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[54] SMOKABLE PRODUCTS AND A  
PROCESS FOR THEIR PRODUCTION

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[56] References Cited

UNITED STATES PATENTS

136,872 3/1873 Stafford et al. ....131/144  
940,181 11/1909 Montag. ....131/141

2,149,179 2/1939 Moser .....131/17 R  
3,298,378 1/1967 Stevens et al. ....131/17 UX  
3,323,524 6/1967 Shamberger .....131/2  
3,424,171 1/1969 Rooker .....131/2 X

FOREIGN PATENTS OR APPLICATIONS

121,598 10/1919 Great Britain .....131/141  
4,855 3/1920 Netherlands .....131/141

OTHER PUBLICATIONS

The Sinister Garden, Wyeth Laboratories, Division of Amer-  
ican Home Products, Philadelphia, Penn., 1966, p. 11 cited.

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[57] ABSTRACT

The aroma of tobacco is improved and artificial tobacco and  
tobacco substitutes are given an improved tobacco aroma  
when smoked by treating such substances with aromatic  
materials extracted from vegetable chlorophyll-containing  
leaf material such as by use of solvents, steam distillation and  
the like.

1 Claims, No Drawings

## SMOKABLE PRODUCTS AND A PROCESS FOR THEIR PRODUCTION

This invention relates to smokable products and to a process for their production. These products are produced by the addition of substances which will aromatize the smoke produced during smoking to a starting material such as tobacco, especially filling tobacco, tobacco leaves, artificial tobaccos, tobacco substitute and other materials which are suitable for smoking for example in cigarette or cigar form.

The object of the invention is to aromatize starting materials such as tobacco, particularly filling tobacco, tobacco leaves, artificial tobacco, and also tobacco substitute and other smokable substances with a completely neutral taste, in such a way that the basic note of the starting material is changed and improved to such an extent that a product which can be smoked in the same way as valuable tobacco products is formed.

These substances which aromatize smoke after they have been incorporated in the starting material are intended to be produced from inexpensive materials, so that a high-grade smokable product is obtained which has a full tobacco flavor.

More particularly, however, the invention is also intended to intensify or simply to produce the basic smoke flavor which is unique to tobacco and which is unaffected by the growing areas, vintages or by grading. Hence tobacco smoke produced from starting materials treated in accordance with the invention provides a greater fullness of flavor even in those cases where the starting material is a tobacco with basically little or no aroma, or neutral substances which although they can be smoked have no aroma at all. These tobaccos or starting materials which naturally are intended to be sold at a low price are given a strong aroma by the process according to the invention and hence are given a flavor generally approaching the flavors of the more expensive tobaccos.

It is already known that the flavor of synthetic tobacco fibers can be improved by subjecting a given tobacco mixture to an extraction treatment in which the water-soluble and alcohol-soluble aromatic substances are successively extracted. It is possible in this way to recover all the aromatic substances present in the tobacco which are then mixed in the form of a dry extract with a carrier of cellulose or methyl cellulose material, after which the mixture is spun into fibers having the same cross section as natural tobacco fibers of the kind from which a cigarette mixture is made.

It is also known that tobacco or tobacco mixtures can be treated with tobacco extracts, or with certain fractions of tobacco extracts, in order to correct variations in the quality of given tobacco mixtures or blends or in order to improve tobaccos which have inadequate flavor. Unfortunately, it is not possible to use this process to alter the flavor of a given tobacco blend any differently than would be possible by incorporating the unextracted tobacco in the tobacco blend which is to be improved. The sole object of this process is to obtain a favorable distribution of the aromatic substances in a tobacco mixture to correct variations in quality, or to arrange the aromatic substances in the tobacco strand forming the cigarette filling, for example, in such a way that they are taken up by the stream of smoke and thus delivered to the smoker, rather than most of them remaining in the cellular structure and being pyrolytically decomposed in the advancing incandescent zone. In this case, too, tobacco is used as the starting material for the extracts used to treat the tobacco or tobacco blends.

Another process has the same object. In this process, tobacco extracts are freeze-dried and applied as a concentrated aromatic powder to tobacco of inferior flavor. Once again, the tobacco extracts used are taken from tobaccos.

In other known processes, tobaccos or tobacco blends have added to them certain chemical compounds which are intended to impart certain flavor notes to the smoke given off from the tobaccos which have been thus treated. In most cases, however, tobacco treatment of this kind usually leads to one-sided displacements of flavor in the bouquet of the smoke. Accordingly articles produced from tobaccos of this

kind are rejected by consumers on the grounds that they do not taste like tobacco. The following are given as examples of chemical compounds which can be used in this way:

4-(2-butenylidene)-3,5,5-trimethyl-2-cyclohexan-1-one, intended to give the tobacco a peppery flavor 4,4a,5,6-tetrahydro-4,4,7-trimethyl-2-(3H)-naphthalenone, 4-(4-oxo-2,6,6-trimethyl-2cyclohexene-1-yl)-1,3-butadiene, or 2-acetyl-5-methyl pyrrole for imparting a cherry-like aroma.

In another known process,  $\alpha,\beta$ -unsaturated gamma lactones are added to the tobacco. However the physiological acceptability of these compounds is in doubt and for this reason alone they cannot legally be used.

The problem of improving the basic aroma of tobaccos without at the same time imparting to them flavor components which have no resemblance to tobacco, cannot be solved at all or can only be ineffectively solved by the processes referred to above where they use non-extracted tobacco ingredients. At the present time the use of tobacco ingredients which have been previously extracted from tobacco is no longer practicable for economic reasons, even in cases where the extract consists for example, of tobacco waste of the kind that accumulates in the tobacco industry. Waste such as this is converted, by methods known in the tobacco-processing industry, into tobacco sheets or foils which can then be reprocessed as a high-grade starting material.

The present invention relates to smokable products such as tobacco, especially filling tobacco, tobacco sheets and tobacco substitutes which contain the extracted aromatic substances formed during the fermentation of vegetable leaf material containing chlorophyll. The smokable products contain preferably from 0.0001 to 2 percent by weight of the extracted aromatic substances. The invention also relates to a process for imparting the properties of a high-grade tobacco product to a smokable starting material, if desired with a completely neutral taste, in which process a vegetable chlorophyll-containing leaf material, preferably of very low ethereal oil and alkaloid content, is fermented after drying in air by prolonged heating at temperatures below 110° C. in the absence of air, after which the aromatic substances formed during fermentation are extracted from the leaf material which has been fermented and added to the starting material as substances which aromatise the smoke given off during smoking. The prolonged heating pyrolysis is preferably carried out at temperatures of from 35° C. to 80° C. and at 60 percent to 90 percent relative humidity. In the present context, the word prolonged refers to a period of from 3 hours to 3 months.

Accordingly, in the process according to the invention vegetable chlorophyll-containing leaf material, after drying sufficiently in air, is subjected to a prolonged heat treatment in the absence of air at temperatures below 100° C. After this the steam-volatile reaction products are extracted with ether and then the solvent-free extracts are added to the starting materials.

The extracts may be added to the starting material, for example, by immersing the starting material in solutions of the extraction products in suitable highly volatile solvents such as ethanol, or by spraying such solutions in suitable concentration on to the starting material. This operation may be carried out at any stage in the process, for example during cigarette production. It has proved to be particularly advantageous to spray the starting material before it is delivered to the cigarette-making machine with a 0.5 to 7 percent solution of the extraction products in ethanol which influence the flavor of the smoke.

In general, it is sufficient to add the extraction products to the starting materials in a quantity of from 0.0001 to 2.0 percent (dry substance), based on the dry weight of the starting material. The quantity in which they are added is governed by a large number of factors: by the type of starting material used, by its flavor, by the conditions under which the vegetable material subjected to heat treatment (pyrolysis) and extraction is dried, by the pyrolytic reaction conditions and by the other aromatizing agents which may additionally be

added, of the kind normally used in the tobacco-processing industry, and so on.

The invention is by no means restricted to the use of an extraction product from the leaf material of a single type of species of plant. On the contrary, it has proved desirable to mix chlorophyll-containing vegetable material, i.e., vegetable material capable of assimilation, of different types of plants in suitable empirically determined ratios and to subject them together to the various treatment steps required to obtain the aromatizing products in order to apply the mixture of the different substances to the starting material without any need for separation beforehand.

According to another aspect of the invention, it is also possible to subject vegetable materials of different origin separately to differing process and temperature conditions and then subsequently to subject them together to the steam distillation and extraction with ether.

In this case, too, the reaction conditions and the ratios in which the individual substances are mixed with one another can be empirically determined by preliminary tests.

Furthermore, it has proved desirable to process different types of vegetable materials separately from one another and then subsequently to mix and dissolve the extraction products in suitable ratios in the quantity of solvent required for application to the starting material and then following this application to subject the starting material to a post-fermentation.

Absorption of the extraction products by the starting material can be increased by evacuating the dry starting material in a suitable vessel and then treating it with appropriate extract solution while at the same time the pressure is suddenly equalized.

Another possible way of carrying out the process according to the invention is to extract thoroughly the starting vegetable material first with water and then with ethanol and chlorinated hydrocarbons in order to produce relatively large quantities of extraction products and then to concentrate the extract and to subject it to the treatment according to the invention either as such or on a neutral substrate such as for example cellulose, burned clay granulates, kieselguhr or the like and to isolate the reaction products from the substrates by steam distillation.

The advantage of this modification of the process according to the invention is that not only can the reaction be better controlled but it is also possible to speed the reaction as required by using suitable catalysts such as for example acid aluminium silicates and aluminium oxides. Naturally this is only possible in those cases where the starting products for the reaction have been isolated from the vegetable cell structure.

The particular course adopted will be governed by the type of starting material, the tobacco end product and the desired influence the additive is required to have.

The invention is illustrated by the following Examples.

#### EXAMPLE 1.

One thousand g. of air-dried chestnut leaves are stored for a period of 2 weeks at 80 percent relative humidity and at a temperature of 50° C. and then subjected to steam distillation at normal pressure. After saturation with common salt, the condensate (3,700 ml., pH 5.5) was thoroughly extracted with ether and the ether gradually distilled off. The residual extract (0.140 g.) was dissolved in ethanol and sprayed onto a filling tobacco, i.e. a tobacco which is substantially free from substances with a conspicuous flavor, (in particular, ethereal oils) in such a quantity that the quantity of extract left on the tobacco after the solvent had been evaporated off amounted to 0.001 percent of the dry weight of the filling tobacco.

After 72 hours' storage at 21° C./67 percent relative humidity, the filling tobacco thus treated was tested for flavor by a panel of experts and was found to be equivalent in its basic tobacco flavor to a high-grade tobacco.

#### EXAMPLE 1a

The comparison tobacco was freed by extraction with water from its aroma carriers or the pyrolytic starting materials of its

aroma carriers so that it was assessed as having no flavor at all. Some of the tobacco material thus prepared was sprayed with 0.05 percent of its weight of the extract according to Example 1 dissolved in ethanol and after 72 hours' storage at 21° C./67 percent relative humidity was compared organoleptically with the starting tobacco by a panel of experts. Compared with the untreated sample, the treated sample was found to have a tobacco-like flavor without any distinct hint in its flavor as to its origin. The basic tobacco flavor was regarded as having been substantially restored.

#### EXAMPLE 2

Two thousand g. of chestnut leaves were thoroughly extracted with water and then with ethanol, dichloromethane and benzene, and the extracts were combined following removal of the organic solvents and then were suspended in a little water and applied to a glass-fiber mat. After drying in vacuo, the impregnated mat was stored in sealed vessels for a period of 4 weeks at a temperature of 55° C. and at 80 percent relative humidity, after which it was subjected to steam distillation at normal pressure. The condensate (4,200 ml., pH 5.7) was saturated with common salt and thoroughly extracted with ether. After the ether had been distilled off on a water bath, a residue of 0.320 g. was left. This residue was taken up in ethanol and sprayed on to tobacco which was free from any synthetic or natural additives in such a quantity that the treated tobacco contained 0.002 percent of its dry weight of extraction products. After 72 hours' storage at 20° C./65 percent relative humidity, this treated tobacco was compared organoleptically with identical but untreated tobacco and was assessed by a panel of experts as being much more refined with a stronger basic flavor than the comparison sample.

#### EXAMPLE 3

Freshly harvested tobacco was dried in the usual way, sprayed as in Example 2 and then fermented in the usual way. This tobacco was found to have a stronger taste than untreated but otherwise identical tobacco so that it was assessed by the panel of expert judges as having a fuller flavor without any change in its specific note.

#### EXAMPLE 4

Five hundred g. of air-dried chestnut leaves were subjected to pyrolysis for 21 days at 85° C. over saturated aqueous potassium chloride solution. Three hundred eight g. of this material with a moisture content of 1.0 percent were steam distilled at normal pressure as in Example 1 and the condensate (3,000 ml., pH 3.8) further processed as described in that Example 1. A sheet of tobacco was sprayed with 0.02 percent of its dry weight of the extraction product (the sheet had been obtained by the method described in U.S. Pat. No. 3,298,378). The untreated comparison sample had a distinctly flatter and expressionless flavor and, unlike the treated sample, was unsuitable as a high-grade filling material for cigarettes.

Like the terebinthales, of which the horse chestnut (*Aesculus hippocastanum*) was investigated in detail as a representative of this species, the assimilating parts of the urticales may also be used for obtaining extraction products suitable for aromatizing tobacco in order to improve an enhanced basic flavor in tobacco smoke.

#### EXAMPLE 5

Four hundred fifty g. of air-dried stinging-nettle leaves (*Fol. urtica dioica*) were pyrolysed in a nitrogen atmosphere in a sealed vessel for a period of 16 days at 50° C./75 percent relative humidity and then subjected to distillation with steam as described in Example 1, giving 0.180 g. of extraction product which even in a quantity as small as 0.00001 percent, based on the dry weight of the tobacco, enhanced the basic flavor.

EXAMPLE 6

Four hundred fifty g. of air-dried stinging nettle (*Urtica dioica*) were treated as described in Example 1, except that 5 percent of their weight of air-dried, unfermented and ground tobacco was added. The yield of the extraction product came to 0.210 g. and this produced an aromatizing effect that showed a distinct improvement in the sense of a better basic tobacco flavor over the end products of examples 1 and 5.

EXAMPLE 7

Four hundred fifty g. of dried stinging nettle (*Urtica dioica*) were treated as described in Example 6 except that 5 percent of their weight of fermented, dried and ground tobacco was added. The yield of extraction product came to 0.195 g. and this had an even more greatly improved quality in terms of aromatising effect in comparison with Examples 1 and 6 as a result of using the extraction product in accordance with the invention.

EXAMPLE 8

Five hundred fifty g. of air-dry stinging nettle (*Urtica dioica*) were treated as described in Example 6 except that 1.5 percent of a tobacco extract prepared as follows was added:

Fifty g. of fresh tobacco leaves (*German Burley*) were cut up finely and homogenised in 125 ml. of 0.05 m tris-(hydroxymethyl)-aminomethane hydrochloric acid. The solids component was separated off through a coarse filter and discarded. The green filtrate was centrifuged for 1 hour at 15,000 g., resulting in the formation of a pale reddish-brown supernatant phase which was decanted off and freeze-dried. The freeze-dried product was used in the form of a 5 percent solution in 0.05 m tris-(hydroxymethyl)-aminomethane hydrochloric acid.

The yield of extraction product came to 0.245 g. with outstanding basic tobacco aroma properties without penetrating the flavor peaks of the tobaccos treated with it.

EXAMPLE 9

Four thousand five hundred g. of fresh coarsely cut stinging nettle leaves (*Fol. urtica dioica*) were covered in a sealed vessel with a solution of 1 l. of the completed tobacco extract according to Example 8 in 10 l. of water, and the vessel evacuated to 100 torr. The vessel was then suddenly vented, the solution penetrating into the vegetable matter. The now transparent product was air-dried and further treated as in Example 1. The yield of extraction product came to 0.240 g. for an initial quantity of 400 g. of air-dried vegetable matter. The extraction product had outstanding basic tobacco aroma properties. The tobaccos treated with this material, compared with untreated comparison tobaccos, showed a strong widened flavor basis without any deterioration or change in the smoke

flavor components of specific type or origin.

EXAMPLE 10

Four thousand g. of fresh stinging nettle leaves were finely cut, homogenized in 0.05 m tris-(hydroxymethyl)-aminomethane hydrochloric acid solution and forced through a coarse filter. The liquid phase was then centrifuged for 75 minutes at 12,500 g., the supernatant phase was discarded and the deposit admixed with 2 percent of its volume of tobacco extract according to Example 8. After freeze-drying, the dried product was blended with the same component by volume of washed quartz sand and pyrolysed at 50° C./80 percent relative humidity. After steam distillation, 0.220 g. of extraction product free from solvent were obtained from the condensate (3,500 ml., pH 5.4) after saturation with common salt and extraction with ether. When used in accordance with the invention on tobacco, this extraction product developed outstanding tobacco-aromatising properties without in any way concealing or interfering with specific smoke flavor components.

In addition to the *terebinthales* of which *Aesculus hippocastanum* was mentioned as a representative in Examples 1 to 4, and the *Urticales* of which *Urtica dioica* was mentioned as a representative in Examples 5 to 10, the assimilating parts of the *Ulotrichales* e.g. *Enteromorpha spec.*, the *Leptosporangiales* e.g. *Dryopteris filix-mas* and, of the *dialypetalae*, the *rosales* e.g. *Rubus fruticosus*, the *leguminosae* e.g. *Vicia faba*, the *guttiferales* e.g. *Camellia sinensis*, the *columniferae* e.g. *Tilia cordata* and *Theobroma cacao* and the *Umbelliflorae* e.g. *Daucus carota*, have all proved suitable for obtaining extraction products.

Equally suitable are the assimilating parts of the *Fagales* e.g. *Fagus silvatica* var. *purpurea*, the *Polygonales* e.g. *Rumex domesticus* and *Theum palmatum*, the *sympetalae*, the *personatae* e.g. *Solanum tuberosum* and *Solanum lycopersicum* the *Rubiales* e.g. *Coffea arabica*, the *Curcubitaes* e.g. *Cucumis sativus* and the *Synandreae* e.g. *Tussilago farfara*. Among the *glumiflorae*, the *gramineae* with *Lolium perenne* and *Zea mays* have been successfully subjected to pyrolysis and the extraction products applied to tobacco in accordance with the invention without outstanding results.

We claim:

1. A smokable product having the taste and flavor of high quality tobacco consisting essentially of a material selected from the group consisting of filling tobaccos, tobacco sheets and tobacco substitute having incorporated therein 0.0001 to 2 percent by weight, calculated on the smokable product, of an aromatic substance obtained by ether extracting steam-volatile, common salt-saturated products from vegetable chlorophyll-containing, non-tobacco, non-toxic leaf material, of low ethereal oil and alkaloid content, which has been subjected to fermentation prior to ether-extraction.

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