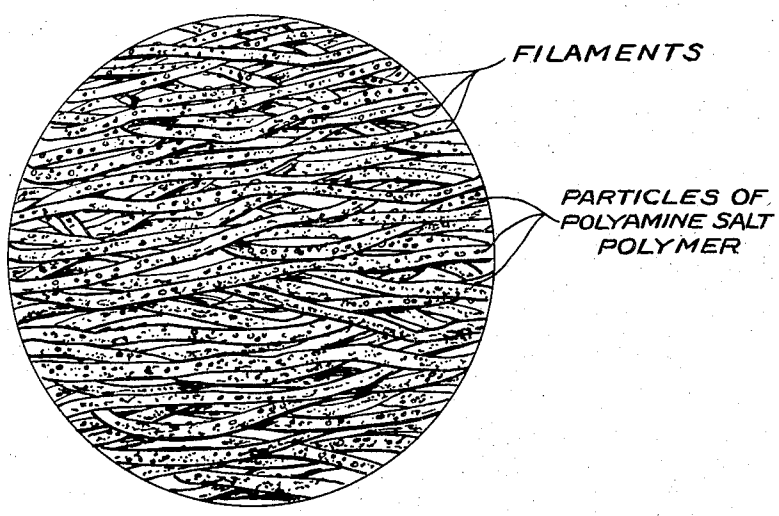
April 14, 1959 G. P. TOUEY ET AL 2,881,772

TOBACCO SMOKE FILTERS

Filed Feb. 29, 1956

FIG. 1.



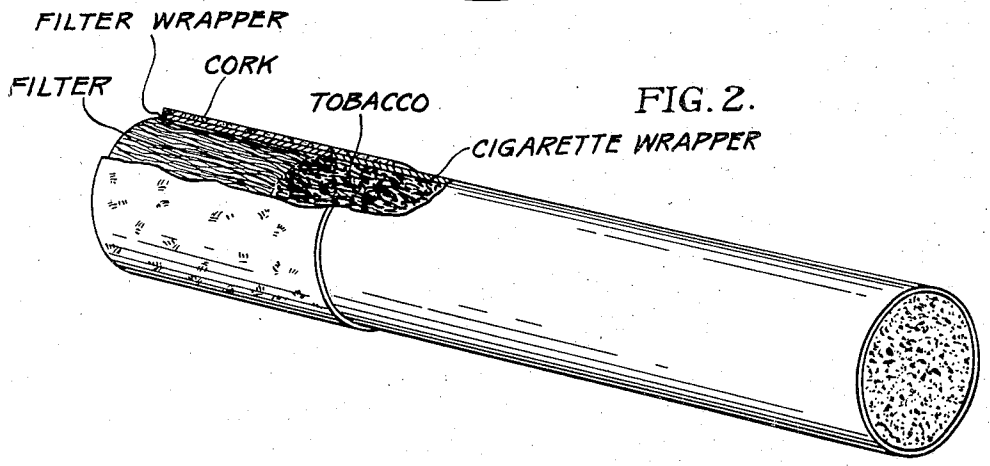


FIG. 2.

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TOBACCO SMOKE FILTERS

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Application February 29, 1956, Serial No. 568,575

9 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. More particularly, the invention is concerned with an improvement in filters of the general type disclosed in pending U.S. patent applications of Crawford and Stevens, Serial No. 324,342, filed December 5, 1952, Serial No. 374,168, filed August 14, 1953, and Serial No. 435,544, filed June 9, 1954, to each of which reference is made.

In the aforementioned applications, 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 thermoplastic 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 coextensive 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 and Ser. No. 503,188, filed April 22, 1955, 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 significantly 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 thought to have the most pronounced effect. 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 parallely oriented filaments, without an accompanying 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 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 a high pressure drop. An additional object is to provide improved tobacco smoke filters prepared from thermoplastic, generally parallel 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 polymeric salts of polyamines, which polyamines contain at least two and preferably three or more primary or secondary amino groups, are selective in removing undesirable aldehydes from tobacco smoke with which they are brought into contact. We have further found that when these polymeric polyamine salts, in the form of finely divided solids are incorporated in tobacco smoke filters, the salts do not exhibit detrimental aging in storage. What is more, when a deposit of finely divided solid polymeric polyamine salt is uniformly dispersed throughout a filamentary filtering mass of the type disclosed by Crawford and Stevens, with the particles of salt being carried on and by the filaments in the manner disclosed by Touey, 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.

In accordance with the invention a filter for the removal of aldehydes from the gaseous phase of tobacco smoke and particulate material from the liquid-solid phase of the smoke comprises a mass of supporting mate-

rial having interstices therethrough and an additive carried by the material, the additive comprising a salt of (A) a polyamine, and (B) a polymeric free acid radical-containing substance selected from the group consisting of: (1) vinyl polymers having a plurality of carboxyl groups, (2) acid esters and ethers of cellulose, (3) mineral acid esters of polyvinyl alcohol, and (4) alginic acid, the additive being present in an amount within the range of about 5% to about 60% by weight of the supporting material plus additive.

The invention will be described in terms of what we have found to be most advantageous embodiments, according to which a tobacco smoke filter is made up of an elongated mass of cellulose acetate filaments, a dispersed deposit of finely divided polyamine salt 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. 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 polyamine salt in the amount of about 5% to 60% by weight of the filter.

The invention is primarily directed to the use as the supporting material of a mass of fibers, particularly parallel thermoplastic fibers, e.g. a tow of cellulose acetate filaments. It will be apparent, however, that the invention will be useful with other types of fibrous masses. When fibers are used, rather than being parallel, they may be in other conventional forms such as wads, or for example, bats 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.

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. triacetin, di(methoxyethyl)phthalate, or methylphthalylethylglycollate, it will be recognized by those skilled in the art that the usefulness of the invention extends to other filters, including for example those prepared from fibers of viscose, cotton, nylon, polyamides, and polyesters. Likewise, the additives of the invention may be employed in other filtering masses than those of fibrous character. For instance, the polyamine salts disclosed herein may be added in solid finely divided form to filtering masses formed either of paper, of granular material, or of other conventional filtering substances. Therefore, while the invention primarily is concerned with polyamine salts supported on pervious fiber masses, the fiber comprising preferably a segment of a continuous filament tow of cellulose acetate or other thermoplastic materials, the supporting mass may be of other substances and may take other structural forms. The invention further contemplates the use of felt-like and web material either of which may be formed into various shapes which are pervious. In fact, those skilled in the art will understand that the invention will find utility where the supporting mass comprises, for instance, only an annular wrapper within which the additive is contained.

The polymeric polyamine salts which have been found to be most effective in the removal of the aldehydes from the gaseous phase of cigarette smoke are those derived by the reaction of the already mentioned acid polymers with polyamines containing at least two and preferably three or more primary or secondary amine groups. Thus, the following polyamines can be employed to form the polyamine salts of the acid polymers in the operation of the invention:

Ethylene diamine
Diethylenetriamine
Triethylenetetramine
Tetraethylenepentamine
1,2-propylene diamine
1,3-propylene diamine
1,4-butanediamine
1,6-hexane diamine

One may also use high molecular weight, non-volatile polyamines such as condensation products containing primary and/or secondary amino groups which are prepared for instance by reacting materials such as for example diethylenetriamine and triethylenetetramine with diketene, ethyl oxalate, methyl acrylate, and diisocyanates.

The free acid radical-containing substance from which the polyamine salt is derived is selected from one of the four groups identified above. Among the useful polymers containing a plurality of free carboxyl groups, alginic acid, carboxy methyl cellulose, polyacrylic acid, and maleic anhydride-vinyl acetate interpolymer provided unusually goood results. The polymer may of course be of either natural or synthetic origin. Thus, for example, alignic acid represents a natural polymer while polyacrylic acid represents one of a synthetic origin. Of a wide variety of synthetic carboxylated polymers which are useful, I may point out particularly polyacrylic acid, copolymers of acrylic acid with other vinyl compounds, various maleic acid copolymers, carboxymethyl cellulose, carboxy ethyl cellulose and copolymers of itaconic and citraconic acids and esters of cellulose and di- or tribasic acids such as cellulose acid citrate or cellulose acid phthalate.

When a mineral acid derivative of cellulose is to be used as the free acid radical containing substance for preparing the polyamine salt, it is preferred to use cellulose acid sulfate, cellulose acid phosphate or sulfoethyl cellulose.

When a mineral acid ester of polyvinyl alcohol is to be used as the free acid radical-containing substance for preparing the polyamine salt, it is preferred to use polyvinyl acid phosphate and polyvinyl acid sulfate.

Filters of the invention are advantageously prepared by adding the polyamine salt to the surface of 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. The polyamine salt may be sprayed on as a liquid solution or suspension or it may be dusted on as a solid powder. The material may be added in a solution which, when dried, will provide either a discontinuous or continuous film on the fiber. The polyamine salt may be added to a fiber filtering mass or formed in situ therein. When applied in a liquid spray, the additive usually is dried so that the liquid adhering to the fibers becomes a dry, solid, finely divided deposit.

The most convenient method of spray application is of course to spray directly onto the mass of fiber which will be the supporting material. This preferably is accomplished by spreading the fibrous mass for the purpose of enabling the spray to be uniformly deposited throughout and then reforming the mass into the desired shape.

When the polyamine salt is to be added as a liquid it may be used in aqueous solution or as a solution or a suspension in a liquid vehicle. The spray is directed onto the fibers and adjusted to form fine droplets so that each fiber theoretically will carry small sprayed deposits of the salt solution. The solvent subsequently is removed by evaporation. As will be evident from the examples below, the polyamine salt may be formed in situ on the

fibers by spraying the fibers first with a solution of the free acid radical-containing polymeric substance and subsequently with a solution of a polyamine, which reacts with the acid material by forming a salt therewith.

When the solution or suspension technique is employed, it has been found that the inclusion of a hygroscopic agent such as for example glycerine, sorbitol or propylene glycol in the solution or suspension aids in preventing polyamine salt particles 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 fine, loosely bound powder is left on the surface of the fibrous material. If the dusting technique is employed for adding the polyamine salt, the hygroscopic agent can be sprayed on the fibrous material either before or after dusting. This will prevent the powder from dusting or sifting out of the end of the filter since the hygroscopic agent keeps the surface of the fibrous material in a moist condition.

Alternately, the material may be added while it is in a 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 in preparing filters of the invention. Thus, for example, the polyamine salt 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 by friction or other suitable means and then to run the fibers through a chamber containing a highly concentrated cloud of polyamine salt 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 salt 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 polyamine salt 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 debundlize 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 an applicator adjacent which the tow passes. The polyamine salt may be added before, simultaneously with, or after the plasticizer, preferably after. When the polyamine salt 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 the material should be capable of passing through a 200 mesh screen. That is to say, most of the particles should have diameters of 20 microns or less. Advantageously, a powder is used which has at least 80% of its particles of a diameter less than the diameter of the fibers of the filter. Probably no substantial number of particles should be as large as twice the filament diameter. A good particle size range is one within the limit of 0.1 micron to 10 microns.

The amount of polyamine salt required in a cigarette filter to remove the volatile aldehydes in the smoke will depend mainly on the particular salt employed, its physical form, and the amount of aldehyde which must be removed in order to make the smoke less irritating to the smoker. I have found that most unfiltered cigarettes manufactured in the U.S. produce about 1 mg. of acetaldehyde per cigarette during normal smoking. (See Touey, "Gaseous Phase of Cigarette Smoke," Anal. Chem. 27, pp. 1788–90, 1955.) Tests have been made with cigarettes containing filters of cotton and of cellulose acetate tow to which had been added various concentrations of various polyamine salts of the type herein described. These tests have shown that at least a three molar excess of these salts must be present on each filter to remove approximately 25% of the aldehyde vapors (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. However, it will be understood that the amount of polyamine salt 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 5% to about 60% by weight of the entire filter mass, particularly when based on the weight of completed cellulose acetate filter elements made as disclosed by Crawford and Stevens.

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 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 dissolved or plastic material in contiguous filaments. 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. Bonds formed by coalescence of the surface solvation type also may be attained through the use of filaments spun with a suitable plasticizer content. It also may be accomplished by use of a filament strand in which only some of the filaments (when spun) contain sufficient plasticizer to be softened at slightly elevated temperatures.

(2) That the filament bonds be formed by coalescence 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 and availability of the particles of polyamine salt. Obviously no plasticizer should be employed which has a detrimental action on the particles.

(3) That substantially all the polyamine salt particles be carried on the surfaces of the filaments, supported by the filaments, and substantially immobile with respect thereto. When the polyamine salt is to be added as a solid, this structure is best accomplished 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 ultimate particles are smaller than the diameters of the filaments, the major portion of the particles being, for instance, less than ½ the filament diameter.

The invention is illustrated in the accompanying drawing 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.—Alginic acid salt of diethylenetriamine

A viscous solution of the diethylenetriamine salt of alginic acid was prepared by suspending 220 g. of alginic acid powder in 1000 cc. of distilled water and adding 50

g. of diethylenetriamine and 20 g. glycerine and stirring the mix for 10 to 15 minutes.

Example 2.—Application of aqueous solution

A cellulose acetate tow of 5 denier per filament, 90,000 total denier was pulled over a compressed air device which spread out the fibers to a total width of about 12 inches. While the tow was in this spread condition, it was sprayed with a portion of the viscous diethylenetriamine alginate solution described in Example 1. The spray was applied from a spray gun of the type in which both the liquid and atomizing air were fed 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 about 78 mm. length, the rods being 26 mm. in circumference. The rods were dried at 100–110° C. The amount of polyamine salt added to the fibers produced a gain in weight in the fibers of about 25% on a dry basis. The plugs were cut into filter tips, 13 mm. in length and these tips were attached to king-size cigarettes of a standard brand retailed in the United States which had been shortened by 13 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 in Industrial and Engineering Chemistry, volume 28, pages 836–9 (1936). The gaseous phase of the smoke was collected and analyzed for acetaldehyde according to the method described by Touey in Anal. Chem. 27, pp. 1788–90 (1955). Ten cigarettes without filters, but having the same total length as the filtered cigarettes, were smoked and the gaseous phase analyzed in the same manner. Calculations made from the experimental data showed that the filters had removed 25–30% of the gaseous aldehydes present in the smoke. Analysis of the liquid-solid phase of the smoke of the cigarettes showed that the filters had also removed a substantial amount of the tarry liquid-solid components.

Example 3.—Application of aqueous solution

The procedure of Example 2 was repeated using in place of the cellulose acetate tow a crimped tow of regenerated cellulose. Smoke analysis showed substantially the same filtration efficiencies as provided by the filters described in Example 2.

Example 4.—Carboxymethyl cellulose salt of triethylenetetramine

In 1500 cc. of water, 200 g. of carboxymethyl cellulose, in the free acid form, was suspended and 35 g. of triethylenetetramine added. The mix was stirred vigorously for a few minutes until it appeared to be homogeneous.

Example 5.—Application of aqueous dispersion

Using the spray technique described in Example 2, a portion of the salt of Example 4 in its aqueous dispersion was sprayed onto a cellulose acetate yarn of 5 denier per filament, 100,000 total denier. Test smoking and smoke analysis were carried out as described in Example 2. Calculations showed that the filters had removed a substantial amount of tarry material and about 30–35% of the aldehydes from the smoke.

Example 6.—Salt formation in situ

Another portion of the tow described in Example 2 was sprayed in the described manner with a solution of 300 g. of polyacrylic acid dissolved in 2000 cc. of water so that the fiber gain in dry weight was about 30–35%. However, while the tow thus sprayed was still wet and in a spread condition, it was sprayed with a solution comprising 200 g. diethylenetriamine, 60 g. glycerine and 200 cc. of water. The polyamine spray was applied in such an amount that the dry deposit provided the fibers with a weight gain of about 15–16%. The dissolved amine reacted immediately with the polyacrylic acid to produce the salt. The tow was dried, condensed, and formed into cylindrical shaped rods, 78 mm. in length and 26 mm. in circumference. These rods were cut into filter tips, 13 mm. in length and ten of the filter tips were attached to the standard cigarettes shortened by 13 mm. Smoking tests conducted as described in Example 2 showed that the filters removed approximately 20–30% of the aldehydes from the smoke.

Example 7.—Salt formation in situ

A viscous solution of maleic anhydride-vinyl acetate interpolymer was prepared by refluxing in 800 cc. of acetone for 12 hours 100 g. maleic anhydride, 86 g. vinyl acetate, and 2.0 g. benzoyl peroxide. The resulting acetone solution was sprayed on a viscose tow of 5 denier for filament, 90,000 total denier, in an amount necessary to give a dry weight gain by the fibers of 40–50%. The spray technique was as described in Example 2. While the tow was spread and still wet with the interpolymer spray, a sufficient amount of triethylenetetramine was sprayed on to produce a gain in weight of the dry fibers (plus interpolymer) of 20–25%. The polyamine reacted with the maleic anhydride units in the polymer to give amide groups and salt groups. The tow was converted into 13 mm. filters as described above, the filters were subjected to smoking tests, from which it was determined that substantial proportions of aldehyde, as well as tar, had been removed from the tobacco smoke.

Example 8.—Salt formation in situ

An elongated web of crepe paper was sprayed with the acetone solution of interpolymer described in Example 7 in an amount sufficient to produce a dry weight gain by the paper of 30–40%. Immediately thereafter the paper was sprayed with a mixture comprising three parts tetraethylene pentamine and one part sorbitol in an amount sufficient to give a dry weight in addition of the paper (and interpolymer) of 25–30%. The sprayed paper was rolled into a cylindrical convolution approximately 25 mm. in circumference and dried. When dry, the paper plugs were cut into 13 mm. segments which were affixed to cigarettes as filters, the longitudinal axis of the paper plugs being aligned with the cigarettes. Smoking tests conducted as described in Example 2 showed that the filters removed a substantial portion of the aldehydes and tars from the smoke.

Example 9.—Salt formation in situ

A mass of cotton wool was combed to spread it out and make the individual fibers accessible to a spray. The combed cotton yarn was subjected to the two successive sprays described in Example 7 above, whereupon portions of the combed cotton were severed from the mass and formed into cylindrical rods within annular paper wrappers having the diameter of cigarettes. The wrapped rods were affixed to cigarettes in the manner described in Example 2 and subjected to smoke tests. Aldehyde removal proved to be approximately the same as that found for the filters of Example 5.

Example 10.—Cellulose acid phosphate salt of diethylenetriamine

A cellulose acid phosphate was prepared by a method described by Coppick and Hall ("Flameproofing Textile Fabrics," by are R. W. Little, A. C. S. Monograph 104, page 179, Reinhold Publishing Corporation, New York, 1947). 250 g. of ground wood pulp were soaked in a solution containing 150 g. 85% phosphoric acid, 210 g. urea, and 250 ml. water. The excess liquid was filtered off, and the impregnated wood pulp was dried in a forced air drying oven at 50° C. The dry powder was put in a 150° C. oven for 2 hours, then washed with water and diluted hydrochloric acid to remove the nitrogen salts. One gram of the cellulose acid phosphate so prepared had a titer of 54.6 cc. of N/10 NaOH. The cellulose acid phosphate was added to a water solution

containing a slight excess of diethylene triamine, slurried 15 minutes at 10° C., filtered and washed with water. The complex salt of cellulose acid phosphate and diethylene triamine formed was found to have a nitrogen content or 8.33%, and a 2% water slurry had a pH of 9.7.

Example 11.—Application of salt dust

A tow of cellulose acetate of approximately 8880 filaments, 8 denier per filament, was slowly pulled over a series of rollers which spread out the fibers to a width of about 12 inches. While the tow was in this spread condition, it was dusted with a powder of the salt prepared in Example 10. The tow was condensed and fed into a conventional cigarette make-up machine which cut and paper-wrapped it into rods of 25 mm. in circumference and 78 mm. in length. The rods contained 28 parts diethylene triamine phosphate salt and 72 parts cellulose acetate. The rods were cut into shorter segments of 13 mm. each, which were attached to king-size cigarettes shortened by 13 mm. and tested in the manner described in Example 2. The result of the smoking experiment was compared with the result obtained from smoking the same brand of cigarettes containing 13 mm. filter tips of the same tow of cellulose acetate fibers without the addition of the diethylene triamine cellulose phosphate salt. Experimental data showed the following:

	Milliequivalents of aldehydes found in smoke
Smoke collected from 5 unfiltered cigarettes (50 mm. of cigarette smoked)	0.24
Smoke collected from 5 filtered cigarettes, filter of cellulose acetate (50 mm. of the cigarette smoked)	0.23
Smoke collected from 5 filtered cigarettes, filter of 72 parts cellulose acetate and 28 parts diethylene triamine cellulose phosphate (50 mm. of the cigarette smoked)	0.18

The values listed above indicate that the filter of cellulose acetate fibers containing no amine salt removed less than 5% of the aldehydes from the smoke stream while the filter containing 28% diethylene triamine cellulose phosphate removed 25% of the aldehydes from the smoke stream.

Example 12.—Application of salt dust

A tetraethylene pentamine salt of cellulose phosphate was prepared by substituting tetraethylene pentamine for the diethylene triamine in Example 10. The cellulose phosphate tetraethylene pentamine salt contained 9.42% N. Cigarette filter tips were prepared and attached to cigarettes in a manner similar to that described in Example 2. The tips contained 25 parts tetraethylene pentamine cellulose phosphate salt and 75 parts cellulose acetate of 8,880 fibers and 8 denier per filament. Calculations from smoking data showed the following:

	Milliequivalents of aldehydes found in smoke
Smoke collected from 5 filtered cigarettes, filter of cellulose acetate (50 mm. of the cigarette smoked)	0.23
Smoke collected from 5 filtered cigarettes, filter of 75 parts cellulose acetate and 25 parts tetraethylene pentamine salt of cellulose phosphate (50 mm. of the cigarette smoked)	0.17

The values listed above indicate that the filter of cellulose acetate fibers containing no amine salt removed less than 5% of the aldehydes from the smoke stream while the filter containing 18% tetraethylene pentamine salt of cellulose phosphate removed 30% of the aldehydes from the smoke stream.

Example 13.—Diethylene triamine cellulose sulfate salt

A cellulose acid sulfate was prepared by the method of Rigby (U.S. Patent 2,025,073, issued December 24, 1935). From the pyridine salt, the diethylene triamine salt was formed by conversion in ethyl alcohol. The salt was filtered, dried and powdered.

Example 14.—Application of salt dust

With the technique described in Example 11, powdered diethylene triamine salt of cellulose sulfate prepared as described in Example 13 was dusted onto another portion of the tow described in Example 1. The tow was converted into filters such that each filter tip contained 18 parts of the salt and 82 parts fiber. Smoking tests gave results from which the following data was calculated.

	Milliequivalents of aldehydes found in smoke
Smoke collected from 5 filtered cigarettes, filter of cellulose acetate (50 mm. of cigarette smoked)	0.23
Smoke collected from 5 filtered cigarettes, filter of 82 parts cellulose acetate and 18 parts diethylene triamine salt of cellulose sulfate	0.19

The values listed above indicate that the filter of cellulose acetate fibers containing no amine salt removed less than 5% of the aldehydes from the smoke stream while the filter containing 18% cellulose sulfate removed 21% of the aldehydes from the smoke stream.

Example 15.—Application of aqueous solution

In this example a tow of 20,000 cellulose acetate filaments, 5 denier per filament was treated with a compressed air device as described in Example 2 and using the technique of Example 2 was sprayed with a 10% aqueous solution of the salt prepared as described in Example 13. The treated tow was converted into filters of 25 mm. circumference and 13 mm. length. The filters contained 14 parts of the salt to 86 parts of acetate. Smoking data was as follows:

	Milliequivalents of Aldehydes found in smoke
Smoke collected from 5 filtered cigarettes, filter of cellulose acetate (50 mm. of the cigarette smoked)	0.23
Smoke collected from 5 filtered cigarettes, filter of 86 parts cellulose acetate and 14 parts diethylene triamine salt of cellulose sulfate	0.17

The values listed above indicate that the filter of cellulose acetate fibers containing no amine salt removed less than 5% of the aldehydes from the smoke stream while the filter containing 14% of the amine salt removed 29% of the aldehyde from the smoke stream.

Example 16.—Polyvinyl acid phosphate salt of ethylene diamine

A solution consisting of 10 parts of polyvinyl alcohol, 4 parts of 85% phosphoric acid, 7.5 parts of urea, and 78.5 parts water was prepared. The solution was heated to 70° C. for 5 minutes, then spread out on a smooth surface and dried at 30° C. The dry film was heated at 155° C. in an oven for 1½ hours, removed, and washed free of water solubles. The sample was then washed in dilute hydrochloric acid to remove the nitrogen salts. One gram of this polyvinyl acid phosphate so prepared had a titer of 41.0 cc. of 0.1 N NaOH. The polyvinyl acid phosphate was added to a water solution containing an excess of ethylenediamine, slurried 10 minutes, and separated from the solution by filtration. The product obtained was washed in water until all of the excess ethylenediamine was removed. Finally it was dried and ground to a powder capable of passing through a 200-mesh screen.

Example 17.—Application of salt dust

By means of the technique of Example 11 and with a portion of the same tow, filters were prepared containing 22 parts dust of the salt prepared as described in Example 16, and 78 parts cellulose acetate fiber. Smok-

ing tests conducted as described in Example 2 showed the following:

	Milliequivalents of aldehydes found in smoke
Smoke collected from 5 unfiltered cigarettes (50 mm. of the cigarette smoked)	0.24
Smoke collected from 5 filtered cigarettes, filter of cellulose acetate (50 mm. of the cigarette smoked)	0.23
Smoke collected from 5 filtered cigarettes, filter of 78 parts cellulose acetate and 22 parts polyvinyl phosphate ethylenediamine salt (50 mm. of the cigarette smoked)	0.19

The values listed above indicate that the filter of cellulose acetate fibers containing no amine salt removed less than 5% of the aldehydes from the smoke stream while the filter containing 22% polyvinyl phosphate ethylenediamine salt removed 21% of the aldehydes from the smoke stream.

Example 18.—Application of salt dust

A polyvinyl phosphate diethylenetriamine salt was prepared in the manner described in Example 16 by substituting diethylenetriamine for the ethylenediamine. Filter tips for cigarettes were prepared as described in Example 17, the tips containing 25 parts salt to 75 parts acetate fiber. Experimental smoking and smoke analysis gave results as follows:

	Milliequivalents of aldehydes found in smoke
Smoke collected from 5 filtered cigarettes, filter of cellulose acetate (50 mm. of the cigarette smoked)	0.23
Smoke collected from 5 filtered cigarettes, filter of 75 parts cellulose acetate and 25 parts polyvinyl phosphate diethylenetriamine salt (50 mm. of the cigarette smoked)	0.18

The values listed above indicate that the filter of cellulose acetate fibers containing no amine salt removed less than 5% of the aldehydes from the smoke stream while the filter containing 18% polyvinyl phosphate diethylenetriamine salt removed 25% of the aldehydes from the smoke stream.

Example 19.—Diethylenetriamine polyvinyl sulfate salt

One hundred and sixty grams of pyridine-sulfur trioxide compound, 44 g. of polyvinyl alcohol, 59 g. of sodium chloride, and 250 g. of pyridine were charged to a reactor. The mass was heated for eight hours at 38° C. Pyridine was then removed and the product washed with methanol. The hard resinous material was dispersed in water and filtered. The clear viscous solution was precipitated by pouring it into a large volume of methanol. The tan precipitate was separated in a centrifuge and extracted with methanol until free of chloride ions. This powder was treated with 150 g. concentrated hydrochloric acid in two liters of methanol. The fine precipitate was separated in a centrifuge and extracted with methanol until free of chloride ions. The polyvinyl acid sulfate was slurried in 2 liters of methanol containing 36 g. of diethylenetriamine. The diethylenetriamine salt was filtered off, washed with methanol, and dried. Finally it was ground to a powder capable of passing through a 200-mesh screen.

Example 20.—Application of salt dust

A tow as described in Example 11 was treated in the manner described in that example for the application of the diethylenetriamine-polyvinyl sulfate salt dust prepared as described in Example 19 after first having been subjected while spread to a spray of dimethoxyethyl phthalate plasticizer. The filter rods resulting from conversion of the treated tow contained 19 parts polyamine-polyvinyl sulfate salt, 10 parts plasticizer and 71 parts acetate fiber. These rods were baked at 80° C. for 30 minutes to set the plasticizer. The cured rods were subjected to smoking tests as described above. Data obtained from these tests was as follows:

	Milliequivalents of aldehydes found in smoke
Smoke collected from 5 filtered cigarettes, filter of 90 parts cellulose acetate and 10 parts dimethoxyethyl phthalate (50 mm. of the cigarette smoked)	0.23
Smoke collected from 5 filtered cigarettes, filter of 71 parts cellulose acetate, 19 parts diethylenetriamine salt of polyvinyl sulfate, and 10 parts dimethoxyethyl phthalate (50 mm. of the cigarette smoked)	0.19

The values listed above indicate that the filter of cellulose acetate fibers containing no amine salt removed less than 5% of the aldehydes from the smoke stream while the filter containing 19% polyvinyl sulfate diethylenetriamine removed 21% of the aldehyde from the smoke stream.

We claim:

1. A tobacco smoke filter comprised essentially of several thousand continuous longitudinally oriented fibers, said fibers carrying on their surface particles of a salt derived from the reaction of a free acid radical-containing compound from the group consisting of alginic acid, carboxy methyl cellulose, polyacrylic acid, maleic anhydride-vinyl acetate, itaconic acid, citraconic acid, cellulose acid citrate and cellulose acid phthalate with a polyamine from the group consisting of ethylene diamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, 1,2-propylene diamine, 1,3-propylene diamine, 1,4-butanediamine, and 1,6-hexane diamine.

2. A tobacco smoke filter comprised of a bundle of at least 8,000 continuous synthetic filaments, which filaments carry on their surface a salt which comprises the reaction product of triethylenetetramine and carboxymethyl cellulose.

3. A tobacco smoke filter comprised of an elongated fibrous base material, said base material carrying on its surface particles of a salt derived from reacting a polyamine with a polymeric material which has a free acid radical.

4. A tobacco smoke filter which consists essentially of a bundle of continuous longitudinally oriented synthetic fibers, which fibers carry on the surface thereof several percent of salt particles, said salt particles being the reaction product of a polyamine with a polymeric material which has a free acid radical.

5. A product in accordance with claim 4 wherein the fibers are continuous crimped cellulose acetate fibers.

6. A tobacco smoke filter consisting essentially of continuous crimped longitudinally oriented cellulose acetate fibers, said fibers carrying on their surface a salt of triethylenetetramine and carboxymethyl cellulose.

7. A tobacco smoke filter element comprised of longitudinally extending continuous filaments, which filaments carry on their surface a deposit of diethylenetriamine alginate.

8. A tobacco smoke filter element comprised of longitudinally extending continuous filaments, which filaments carry on their surface a deposit of diethylenetriamine and a salt of cellulose acid phosphate.

9. A tobacco smoke filter element comprised of longitudinally extending continuous filaments, which filaments carry on their surface a deposit of a salt of polyvinyl acid phosphate and ethylene diamine.

References Cited in the file of this patent

UNITED STATES PATENTS

2,172,946	Sutter	Sept. 12, 1939
2,763,267	Muller	Sept. 18, 1956

FOREIGN PATENTS

717,029	Great Britain	Oct. 20, 1954