic number between 25 and 28, inclusive, fermenting said tobacco containing said catalyst with an oxygen-containing gas and moisture and continuing the fermentation until said nicotine has been substantially completely consumed and the smoking qualities of said tobacco have been destroyed, whereby nicotinic acid is produced.

13. The process of claim 12 wherein the catalyst comprises a water-soluble iron compound.

14. The fluidized process for the production of nicotinic acid which comprises fluidizing a mass of comminuted tobacco containing nicotine with an oxygen-containing gas in the presence of moisture, the fluidized mass having a turbulence resembling that of a boiling liquid, and effecting fermentation of said tobacco and simultaneous conversion of said nicotine to nicotinic acid with-

in said fluidized mass until said nicotine has substantially completely disappeared.

15. The process of claim 14 wherein said fermentation and simultaneous conversion are effected at a temperature in the range of about 150° to 220° F.

WALTER G. FRANKENBURG.

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