ABSTRACT: A method of cooling cigarette smoke is disclosed utilizing ethanol-filled rupturable capsules contained within the filter section of a cigarette. The filter material utilized is preferably a crepe paper of high absorbency and porosity and is free of absorbent material or other material for which the ethanol is a solvent to the extent of releasing a sensible heat of solution when the ethanol is released into the filter.

The invention relates to a method of effecting cooling of cigarette smoke and more particularly to the incorporation of frangible ethanol-filled rupturable capsules in a filter to effect this.

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3,366,121 1/1968 Carty............................. 131/10.1
3,390,686 7/1968 Irby et al........................ 131/10.1X
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OTHER REFERENCES


Primary Examiner—Melvin D. Rein
Attorney—Pennie, Edmonds, Morton, Taylor and Adams
3,547,130

METHOD OF COOLING CIGARETTE SMOKE

It has been proposed heretofore to provide a tobacco smoke filter with a liquid such as water to cool the smoke. In the more effective embodiments of this type of filter, the water is contained in at least one capsule positioned within the filter where water when the capsule is ruptured by compression. In order to control the release of water vapor progressively into successive puffs of smoke, it has been necessary to provide absorbent material within the filter so that the smoke passing through the filter can, by selective adsorption, exchange some of its constituents for water held by the absorbent material. Such an arrangement will slightly lower the temperature of the smoke, but its cooling effect is not its primary attribute.

We have experimented extensively with other liquids more volatile than water with the aim of producing a more pronounced cooling effect on the smoke. Sensitve instrument demonstration, however, that puffing on an unlit cigarette provided with an active carbon-containing filter or with a cellulose acetate tow filter injected with such a volatile liquid shows a temperature rise in the air drawn through the filter in at least the early puffs, and the same temperature rise appears when the cigarette is smoked. Our investigations have shown that both the heat evolved by adsorption of the vaporized liquid on the adsorptive material and the heat evolved by dissolution of condensate plastics in the volatile liquid tend to defeat the cooling effect of vaporization of the liquid. We have discovered, accordingly, that a tobacco smoke filter capable of cooling the smoke can be obtained by positioning within a flexible outer wrapper, and in contact with a filler therewithin capable of entraining a cooling liquid for the smoke, at least one capsule having walls rupturable by compressive pressure and containing a nontoxic liquid substantially more volatile than water, provided that the filler is substantially free of absorbent material and free of substances sufficiently soluble in the liquid to evolve a sensible amount of heat of solution when the capsule is ruptured and releases the liquid into the filter.

The invention will be more fully understood from the following description taken in conjunction with the drawing in which the single FIG. is a longitudinal cross-sectional view of a filter embodying the invention.

As shown in the drawing, utilized in the method the filter element of the invention.

As shown in the drawing, the filter element utilized in the method of the invention comprises a resilient outer wrapper surrounding a filler 6 having passages 7 arranged to permit axial flow of smoke therethrough with the customary total resistance to air and smoke flow through a cigarette with the filter attached of, say, about 5 to 30 cc. per second under a suction pressure of 2% inches of water. The filler further comprises at least one fragile capsule 8 containing a smoke-cooling liquid 9.

The tubelike outer wrapper 5 can be conventional plug wrap paper used in making cigarette filter plugs. It does not have to possess significant wet strength because the liquid in the microcapsules is not released until after the filter element is enclosed in the stronger tipping paper conventionally used to secure the filter element to a cigarette or cigar, or the like. It should, however, have sufficient resilience so that it can permit the filter element to be compressed when the tube is squeezed yet will return substantially to its initial tubular shape when this squeezing pressure is released.

The filler material used in the filter element of the invention must be capable of entraining a significant amount of the released liquid so as to hold the liquid in the pores or passages of the filler material through and past which the smoke is to be drawn. By entraining the released liquid, the liquid is restrained from passing into the tobacco portion of a cigarette or cigar, or into the smoker's mouth, or into an adjacent section of a multiple-component filter assembly. The degree of entrainment of the liquid is also generally commensurate with its surface area available for contact with the liquid. The greater this area, the greater the amount of liquid which can be exposed to the smoke stream for evaporation cooling. Thus, the filler should be characterized by a high degree of porosity such as that provided by fibrous or granular filler materials. If the filler material is fibrous, it is advantageously resilient not only when dry but also when wet with the liquid so as to permit the filter element to be distorted for the purpose of rupturing the liquid-containing capsules yet spring back substantially to its precompressed smoke-filtering form in order to resume its normal filtering position within the filter tube. If the filler material is granular, it need not be resilient because when it is admixed with a number of small microcapsules containing the liquid, the shells of the microcapsules constitute a major portion of their volume test data that a filler after their cooling liquid content has been released by rupture of the microcapsules. Thus, although the filler may be a fibrous mass, such for example as cotton, or a granular mass, such as expanded mica or minute clay pellets, our present preference for the filler material is conventional smoke filter paper having both good absorbency and wet strength. Paper of this type is generally of sufficient resiliency, even when wet, to satisfy the most demanding requirements of a filter element, but further resilience can be imparted to the paper by coating it with starch or other porous stiffening material.

We have found, however, that certain components frequently present in tobacco smoke filters are incompatible with the smoke-cooling effect of the aforementioned liquids. For example, we have ascertained from test data that the presence of an adsorbent material in the stream of smoke cooled by evaporation of the cooling liquid selectively adsorbs at least a portion of the cooling liquid vapor and in doing so liberates sufficient heat to offset the cooling effect of the evaporated liquid. Accordingly, absorbent materials such as active carbon and silica should not be a part of our invention or in any other filter element downstream of the smoke passage. In addition, we have ascertained from test data that substances which are significantly soluble in the cooling liquid or its vapor liberate, by their exothermic heat of solution, enough heat to warm the smoke. Cellulose acetate tow and plasticizers such as triacetin appear to be dissolved to a significant extent by the cooling liquids and, when present in the smoke stream containing the cooling liquid or its vapor, cause a temperature rise rather than a temperature drop in the smoke. Tobacco produces the same effect, and therefore the cooling effect of the volatile liquid is lost if the liquid-containing capsules are embedded in the tobacco portion of a cigarette or cigar.

The liquid-containing capsules positioned within the filler portion of the filter element utilized in the method of the invention can be a single relatively large capsule or can be a number of capsules which range in diameter between about 0.001 and 0.12 inch. The large size capsules are generally made by conventional techniques used in the pharmaceutical industry, and the miniature capsules can be made by a coacervation process of liquid-solid exchange process. Suitable microcapsules can also be produced mechanically with a single or multiorifice encapsulating device which forces drops of a liquid to be encapsulated through a thin film of coating-forming material. Centrifugal devices can also be used in a similar fashion. Some of these and other microencapsulating procedures, are described in U.S. Pat. Nos. 2,800,457, 2,800,458, 2,969,330, 2,969,331, 3,015,128 and 3,041,289, in an article by H. W. Mattson entitled "Microcapsules," published in the Apr. 1965, issue of International Science and Technology (New York, N.Y.) pages 66 et seq., in "Microencapsulation" by C. E. Anderson et al. Management Reports, (American Management Association), pp. 1-103, 1963.

The capsule used pursuant to our invention comprises an outer fragile sheath enclosing the smoke-cooling liquid and consists of a material which is not reacted upon or dissolved by the liquid. The sheath advantageously is composed of a hard petroleum wax or of a thermoplastic or thermosetting resin such as vinylidene chloride copolymers, polyethylene,
polypropylene, ethylene-vinylacetate copolymers, polyesters, phenol-formaldehyde and urea-formaldehyde resins, or of gelatin, or the like. There is no limitation on the composition of the sheath material other than its ability to form and maintain an encapsulating but fragmentable sheath about the treating liquid.

The cooling liquid within the rupturable capsules is one which is nontoxic and which is significantly more volatile than water but capable of being stored in fragmentable capsules. Such liquids generally have high vapor pressure at ambient temperature and have a relatively high heat of vaporization. Advantageously, the liquid has a boiling point above about 35°C and below about 120°C so that it will evaporate quickly when exposed to a puff of smoke drawn through the filter but will not be so volatile as to cause the capsule to rupture at ambient temperatures. However, if the cooling liquid is combined with another less volatile solvent liquid, the boiling point of the cooling liquid can be as low as about minus 21.6°F, as in the case of dichlorodifluoromethane, and as low as minus 35°C, in the case of other volatile cooling materials dissolved in a normally liquid solvent therefrom. The heat of evaporation of the cooling liquid, being endothermic, causes the evaporating liquid to remove heat from the surrounding tissue, and thus reduce the likelihood of injury to the tissue. Examples of suitable cooling liquids include: alcohols such as ethanol, methanol, ethyl, n-butyl, n-amyl, iso-butyyl, sec-amyl, t-butyl, n-propyl and iso-propyl acetates, methyl, ethyl and iso-propyl formates; methyl, ethyl, propyl, iso-propyl, and allyl propionates; methyl and ethyl butyrates; and ethyl isobutyrate; hydrocarbons such as n-pentane, n-hexane, cyclohexane and cyclohexene; ketones such as acetone; aldehydes such as acetaldehyde; and halogenated hydrocarbons such as dichlorofluoromethane, bromotrifluoromethane, dichlorodifluoromethane, 1,2-dichloro, 1,1,2,2-tetrafluoroethane and 1,1,2,2-tetrachloro, 1,2-difluoromethane. These cooling liquids can be used either alone or in admixture with up to about 70 percent water, ethyl acetate, methyl acetate or other liquid solvents for the cooling liquid, and mixtures thereof.

Flavoring agents and other smoke additives can be incorporated in the cooling liquid either by deliberate addition or by choice of a flavored cooling liquid such as whiskey, brandy, rum or liqueur as the cooling liquid.

The amount of cooling liquid which, in encapsulated form, is incorporated in the filter element should be substantially that which, when completely evaporated during smoking, will effect the desired cooling of all of the smoke. The amount of liquid should be selected such that while the filter material is capable of holding in dispersed form, but the greater the surface area offered by the filter the greater the amount of liquid it can hold for surface evaporation. Of course, an amount of cooling liquid in excess of that which can be evaporated during smoking is wasteful.

EXAMPLE

As an example of the practice of the invention, a series of tests was run to show the extent and mechanism of the lowering of mainstream smoke temperature due to the presence of a smoke-cooling liquid in the filter portion of a cigarette. All cigarettes used in the experiments were composed of a 65 mm. tobacco column and a 20 mm. dual filter of an inner 10 mm. plug of crepe paper and an outer 10 mm. plug of triacetin-plasticized cellulose acetate. The solvents to be tested were injected into the paper section of the filter 15 mm. from the butt end of the cigarette.

The cigarettes were inserted into a plastic holder and were sealed by means of dental dam and O-ring. The holder was equipped with a bare Chromel-Alumel thermocouple 0.002 inch in diameter. The thermocouple was perpendicularly cemented in the holder with the junction exactly on the axis and located 1 mm. from the end of the cigarette filter tip. The thermocouple leads, which were brought out on opposite sides of the holder, led to the reference junction at ambient temperature and then to the Y-input terminals of of an X-Y recorder. An amplifier was used to boost the thermocouple signal to a level affording a recorder sensitivity of 0.2 inch per Centigrade degree. The X-inputs were supplied with a signal from an external time-base signal generator providing a 1 inch-per-minute scan rate. The standard smoking procedure was adopted, using one head of a smoking machine adjusted to take a 35 cc., 2 second puff once per minute.

The maximum temperature difference which could be recorded with this apparatus under these test conditions was 35°C with ambient temperature being set arbitrarily on the recorder chart by means of a zeroing control on the recorder. Temperature differences observed during smoking then showed on the recorder chart as either positive or negative deflections of the recorder pen depending on whether the probe junction was hotter or cooler, respectively, than the ambient temperature.

1. Ten of the filter cigarettes were smoked to determine the temperature level of smoke on a normal cigarette. No solvent was injected into the filter. A slight heating of about 0.25°C to 0.5°C was observed during each puff up to puffs nos. 6 or 7 with the subsequent puffs displaying an additional temperature rise due to the shorter lengths of the unsmoked portion of the cigarette. The temperature difference during the puffs was attributed to the sum of diabatic cooling and smoke temperature.

2. Cigarettes were puffed in the standard manner but contained no solvent and were not lit. A decrease in temperature was observed during each puff and was attributed to diabatic cooling. This temperature difference was of the order of 0.5°C and remained fairly constant throughout the first ten puffs.

3. Ten cigarettes were smoked to determine the cooling, during each puff, due to the evaporation of 50 mcl. of 95 percent ethanol injected into the filter. A definite lowering of the mainstream smoke temperature was observed and was attributed mainly to the evaporation of the solvent. A slight initial temperature rise of about 5°C for the first puff and less than 1°C for the second and third puffs was observed which was followed by cooling on each of the 3 puffs. We have attributed this initial heating mainly to the heat of solution provided by the dissolution of the cellulose acetate plasticizer (triacetin) by the alcohol.

4. A cigarette was "smoked" with 50 mcl. of ethanol in the filter. The effects due to smoke temperature were thereby eliminated. The observed temperature difference was then the sum of the effects due to diabatic cooling, the heat of solution by the cellulose acetate, and evaporation of solvent. Significant heating was observed on the first few puffs and was attributed mainly to heat of solution of the cellulose acetate plasticizer in the alcohol.

5. The cigarette puffed in test No. 4 was lighted and smoked in normal fashion. Cooling was observed. Lighting the cigarette did not affect the level of cooling.

6. A cigarette was tested after removing the cellulose acetate plug and injecting 50 mcl. of ethanol into the paper section. Much greater cooling was observed compared to test No. 3. No initial heating was observed on puffs 1, 2 and 3. This test demonstrated that the cellulose acetate plasticizer played an important role in the heating and cooling of the smoke.

7. Cigarettes were smoked with 50 mcl. of methyl acetate injected into the paper section of the filter. Intense initial heating (puffs 1 and 2) was observed. Cooling of subsequent puffs was intense but tapered off rapidly, due to the high vapor pressure of the methyl acetate. Cooling as much as 9°C was maintained.

8. Ten cigarettes were injected with 25 mcl. of methyl acetate. Essentially the same effect was noted as for the 50 mcl. addition in test No. 7 except that the heating and cooling intensities were halved.
Ten cigarettes were injected with 25 mcl. of ethanol. The same effect was observed as for the 50 mcl. addition in test No. 3 except that the cooling and heating intensities were halved. Cooling by 3-4°C with about 25 m.1. of injected ethanol was considered to be equivalent to the cooling attainable with an amount of ethanol which could be added readily to the filter in encapsulated form.

Cigarettes having 20 mm. paper filter, injected with 25 mcl. of ethanol, were smoked and were observed to show no initial heating. Cooling of the puffs averaged about 2°C.

The cigarettes used in test No. 10 were injected with 25 mcl. of ethyl acetate. Very little initial heating was observed and cooling tapered off sharply as puffs were taken.

Cigarettes having a 20 mm. paper filter into which 25 mcl. of 50-50 ethyl acetate-ethanol mixture was injected were smoked. No initial heating was observed. The temperature-time trace appeared to be a combination of that of tests Nos. 10 and 11.

Runs were made of cigarettes with plain absorbent cotton filters, with filters of absorbent cotton plus 60 mg. active carbon, and with filters of absorbent cotton plus 50 mg. of active carbon which had previously been wetted with 95 percent ethanol and allowed to dry. Heating was observed for all three types of cigarettes, but those containing carbon showed a greater temperature rise than those containing cotton alone.

Cigarettes were prepared with microcapsules containing a 50-50 ethanol-water solution embedded in the paper section of the filter. The capsules weighed about 50 mg. per cigarette of which about 50 percent comprised the alcohol-water mixture. The smoke was cooled by about 1.5°C.

Cigarettes whose filters were injected with 25 mcl. of various concentrations of ethanol in water were smoked. On the basis of puffs 4, 5, 6 and 7, the following average results were obtained:

<table>
<thead>
<tr>
<th>Ethanol:</th>
<th>Cooling, °C.</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>0.505</td>
</tr>
<tr>
<td>25%</td>
<td>1.22</td>
</tr>
<tr>
<td>37.5%</td>
<td>1.56</td>
</tr>
<tr>
<td>50%</td>
<td>2.06</td>
</tr>
<tr>
<td>67.5%</td>
<td>2.52</td>
</tr>
<tr>
<td>75%</td>
<td>2.26</td>
</tr>
<tr>
<td>95%</td>
<td>3.82</td>
</tr>
</tbody>
</table>

It will be readily seen from the tests reported in the foregoing example that a tobacco smoke filter can be obtained by positioning within a flexible outer wrapper, and in contact with a filler therewithin capable of entraining a cooling liquid, at least one rupturable capsule containing a liquid substantially more volatile than water, provided that the filler is substantially free of absorbent material and free of substances sufficiently soluble in the liquid to evolve a significant amount of heat of solution when the capsule is ruptured and releases the liquid into the filler.

I claim:

1. The method of effecting cooling of cigarette smoke which comprises locating a plurality of spaced, rupturable capsules containing ethanol within the body of an absorbent free filter of crepe paper at the mouth end of a cigarette, said paper being characterized by good absorbercy, resiliency and wet strength, said filter being encased within an outer resilient wrapper of high wet strength and further characterized by being free of substances sufficiently soluble in the ethanol to evolve a sensible heat of solution when the ethanol is released from the capsules, said filter being highly porous so as to further constitute a smoke filter of high exposed surface area and which permits the axial flow of the cigarette smoke therethrough, said capsules being ruptured by the smoker by compression immediately prior to smoking to effect the desired cooling.
CERTIFICATE OF CORRECTION


Inventor(s) EDWARD S. HARLOW et al.

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

Column 1, lines 44-45, "As shown in the drawing, utilized in the method the filter element of the invention.", should be deleted.

Column 3, line 5, "en" should read --an--.

Column 5, line 23, "plug" should read --plus--.

SIGNED AND SEALED

(SEAL)

Attest:
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHULTZ, JR.
Commissioner of Patents