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TOBACCO SMOKE FILTER CAPABLE OF SELECTIVE REMOVAL OF ALDEHYDES

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FIG. 1.

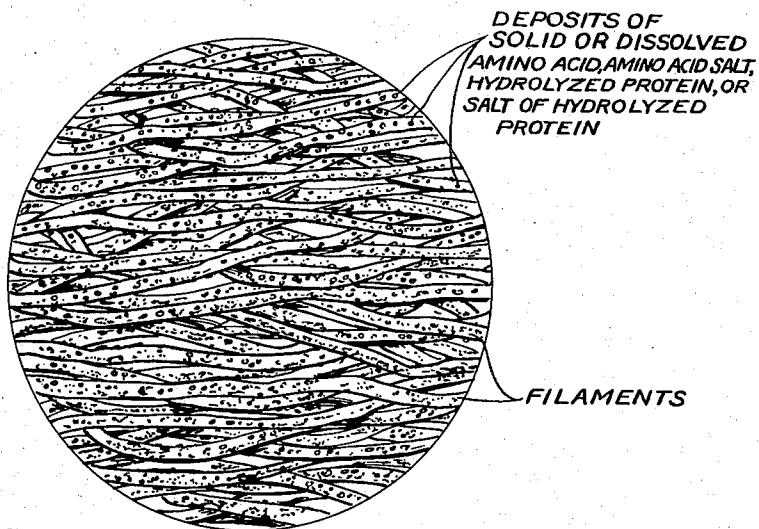
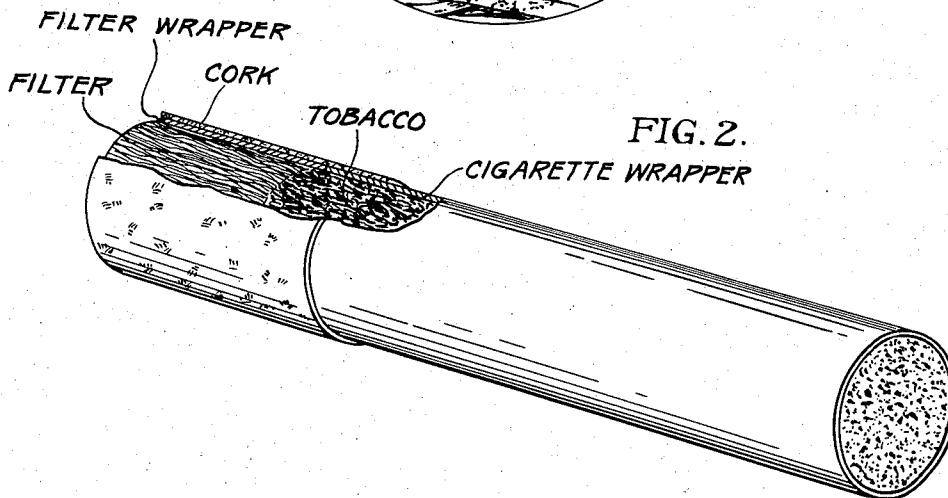


FIG. 2.

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TOBACCO SMOKE FILTER CAPABLE OF SELECTIVE REMOVAL OF ALDEHYDES

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5 Claims. (Cl. 131-208)

The present invention relates to tobacco smoke filtering material and structurally unitary rods thereof suitable for use in cigarettes, pipes, cigarette holders, and cigar holders. Further information concerning the particular type of filter with respect to which the present invention is an improvement may be had by reference to Crawford and Stevens Patents 2,794,480 and 2,794,239.

In the aforementioned patents, advantages of a newly discovered type of fibrous tobacco smoke filter are discussed. The filter therein described is prepared from a specially conditioned tow of synthetically spun continuous filaments and comprises an elongated structurally unitary rod-like mass of filaments and a wrapper encircling the mass, each filament of the mass being substantially co-extensive therewith, the filaments as a whole being in substantially parallel orientation longitudinally of the mass but substantially each of the individual filaments having a plurality of short portions thereof crimped into diverging and converging relationship to the main filament axis, a plurality of the filaments having surface solvation bonds to contiguous filaments at random points of contact. Very good results have been obtained in the use of such filters for the removal of nicotine and tars from tobacco smoke, especially in view of the fact that the filters supply other requirements, such as a unitary nature, rigidity, and resiliency, which are equally as necessary to the success of a tobacco smoke filter. These filters also have a marked processing advantage over other filters known in the art.

The filtering action of known fibrous filters ordinarily is limited to the liquid-solid phase of the tobacco smoke, e.g. the high boiling tar particles. While particulate liquid and solid components of the smoke may contain within them a small portion of the gaseous constituents in occluded or dissolved form, ordinarily the components of the gaseous phase of the smoke readily pass through the filters since the filters have little absorptive or adsorptive capacity for the gases. This is true even though the filters generally are made as dense as possible within the allowable limits of pressure drop. In copending Touey U.S. patent applications Ser. No. 413,950, filed March 3, 1954, now U.S. Patent No. 2,881,769, and Ser. No. 503,188, filed April 22, 1955, now U.S. Patent No. 2,917,054, it has been disclosed that the addition of certain finely divided organic solids to fibrous filters of the type taught by Crawford and Stevens improves filter efficiency without a further significant increase in pressure drop. This improvement is accomplished entirely by removal of additional quantities of components of the liquid-solid phase and does not affect components forming the gaseous phase.

It is known that although some of the gaseous constituents of tobacco smoke are desirable from the standpoint of taste, flavor, and aroma, other gaseous constituents are undesirable and are quite irritating to the smoker's throat and lungs. Among the major irritating gases in tobacco smoke low molecular weight aldehydes are

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thought to be the most detrimental. In particular, acetaldehyde, a well-known irritant, is always present in cigarette smoke in relatively large amounts. In order to remove gaseous irritants from cigarette smoke, various adsorbents have been incorporated into fibrous filters. Thus, adsorbents such as activated silica gel, activated carbon, activated aluminum oxide, and the various diatomaceous earths have been used. However, these adsorbents leave room for improvement in several respects. One disadvantage is the fact that on storage in a closed container in the presence of tobacco they may adsorb moisture vapor or tobacco odors and lose their "activity" for removing other gases. Another disadvantage is that they are not selective for the irritating aldehydes but also remove those gaseous constituents which are desirable and should be allowed to remain in the smoke. Therefore the incorporation of such products into a fibrous filter for cigarettes may give the filtered smoke a harshness that is irritating to the smoker's tongue.

It is an object of the present invention to provide filters capable of removing undesirable gaseous aldehydes from tobacco smoke while allowing other gaseous components of the smoke to pass through. It is another object of the invention to provide in a filter of longitudinally and parallelly oriented filaments, without an intolerable increase in pressure drop, a capacity for selective removal of undesirable constituents of the gaseous phase of the smoke together with an increased capacity for removal of particulate material from the liquid-solid phase of the smoke. A further object is to provide a filter which will remain effective for the removal of acetaldehyde and other volatile low molecular weight aldehydes even after prolonged exposure to moisture vapor or tobacco odors such as would normally be encountered in a sealed package of cigarettes. A still further object of the invention is to provide a filter which can effectively remove low molecular weight e.g. gaseous aldehydes from tobacco smoke vapors without destroying the taste or aroma of the smoke. Still another object is to increase the efficiency of tobacco smoke filters of the type described by Crawford and Stevens with respect to gaseous, liquid, and solid components without creating an intolerably high pressure drop. An additional object is to provide for firm adherence of particulate additive for filamentary tobacco smoke filters, particularly those filamentary filters prepared with filaments bonded by surface solvation and coalescence obtained by means of the application of a spray of a liquid, solvent-type plasticizer. Other objects will be obvious from the present specification and claims.

We have discovered that certain amino acids and certain amino acid derivatives are selective in removing undesirable gaseous aldehydes from tobacco smoke with which they are brought into contact. We have further found that when these amino acids and amino acid derivatives are incorporated as additives in tobacco smoke filters, the additives do not exhibit detrimental aging in storage. What is more, when a deposit of three dimensional particles of finely divided solid, gummy, or viscous additive of the present invention is uniformly dispersed throughout a filamentary filtering mass of the type disclosed by Crawford and Stevens with the particles of additive being carried on and by the filaments in the manner disclosed by Touey in the above-identified prior applications, the filamentary filter mass not only selectively removes large quantities of irritating aldehyde gases but also has greater efficiency in the removal of particles from the liquid-solid phase of the smoke, all with relatively little increase in the pressure drop through the mass.

The invention will be described in terms of what we

have found to be a most advantageous embodiment, according to which a tobacco smoke filter is made up of an elongated, cylindrical mass of cellulose acetate filaments, a dispersed deposit of finely divided additive carried by and on the filaments, and a paper wrapper encircling the filament mass, the filaments of the mass being coextensive therewith, being in substantially parallel orientation longitudinally of the mass, being provided with short crimped portions disposed in diverging and converging relationship to the main filament axis, and being bonded at random points of contact with adjacent filaments by means of surface solvation bonds comprising coalesced portions of the filaments making up the bonds, and the additive being a gummy, spray deposited material selected from the group consisting of amino acids and alkali metal and alkaline earth metal-carboxyl salts of amino acids, which acids and salts have at least one free and uncombined amino group in their molecular structure. Most advantageously, the invention comprises a filter of cellulose acetate fibers having surface solvation bonds achieved through the application of a plasticizer spray, the filter carrying uniformly dispersed particles (either solid, semi-solid, or liquid) particles of the additive in the amount of about 15% ($\pm 10\%$) by weight of the filter.

As indicated above, the additive of amino acid or derivative must have free amino groups. We have found that sufficient water is present in tobacco combustion products so that a dry form of the additive becomes quite reactive, but we have also found it is to be necessary that, whether wet or dry, the additive be in such a condition chemically that one or more primary or secondary amino groups per molecule of additive are free, uncombined, readily available for reaction with the aldehyde, and not tied up in the form of an inner salt, or a salt formed through the amino group. For instance, glycine and glycine hydrochloride both have their amino groups tied up and therefore are not significantly effective in aldehyde removal. Thus, any amino acid which is to be used in its pure form should be one which has a plurality of amino groups and is an alkaline amino acid, i.e. has an excess of amino groups over carboxyl groups. Otherwise, the amino acid should be present in the form of its carboxyl salt (formed through the carboxyl group or groups of the acid) of an alkali metal or an alkaline earth metal so that at least one amino group is free and readily available for reaction with the aldehyde. The acid or its salt may be in an impure and unconcentrated form such as alkali hydrolyzed protein. All of these forms are intended to be included by the term "amino acid material" used hereinafter.

The amino materials which have been found to be most effective in the removal of the aldehydes from the gaseous phase of cigarette smoke are those which, in addition to meeting the specifications given above, contain no more than six carbon atoms for each primary or secondary amine group. Preferably, there should be an even lower ratio of carbon atoms to amine groups. Thus, the following amino acids and amino acid salts, for example, can be employed in the operation of the invention, it being obvious that where a sodium salt is listed other water soluble alkali metal salts or water soluble alkaline earth metal salts will be operative:

- (1) Sodium salt of glycine (amino acetic acid)



- (2) Sodium salt of alanine (1-amino propionic acid)



- (3) Sodium salt of β -alanine (2-amino propionic acid)



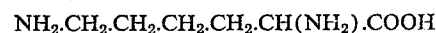
- (4) Arginine NH_2C



- (5) Sodium salt of arginine

- (6) Di-sodium salt of glutamic acid (2-amino pentanedioic acid) $\text{HOOC.CH(NH}_2\text{).CH}_2\text{CH}_2\text{COOH}$

- (7) Lysine (2,6-diaminohexanoic acid)



- (8) Sodium salt of lysine

Although all the amino acids listed above are operative, the two simple compounds, e.g. sodium glycinate and sodium alaninate, glycine and alanine, are preferred. When hydrolyzed proteins are to be used as the source of the amino acid the protein may be hydrolyzed into its amino acid constituents by any convenient procedure before being incorporated into cigarette filters. For example, it may be dissolved in a solution containing enough alkali to effect partial or complete hydrolysis of the protein and this solution subsequently sprayed onto the surface of the fibrous material, the material then being processed into a filter by the known procedures. This method of course contemplates the use of alkaline hydrolysis.

The proteins which have proven to be most effective in the practice of the invention, are those proteins which, on their alkaline hydrolysis, form amino acids (or amino acid salts) containing a high percentage of primary amine groups. As indicated above, at least one free primary or secondary amine group per six carbon atoms is desirable. Examples of proteins that are useful are gelatin, casein and zein.

The amount of amino acid material required in a cigarette filter to remove a sufficient amount of the gaseous aldehydes in the smoke in order to make the smoke less irritating to the smoker will depend mainly on the type of material employed. Most unfiltered cigarettes manufactured in the U.S. have been found to produce about 1 mg. of gaseous aldehyde (calculated as acetaldehyde) per cigarette during normal smoking. See Touey, "Gaseous Phase of Cigarette Smoke, Isolation and Analysis of Total Aldehydes," Anal. Chem. 27, 1788 (1955). Tests made with similar cigarettes containing filters of cotton and of cellulose acetate tow to which had been added various concentrations of the sodium salts of glycine and alanine, have shown that at least a fivefold molar excess of these amino acid salts must be present on the filter to remove approximately 25% of the gaseous aldehydes (approximately 0.25 mg. aldehyde per cigarette). When this amount was removed from the smoke of the cigarettes, the smoke was considerably improved with respect to its irritating characteristics. The amount of hydrolyzed protein required in a cigarette filter to remove significant quantities of the gaseous aldehydes in the smoke will depend upon (1) the type protein employed, and (2) the degree of hydrolysis of the protein. There should be enough alkali hydrolyzed protein present to provide a fivefold molar equivalent excess of amino acid in each filter in order to remove approximately 25% of the aldehyde gases. However, it will be understood that the amount of amino acid material required for the purpose of the invention is not critical but is relative, depending on the particular material used and the results desired. The amount normally will be about $15\% \pm 10\%$, particularly when based on the weight of completed cellulose acetate filter elements made as disclosed by Crawford and Stevens. When used with other types of supporting masses, much more or possibly less material may be preferred.

Filters of the invention are prepared preferably but not necessarily by adding the amino acid material to the surface of a pervious supporting mass such as a fibrous filter material prior to its fabrication into a filter cartridge, e.g. a tip for a cigarette. Various methods are suitable for carrying out the addition since the physical form of the deposit is not critical. The material may be added as a dry powder or as a powder kept damp

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by use of a hygroscopic agent, i.e. a humectant, for example, glycerine. It may be added in suspension in a liquid or as a true solution which, when partially or completely dried, will provide either a discontinuous particulate film or a continuous coating on the fiber. The addition may be made in such form, i.e. spray of a true solution of the acid or its salt or of a hydrolyzed protein with or without added hygroscopic agent, that even after drying for removal of most of the solvent, the particulate deposits of the material will not be solid in the true sense, that is, they will be minute masses of viscous, gummy, or semi-solid material. Deposits in this form have proven advantageous in that they appear to be more reactive.

When the material is to be added in a dry, solid, finely divided form, any suitable means known to the art for spreading a powder onto a fibrous surface or through a fibrous mass may be employed. Thus, for example, the amino acid material can be blown onto the fibers or it can be applied as a slurry in a non-solvent liquid, in a volatile organic vehicle or in a plasticizer for the fiber. Another method is to apply the material to the fibers electrostatically, i.e. to induce a charge on the fibers through a chamber containing a highly concentrated cloud of amino acid material dust. Preferably this is done with the fibers in the form of a tow and in a banded, i.e. spread-out condition. Still another method for applying the acid particles is to wet the surface of the fibers with an adhesive or a plasticizer before exposing them to a powder spraying device. Preferably, the amino acid material is continuously applied to an opened and banded moving tow formed as described in the Crawford and Stevens applications. That is to say, tow from a supply roll is opened to debundle the filaments and provide a larger and more uniform tow cross section, and the opened tow is spread uniformly to a much larger width of e.g., 10 times its original width, thereby exposing substantially all of the filaments to material, e.g. plasticizer, issuing from a dispenser adjacent which the tow passes. The amino acid material may be added before, simultaneously with, or after the plasticizer, preferably after. When the amino acid material is added as a powder it should be sufficiently finely divided so that it can be suspended in a gas, such as air, for dusting, or readily slurried in a liquid and passed through a spraying nozzle. While the exact size of the particle does not appear to be critical, it is indicated that substantially all of the material preferably should be capable of passing through a 200 mesh screen.

If the solution or suspension technique is employed, it has been found that the inclusion of a hygroscopic agent such as glycerine, sorbitol, propylene glycol, etc., in the solution or suspension aids not only in promoting selective reaction with aldehydes but also in preventing the amino acid material from dusting out of the finished filter. In other words, the hygroscopic agent does not allow the solution or suspension to evaporate down to the point where a loosely bound solid is left on the surface of the fibrous material. If the dusting technique is employed for adding the amino acid material, the hygroscopic agent can be sprayed on the supporting mass either before or after dusting.

While unusually good results have been obtained with filters prepared from a crimped continuous filament tow of cellulose acetate fibers sprayed with a plasticizer, e.g. glycerol acetate, di-(methoxyethyl)phthalate, or methylphthalylethylglycolate, it will be recognized by those skilled in the art that the usefulness of the invention extends to other filters, including those prepared from fibers of viscose, cotton, nylon, polyamides, polyesters, etc. Likewise, the additives of the invention may be employed in other filtering masses than those of a textile character. For instance, the amino acid materials disclosed herein may be added in finely divided form to filtering masses formed either of paper, asbestos or even granular material, or of other conventional tobacco smoke filtering sub-

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stances. When fibers are used, rather than being in tow form, i.e. parallel, they may be in other conventional forms such as wads, or fibrous masses interleaved with paper and rolled into a convoluted configuration. However, cellulose acetate and other synthetic thermoplastic fibers will be particularly useful where the fibers are in substantial longitudinal parallelism and are coextensive with the body of the filter. It is preferred to use for filter preparation in accordance with the present invention a continuous strand, e.g. tow, of 4,000 to 35,000 filaments, the filaments being of 16 to 3 denier and having about 4 to 10 crimps per inch.

By the expression "surface solvation" as used herein is meant the creation, by the action of a solvent or plasticizer and/or heat, of an adhesive, tacky or readily bonding condition of the filaments by solution or incipient solution of surface portions of the filament material whereby there is produced a welding and adhesion between adjacent filaments contacting at such portions, and by "coalescence" is meant the situation caused by partial or incipient melting, fusion, and/or solvation of surface portions of the filaments and resulting in a condition within those portions under which the portions will flow into or unite with similar portions of melted, fused and/or dissolved material in contiguous filaments. Coalesced (including surface solvation) bonds between fibers are sometimes also referred to as "fused" or "welded" bonds.

The more important structural factors found in the most advantageous form of the invention seem to be:

(1) That the aligned filaments be randomly bonded at randomly spaced intervals. This may be achieved by spraying a solvent type of plasticizer onto a spread tow of synthetic thermoplastic filaments as described above. It also may be accomplished by use of a filament strand in which at least some of the filaments contain sufficient plasticizer to be softened at slightly elevated temperatures.

(2) That the filament bonds be formed by coalescence, particularly of the surface solvation type. In other words, no material should be employed for adhering the filaments which would coat, destroy or otherwise substantially interfere with the integrity of the amino acid material. Obviously no plasticizer should be employed which has a detrimental action on the activity of the amino acid material. Bonds formed by coalescence of the surface solvation type also may be attained through the use of filaments spun with a suitable plasticizer content.

(3) That substantially all the amino acid material be carried on the surfaces of the filaments, supported by the filaments, and substantially immobile with respect thereto. This structure is best accomplished, when the material is to be added in dry form, by softening of portions of the filament surfaces whereby the particles may be slightly embedded therein without being coated or covered. It is also most easily accomplished when the diameters of the particles are not too different from the diameters of the filaments, the major portion of the particles being, for instance, less than twice the filament diameter, but more than one-tenth of the filament diameter.

The invention is illustrated in the accompanying drawings in which

Fig. 1 represents a magnified view of the interior of a mass of filtering material prepared in accordance with one embodiment of the invention, and

Fig. 2 is a view of a cigarette having attached thereto a tip prepared from a filtering material of the invention.

The invention is further illustrated in the following examples:

Example 1

A cellulose acetate tow of 5 denier per filament, 60,000 total denier, was pulled over a compressed air device which spread out the fibers to a width of twelve inches. While the tow was in this spread condition, it was sprayed with a solution consisting of 1 part sodium glycinate, 1 part propylene glycol, and 2 parts water. The solution was prepared by dissolving pure glycine in an aqueous

solution of an equivalent amount of sodium hydroxide and adding the propylene glycol. The pH of the solution was 8.6. The spray was applied from a conventional paint spray gun using air under pressure. The sprayed tow was fed through a conventional cigarette make-up machine which wrapped it with paper and cut it into rods of 66 mm. lengths and 25 mm. circumference. The plugs were dried at 30° C. for 16 hours. Each plug weighed 1.45–1.55 grams and contained 65% cellulose acetate, 15% sodium glycinate ($\text{H}_2\text{NCH}_2\text{COONa}$), 15% propylene glycol, and 10% water. The glycinate deposit on the dry plugs remained in the form of particulate minute viscous masses or gummy droplets of a concentrated water-glycol solution of the glycinate. These plugs were cut into 15 mm. filter tips (0.335–0.345 g.), attached to king size cigarettes of a standard brand retailed in the United States which had been shortened by 15 mm. Ten of these filtered cigarettes were smoked on a smoking machine similar in design and operation to the smoking machine described by J. A. Bradford, W. R. Harlan, and H. R. Hanmer, *Industrial and Engineering Chemistry*, vol. 28, pp. 836–9 (1936). The gaseous phase of the smoke was collected and analyzed for acetaldehydes. Ten unfiltered cigarettes, 85 mm. in length, were smoked and the gaseous phase analyzed in the same manner.

Acetaldehyde found in smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in smoke of 10 filtered cigarettes—4.7 mg.

Acetaldehyde removed—52%.

Example 2

A cellulose acetate tow of 5 denier per filament, 60,000 total denier, was sprayed with a solution of 1 part sodium glycinate, 1.5 parts water, and 1.5 parts sorbitol. The solution had a pH of 8.9. The sprayed tow was processed into filter tips (0.30–0.31 g.), containing 13% sodium glycinate, 20% sorbitol, 8% water, and 59% cellulose acetate. The tips were attached to cigarettes and smoked as in Example 1.

Acetaldehyde found in smoke of 10 unfiltered cigarettes—9.9 mg. to 10.0 mg.

Acetaldehyde found in smoke of 10 filtered cigarettes—7.4 mg. to 7.5 mg.

Acetaldehyde removed—25%

Example 3

A cellulose acetate tow of 5 denier per filament, 60,000 total denier, was sprayed with a solution of 1 part sodium glycinate, 1 part glycerol, and 2 parts water. The tow was processed into filter tips (0.30–0.32 g.), containing 14% sodium glycinate, 14% glycerol, 12% water, and 60% cellulose acetate. The tips were attached to cigarettes and smoked as in Example 1.

Acetaldehyde found in smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in smoke of 10 filtered cigarettes—5.9 mg.

Acetaldehyde removed—40%

Example 4

The procedure in Example 3 was repeated substituting the sodium salt of 2-amino-propionic acid (alanine) for the sodium glycinate. The 15-mm. filter tips (0.32–0.33 g.) contained 15% of the alanine salt, 13% glycerol, and 11.5% water, the remainder being cellulose acetate. The tips were attached to 85 mm. (king size) cigarettes shortened by 15 mm. and smoked as in Example 1.

Acetaldehyde found in the smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in the smoke of 10 filtered cigarettes—5.1 mg.

Acetaldehyde removed—48.5%

Example 5

This example points out the fact that a cellulose acetate filter without the amino acid salt removes only a trace of the aldehydes from the gaseous phase of cigarette smoke. It also points out that high alkalinity of the filter is not the basis of aldehyde removal, i.e. the mechanism of the reaction does not involve aldol condensation.

A cellulose acetate tow of 5 denier per filament, 60,000 total denier, was sprayed with a solution containing 35% glycerine, 65% water, and 1.3 grams of dissolved sodium bicarbonate. The pH of the solution was 9.0. The sprayed tow was processed into filter tips (0.34 g.) containing 18% glycerol and 18% water. The tips were attached to the king size cigarettes and smoked as in Example 1.

Acetaldehyde found in the smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in the smoke of 10 filtered cigarettes—9.7 mg.

Acetaldehyde removed—2%

Example 6

A piece of cotton weighing 5 g. was dipped into a solution of 1 part sodium glycinate, 1 part propylene glycol, and 2 parts water. The pH of the solution was 8.6. The cotton was removed and pressed to a weight of 15 g. and then allowed to dry at 25° C. and 40% relative humidity for 24 hours. The air-dry product weighed 11 g. and contained 5 g. cotton, 2.5 g. sodium glycinate, 2.5 g. propylene glycol, and 1 g. water. Wads of this material, weighing approximately 0.4 g., were inserted into paper tubes, 25 mm. in length and 25 mm. in circumference. These wads containing 22.8% sodium glycinate were attached to king size cigarettes shortened by 15 mm. and the cigarettes were smoked on the smoking machine as in Example 1.

Acetaldehyde found in smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in smoke of 10 filtered cigarettes—3.5 mg.

Acetaldehyde removed—65%

Example 7

As a comparison for judging the effectiveness of the amino acid material in aldehyde removal, a filter was prepared without the acid additive. A piece of cotton similar in construction to that employed in Example 6 was sprayed (a fine spray gun) with a 50% glycerine water solution until it contained 10% glycerine and 10% water. This cotton was converted into a filter 25 mm. in length as in Example 6 and tested on a king size cigarette shortened by 15 mm. It removed less than 2% of the acetaldehyde in the cigarette smoke.

Example 8

A cellulose acetate tow of 5 denier per filament, 60,000 total denier, was pulled over a compressed air device which spread out the fibers to a width of twelve inches. While the tow was in this spread condition it was sprayed with a solution consisting of (5 parts gelatin, 1 part sodium hydroxide, and 6 parts water). The sprayed tow was fed through a conventional cigarette make-up machine which paper wrapped it and cut it into rods of 66 mm. lengths and 25 mm. circumference. The plugs were dried at 60° C. for 2 hours. Each plug weighed 0.80–0.85 g. and contained 88% cellulose acetate and 12% hydrolyzed gelatin. These plugs were cut into 15 mm. tips weighing 0.18–0.19 g., and the tips attached to standard king size cigarettes (purchased on the retail market in the United States) which had been shortened by 15 mm. Ten of these filtered cigarettes were smoked on a smoking machine similar in design and operation to the smoking machine described by T. A. Bradford,

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W. R. Harlan, and H. R. Hanmer, Industrial and Engineering Chemistry, 28, 836-9 (1936). The gaseous phase of the smoke was collected and analyzed for acetaldehyde. Ten unfiltered cigarettes, 85 mm. in length, were smoked, and the gaseous phase analyzed in the same manner.

Acetaldehyde found in smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in smoke of 10 filtered cigarettes—6.2 mg.

Acetaldehyde removed—37%

Example 9

The procedure in Example 8 was repeated substituting casein for the gelatin. The 15 mm. filter tips (0.19-0.20 g.) contained 86% cellulose acetate tow and 14% of the hydrolyzed casein. The tips were attached to 85 mm. (king size) cigarettes shortened by 15 mm. and smoked as in Example 1.

Acetaldehyde found in the smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in the smoke of 10 filtered cigarettes—6.8 mg.

Acetaldehyde removed—31%

Example 10

The procedure in Example 8 was repeated substituting zein for the gelatin. The 15 mm. filter tips (0.18-0.20 g.) contained 85% cellulose acetate tow and 15% of the hydrolyzed zein. The tips were attached to 85 mm. (king size) cigarettes shortened by 15 mm. and smoked as in Example 8.

Acetaldehyde found in the smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in the smoke of 10 filtered cigarettes—7.4 mg.

Acetaldehyde removed—31%.

Example 11

This example points out the fact that a cellulose acetate filter without the hydrolyzed protein removes only a trace of the aldehydes from the gaseous phase of cigarette smoke.

A cellulose acetate tow of 5 denier per filament, 60,000 total denier, was sprayed with a 5% solution of sodium hydroxide. The sprayed tow was processed into filter tips (0.16-0.17 g.) containing 2% sodium hydroxide. The tips were attached to the king size cigarettes and smoked as in Example 8.

Acetaldehyde found in the smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in the smoke of 10 filtered cigarettes—9.5 mg.

Acetaldehyde removed—4%.

Example 12

A piece of cotton weighing 10 g. was dipped into a solution of 5 parts gelatin, 1 part sodium hydroxide, and 14 parts water. The cotton was pressed to a weight of 16 g. and then allowed to dry at 25° C. and 40% relative humidity for 24 hours. The air dry product weighed 12 g. and contained 83% cotton and 17% hydrolyzed gelatin. Wads of this material weighing 0.2 g. were inserted into paper tubes 15 mm. in length and 25 mm. in circumference. Tips of the same dimensions and weight were prepared from cotton, and both the treated and untreated tips were attached to king size cigarettes shortened by 15 mm. The cigarettes were smoked on the smoking machine as in Example 8.

Acetaldehyde found in smoke of 10 unfiltered cigarettes—9.9 mg.

Acetaldehyde found in smoke of 10 cigarettes containing a cotton filter—9.5 mg.

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Acetaldehyde found in smoke of 10 cigarettes containing a cotton filter treated with hydrolyzed gelatin—6.9 mg. Acetaldehyde removed by cotton—4%.

Acetaldehyde removed by treated cotton—30%.

Example 13

A solution of sodium glycinate was prepared by dissolving 45 parts glycine and 20 parts sodium hydroxide in 19 parts of water. To this solution there was added 15 parts of propylene glycol. All of the parts were on a weight basis.

A cellulose acetate tow of 5 denier per filament, 60,000 total denier, was pulled over a compressed air device which spread the fibers to a width of twelve inches. While the tow was in this spread condition, it was sprayed with the sodium glycinate solution until it contained 15% of the solution based on the total weight of the combination. The sprayed tow was fed through a conventional cigarette make-up machine which paper wrapped it and cut it into rods of 66 mm. lengths and 25 mm. circumference. The plugs were dried at 30° C. for 16 hours.

The dried plugs were cut into 15 mm. filter tips and attached to standard king size cigarettes retailed in the United States which had been shortened by 15 mm.

Ten of these filtered cigarettes were smoked on the standard smoking machine and the gaseous phase of the smoke was collected and analyzed for acetaldehyde. Ten unfiltered cigarettes, 85 mm. in length were smoked in a similar manner and the gaseous phase of this smoke was also analyzed for acetaldehyde.

Acetaldehyde found in smoke of 10 unfiltered cigarettes—9.8 mg.

Acetaldehyde found in the smoke of 10 filtered cigarettes—5.1 mg.

Acetaldehyde removed—48%.

Example 14

A glycine solution of 30.2% glycine, 14.3% sodium hydroxide, 25.2% water, 24.4% propylene glycol, and 5.9% glycerine was sprayed onto a 5 D/F, 80,000 total denier regular cross-section baled tow of cellulose acetate in the tow processing machine described above. Glyceryl triacetate plasticizer was sprayed onto the tow separately from the glycine solution. Results obtained from the preparation and testing of five samples were as follows using standard test procedures.

Percent by Weight in Completed Filter		Performance of 15 mm. Filter Tip On A King Size Cigarette Compared To Equivalent Length of Tobacco	
Plasticizer	Glycine Solution	Pressure Drop in Inches of Water	Aldehyde Removal
10.8	6.3	3.6-4.4; av. 4.1	14%.
10.8	10.7	4.0-4.6; av. 4.3	16%.
10.8	14.1	3.1-4.0; av. 3.6	25% (20% tars, 20% nicotine).
10.8	25.4	3.8-4.2; av. 4.0	25%.
9.6	12.6	3.4-3.7; av. 3.5	16% (15% tars).

We claim:

1. A tobacco smoke filter adapted to remove aldehyde impurities from tobacco smoke, said filter being comprised of a bundle of crimped, continuous filaments, the number of filaments in the bundle being greater than 4,000, the denier per filament being less than 16, the crimp being greater than 4 crimps per inch, substantially all the filaments being generally aligned longitudinally of the filter, a wrapper enclosing the periphery of the bundle, the filter being further characterized in that (a) the filaments contain a plasticizer and (b) the filaments carry on their surface particles of an amino acid material which is a nontoxic, nonvolatile, substantially non-odorous solid and which amino acid solid is a chemical compound having more than one carbon atom but not more than six carbon atoms and which has at least one

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free amino group in its molecular structure whereby said solid amino acid material not only is present to remove aldehydes, but as a solid is available on the filter to assist the filter in removing tar particles from the tobacco smoke stream.

2. A filter in accordance with claim 1 wherein the filaments are essentially comprised of cellulose acetate and the plasticizer is essentially comprised of an organic ester which will soften the cellulose acetate filaments.

3. A filter in accordance with claim 1 wherein there is also present with the amino acid material a content of a polyhydroxy organic compound.

4. A filter in accordance with claim 1 wherein the polyhydroxy organic compound present with the amino acid material is a compound selected from the group consisting of glycerol, sorbitol and glycol compounds.

5. A filter in accordance with claim 1 wherein the amino acid material is a compound selected from the group consisting of glycine, alanine, arginine, lysine, glutamic acid and salts thereof.

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