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SELECTIVE TOBACCO SMOKE FILTER

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This invention relates to a tobacco smoke filter. More particularly this invention concerns a filter that is selective in the removal of aldehydes from tobacco smoke.

In our companion U.S. patent application Serial No. 568,575, now Patent No. 2,881,772, of which the present application is a continuation-in-part, we have already discussed to some extent filtering tobacco smoke and filters and pointed out the desirability of removing aldehydes from such tobacco smoke. However, briefly these matters will be further discussed below.

A wide variety of materials have been suggested in the prior art as filters for tobacco smoke. Thus, such products as cotton, paper, asbestos, regenerated cellulose and certain synthetic fibers have been disclosed as filter media for tars and nicotine of cigarette, pipe and cigar smoke.

Although materials as aforesaid remove a certain proportion of the particulate, or liquid-solid phase of tobacco smoke, such as the high boiling tar and nicotine particles, these materials are of little value in removing the constituents in the gaseous phase of the smoke. It is known that, although some of the gaseous constituents of tobacco smoke are desirable from the standpoint of taste, flavor and aroma, others are undesirable and are quite irritating to the smoker's throat and lungs. Many of the major irritating gases in tobacco smoke are low molecular weight aldehydes. In particular, acetaldehyde, a well-known irritant, is always present in cigarette smoke in significant amounts.

In order to remove such vapors from cigarette smoke, various adsorbents have been suggested in such prior filters. Thus, materials as activated silica gel, activated aluminum oxide and the diatomaceous earths have been used. Such products, however, have several undesirable features. One disadvantage is the fact that, on storage in the presence of tobacco, they adsorb moisture and tobacco flavors and odors. This not only impairs the quality of the cigarette but also "deactivates" the adsorbent rendering it incapable of removing aldehyde vapors. Also, the adsorbents are not selective for the irritating aldehydes but also remove other gaseous constituents which are desirable. In addition, filters of these adsorbents may be harsh and irritating to the smoker's tongue and, from an economical standpoint, they cannot be readily prepared on standard filter making equipment.

It is believed apparent, therefore, that the development of a filter which is somewhat selective in its removal action, and which in particular removes the undesired aldehydic components represents a highly desirable result. We have now found that it is possible to selectively remove a substantial portion of the irritating aldehyde vapors from cigarette smoke by employing a filament filter containing a finely divided polymer of a certain type uniformly spread over the surface of the filaments in the filter.

One object of the invention, therefore, is to provide a filament type of tobacco smoke filter which will remove a substantial portion of the particulate (liquid-solid) phase of tobacco smoke by physical means such as adsorption or impingement, and which, in addition, will chemically or otherwise remove acetaldehyde and other aldehyde vapors present in the smoke. Another object is to provide a filter which will selectively remove the undesirable aldehyde vapors without removing certain vapors or

aromas that contribute to the enjoyment of smoking. A further object is to provide a filter which will remain effective for the removal of the aldehyde vapors even after prolonged exposure to moisture vapor or tobacco odors as would normally be encountered in a sealed package of cigarettes. Still another object is to provide suitable methods for manufacturing filters of the class referred to. Other objects will appear hereinafter.

We have found that there are certain polymeric compounds, namely insoluble polymeric amine powders, which polymeric compounds have functional amino groups therein that will remove the undesired aldehydes from cigarette smoke and yet not materially adversely affect the aroma, taste and the properties of the smoke either during storage of the filter cigarettes or during the smoking thereof. The reaction of such polymers with the aldehydes may be illustrated by the following equations wherein R′ represents the polymer nucleus.

(1) $RCHO+R'NH_2 \rightarrow RCH[OH].NH.R' \rightarrow RCH{=}NR'+H_2O$

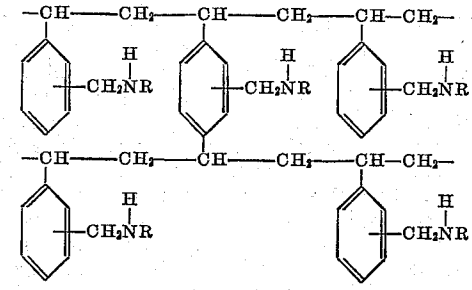
(2) $RCHO+2[R']_2NH \rightarrow RCH[NR']_2+H_2O$

The particular types of insoluble polymers which have been found to be most effective in the removal of the aldehydes from the gaseous phase of cigarette smoke are those containing primary and secondary amine groups in their free amine form as generally illustrated in the above formulas.

The preferred polymer, which would be employed in powered form, as will be explained hereinafter consists of a polystyrene polymer cross-linked with divinyl benzene and which contains aliphatic primary and secondary amine groups attached to its benzene rings. The number of amine-containing substituent groups can vary between an average of 0.7 and 1.5 for each benzene ring in the polymer. The amount of divinyl benzene constituent in the cross-linked polymer can vary between 2 and 15%.

In FIG. 1 is shown the formula for the insoluble polymeric amine powder which we have found to be highly effective in combining with the aldehyde gases of cigarette smoke.

FIGURE 1



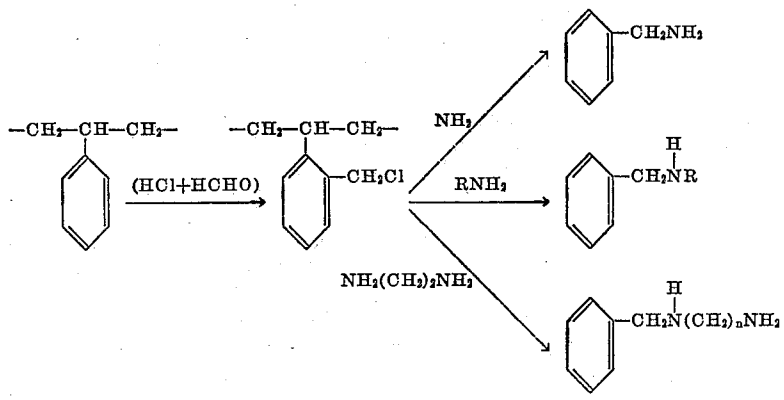
where

R=H, CH_3, $C_nH_{(2n+1)}$, $(CH_2)_n\left[\begin{matrix}H\\|\\N(CH_2)_n\end{matrix}\right]_mNH_2$

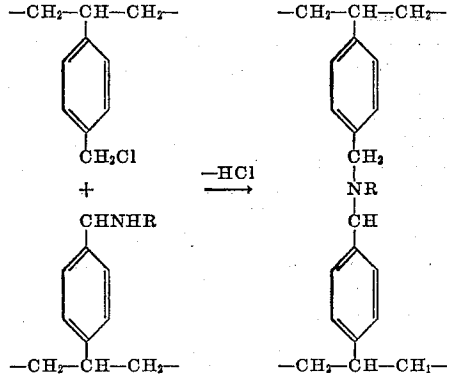
n=2–5 and m=0–5

The insoluble polymeric amines of this invention may be prepared by known procedures which involve a three-step process. The first step consists of the preparation of the styrene-divinyl benzene cross-linked polymer by the polymerization of styrene in the presence of 2–15% divinyl benzene, based on the total monomer weight. After the cross-linked polymer is prepared it is then chloromethylated by conventional procedures. Finally, the chloromethylated product is treated with ammonia or a monoamine.

It is by this last reaction that the alkylamino groups are incorporated into the polymer structure:



In order for the cross-linked polyamine polymer to best function in removing aldehydes from cigarette smoke at least 20% and preferably 50% or more of the alkylamino groups in the polymer preferably are primary or secondary. In other words, there should be active hydrogens still on the amino-nitrogen in most instances. This does not exclude, however, the possibility of the presence of tertiary amino groups on some of the benzene rings. Such groups can form by a reaction of an introduced secondary amine group on one benzene unit with a residual chloromethyl group on an adjacent benzene unit. This is shown by the following equation:



A wide variety of primary alkylamines can be used to react with the chloromethylated cross-linked polymer to give the desired product. Examples of such amines are methylamine, ethylamine, propylamine, isopropylamine, butylamine, isobutylamine, cyclohexylamine, ethylenediamine, tetraethylenediamine, diethylenetetraamine and diethylenetriamine. It is also understood that the amine can carry additional substituent groups on their alkyl components such as hydroxyl, amido, methoxy and the like. Thus, the primary alkanol amines such as ethanolamine can be used to react with the chloromethyl groups on the styrene-divinyl benzene polymer.

The size of the insoluble polymeric material above described is also an important part of this invention. In order to incorporate the powder into the finished filament filter it has been found that the product should be ground to the point where it can pass through a 100 mesh screen or finer. In this condition it can be readily dusted onto the surface of the spread out filaments of cellulose acetate prior to the fabrication of the filter. It is also desirable to spray the spread-out filaments with a cellulose ester type of organic plasticizer either before or after it is dusted with the powder. The plasticizer functions as a curing or bonding agent for the filter by partially solvating the cellulose filaments at random spots within the filter.

Satisfactory plasticizers for this purpose are glycerol diacetate, glycerol triacetate, glycerol dipropionate, glycerol tripropionate, propylene glycol mono- and diacetate, di(methoxyethyl)phthalate, methylphthalylethyl glycollate and triethyl citrate. Aside from forming a firm or rigid filter, the plasticizer aids in bonding the above described polymer powder to the filaments. This is because the powder becomes partially embedded in the filaments after the plasticizer has softened their surface.

A very desirable form of the insoluble amino polymer is a powder which will pass through a 200 mesh screen or finer. This is because such a powder can be suspended in the plasticizer used as the hardening agent for the filter and sprayed on the filaments rather than being dusted thereon. This simplifies the operation somewhat by eliminating a dusting booth or other suitable dusting apparatus in the fabrication of the filter. If desired, the plasticizer or hardening agent can be diluted with a solvent prior to the addition of the powder if the suspension or slurry technique is to be used for applying the powder. Suitable solvents which can be used as diluents for the plasticizer are the alkylene glycols and glycerine. In those cases where the plasticizer or filter hardening agent is water-miscible such as glycerol diacetate, propylene glycol acetate, etc., the plasticizer may be diluted with water.

The amount of the powdered polymer which we prefer to add to the finished filter will vary with the number of primary and secondary amino groups in its structure and the amount of aldehydes which one desires to remove from the cigarette smoke. When the polymer contains a nitrogen content of within the range of 5 to 15%, the amount of powdered additive required will be within the range of 5–30%. This percentage value is based on the weight of the combination of cellulose acetate filaments and powder only and does not include the weight of the plasticizer (or plasticizer and diluent) and paper wrapper. On this basis when 5% powder (nitrogen content 5%) is added to the filter, the filter will remove at least 5% of the gaseous aldehydes calculated as acetaldehyde. When 30% of the powder (nitrogen content 9–10%) is added, the filter will remove up to 60% of the gaseous aldehydes.

A method for determining if a cigarette filter removes gaseous aldehydes has been developed and published:

"Gaseous Phase of Cigarette Smoke—Isolation and Analysis for Total Aldehydes," G. P. Touey, Anal. Chem. 27, 1788–90 (1955).

Another advantage of using the insoluble amine polymer in a finely divided form is that when properly applied to the tow filaments it also aids in removing the tar and nicotine particles in the particulate phase of cigarette smoke. This is because the particles are deposited on the filaments and function as protrusions or humps. These protrusions extend into the spaces between the filaments in a cellulose acetate filament-type filter. Part of the nicotine and tar particles, therefore, which might normally

channel through such a filter are impinged on these protrusions.

The cross-linked insoluble polymer powders of this invention can be added to any type of cellulose acetate crimped tow filter which can be used for cigarette filter manufacture. Normally, this material consists of 5,000–40,000 filaments depending on the denier per filament. The denier per filament range is between 0.6 and 16. The ratio of denier per filament to the number of filaments present in the filter is in reverse proportions. Thus, when the heaviest denier per filament is used (16 d./f.) the number of filaments present in the filter will range from 5,000 to 10,000. When the finest denier per filament is used (0.6 d./f.) the number of filaments present in the filter will range from 30,000 to 40,000.

The number of crimps in the cellulose acetate tow can range from 8 to 25 crimps per inch. The more desirable number of crimps will range from 12–18.

For a still further understanding of our invention, reference may be made to the following examples which illustrate certain of our preferred embodiments.

EXAMPLE I

A length of cellulose acetate crimped tow of 5 denier per filament and containing 17,000 filaments was bloomed out with an air jet device to a width of 10 inches. While in this spread out condition the tow was sprayed on both sides with a plasticizer-type bonding agent (glycerol triacetate). It was then dusted on both sides with a powder consisting of a styrene-divinyl benzene copolymer containing primary and secondary alkylamine groups chemically bound to its benzene units. The nitrogen content of the polymer was 9.8% and it had been ground until it was capable of passing through a 200 mesh screen. After the spraying and dusting operation the tow was pulled back together into the form of a cord and pulled through a cigarette filter rod making device which converted it to paper-wrapped cylindrical rods 90 mm. in length and the circumference of a king size cigarette. These rods were cut into filter tips 15 mm. in length. Analyses of the rods disclosed that they consisted of 70% cellulose acetate filaments, 15% plasticizer and 15% polymeric amine powder, based on the weight of the combination without the paper. Microscopic observation of a few of the opened rods revealed that the powder was uniformly distributed on the filaments in the tow.

Ten of these filters were attached to commercial king size cigarettes which had been shortened by 15 mm. to compensate for the length of the filter tips. These cigarettes were smoked to 30-mm. butt lengths on an automatic smoking apparatus designed for determining the tar and nicotine content of the smoke as well as the aldehyde content of the gaseous phase of the smoke. The equipment and method have been described in Analytical Chemistry, vol 27, pp. 1788–90 (1955). The smoke was pulled by each puff through an absolute filter unit, followed by two gas absorption flasks containing a dilute aqueous solution of dimedon, a specific reagent for aldehydes. As each cigarette was smoked, the absolute filter removed all of nicotine and tars not removed by the filter tip while the dimedon solution scrubbed the smoke gases free of aldehydes. By analyzing the material on the absolute filter after the smoking test (10 cigarettes) it was possible to determine how much tar and nicotine came through the cigarettes. By analyzing the contents of the absorption flasks it was possible to determine how much of the low molecular weight aldehydes (calculated as acetaldehyde) were produced by the cigarettes. Finally, by smoking another set (10) of the same cigarettes, 35 mm. in length, and unfiltered, in the same manner it was possible to determine how much nicotine, tar and gaseous aldehydes were produced by the cigarette without a filter. The results of these two tests are listed in Table 1.

Control filters (15 mm.) without the cross-linked polymeric amine polymer but containing 15% glycerol triacetate were also prepared from another length of the tow and converted into 15-mm. filters in the manner described. These filters were attached to another set of the same brand of king size cigarettes (mentioned above) which had been shortened by 15 mm. This set of cigarettes was also smoked to butt lengths of 30 mm. on the smoking apparatus and the amounts of nicotine, tar and gaseous aldehydes delivered by the cigarettes were determined. The results of this test are also listed in Table 1.

Table 1

Type of Filter on Cigarette	Mg. Tar from 10 Cigarettes	Mg. Nicotine from 10 Cigarettes	Mg. Aldehydes from 10 Cigarettes	Cigarette Pressure Drop [1] (Average of 10)
Cellulose acetate tow containing the cross-linked polyamine powder	305	21	7.0	4.0
Cellulose acetate tow control	360	23.5	11.2	3.8
No filter	400	28.0	11.5	3.1

[1] Pressure drop expressed in inches of water at an air flow rate of 17.5 ml. per second through the cigarette.

The results in the table above show that the control filter removed 15% more tar and 16% more nicotine than the 15-mm. length of tobacco which it replaced. However, it was no better than the tobacco (15 mm.) in removing the gaseous aldehydes. The filter containing the cross-linked polystyrene powder removed 24% more tar, 25% more nicotine, and 37% more aldehydes than the 15 mm. length of tobacco it replaced.

EXAMPLE II

A length of cellulose acetate crimped tow of 2.1 denier per filament and containing 26,000 filaments was bloomed out to a width of 10 inches. It was then sprayed on both sides with a suspension consisting of 30 parts cross-linked polymer powder containing reactive amino groups, 35 parts propylene glycol and 35 parts glycerol triacetate. The polymer powder was a finely ground styrene-divinyl benzene copolymer containing primary and secondary alkylamine groups chemically bound to its benzene units. Its nitrogen content was 8.3% and the average size of its particles was 8 microns.

After being sprayed with this slurry the tow was pulled back together into the form of a cord and converted into 15-mm. filter tips as described in Example I. Analysis of the tips disclosed that they consisted of 67% cellulose acetate, 11.5% glycerol triacetate, 11.5% propylene glycol and 10% powder, based on the weight of the combination without the paper. Microscopic observation of a few of the opened filters revealed that the powder was uniformly distributed on the filaments. Ten of the filters were attached to commercial king size cigarettes (same brand as used for Example I) which had been shortened by 15 mm. These cigarettes were smoked on the smoking apparatus (Example I) to 30-mm. butt lengths and the amounts of nicotine, tar and gaseous aldehydes (calculated as acetaldehyde) delivered by the cigarettes were determined (Table 2).

Control filters (15 mm.) which had been sprayed with a 50/50 (by weight) glycerol triacetate-propylene glycol solution containing no polymer powder were also prepared from the same 2.1 d./f. tow. These filters contained 15% glycerol triacetate, 15% propylene glycol and 70% cellulose acetate, based on the weight of the com-

bination without the paper. Ten of the filters were attached to the king size cigarettes (same as Example I) which had been shortened by 15 mm. These cigarettes were smoked on the smoking apparatus (Example I) to 30-mm. butt lengths and the amounts of nicotine, tar and gaseous aldehydes delivered were determined. (Table 2.)

Table 2

Type of Filter on Cigarette	Mg. Tar from 10 Cigarettes	Mg. Nicotine from 10 Cigarettes	Mg. Aldehydes from 10 Cigarettes	Cigarette Pressure Drop
Cellulose acetate tow containing cross-linked amine powder	270	20	8.5	4.2
Cellulose acetate tow control	307	22	11.2	4.0

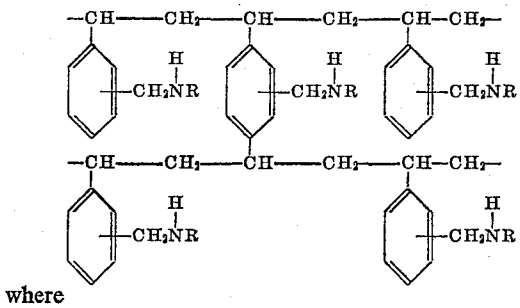
When these results are compared with those obtained from the unfiltered cigarette of Example I it is found that only the filter with the cross-linked amine powder removed aldehydes (26%). Also, the filter containing the powder removed 32% more tar and 29% more nicotine than the 15-mm. length of tobacco it replaced. The control filter removed 23% more tar and 22% more nicotine than the 15-mm. length of tobacco it replaced.

It is believed apparent from the foregoing that we have shown an improved tobacco smoke filter that is especially useful in removing undesired aldehyde components from tobacco smoke.

The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A tobacco smoke filter adapted to remove undesirable aldehyde components from tobacco smoke comprising an elongated filter body portion which is made up of several thousand longitudinally oriented synthetic filaments, the filaments being encircled about their circumference by a wrapper, the filter being characterized in that the filaments carry on their surface a substantial content of a polymeric powder material that has amine groups in its molecule, said polymer composition being in accordance with the following general formula:



where

R=H, CH_2, $C_nH_{(2n+1)}$, $(CH_2)_n\left[\begin{matrix}H\\|\\N\end{matrix}(CH_2)_n\right]_mNH_2$

n=2–5 and m=0–5

2. A filter in accordance with claim 1 wherein the filaments are essentially comprised of cellulose acetate which contains plasticizer.

3. A filter in accordance with claim 1 wherein the filaments are crimped continuous cellulose acetate filaments of a denier per filament of less than 16.

4. A filter adapted for removing aldehyde components from tobacco smoke comprised of a bundle of several thousand cellulose ester filaments, a content of plasticizer, at least 10% by weight of the filaments, contained in the cellulose ester, and a content of styrene-divinyl benzene copolymer which contains primary and secondary alkyl amine groups chemically bound to the benzene units of the copolymer carried on the surface of said filaments in finely divided form.

5. A product in accordance with claim 4 wherein the plasticizer is from the group consisting of glycerol diacetate, glycerol triacetate, glycerol dipropionate, glycerol tripropionate, propylene glycol mono- and diacetate, di (methoxyethyl) phthalate, methylphthalylethyl glycollate and triethyl citrate.

6. The product of claim 4 wherein the amount of powdered copolymer is 5–30% by weight of the filaments.

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