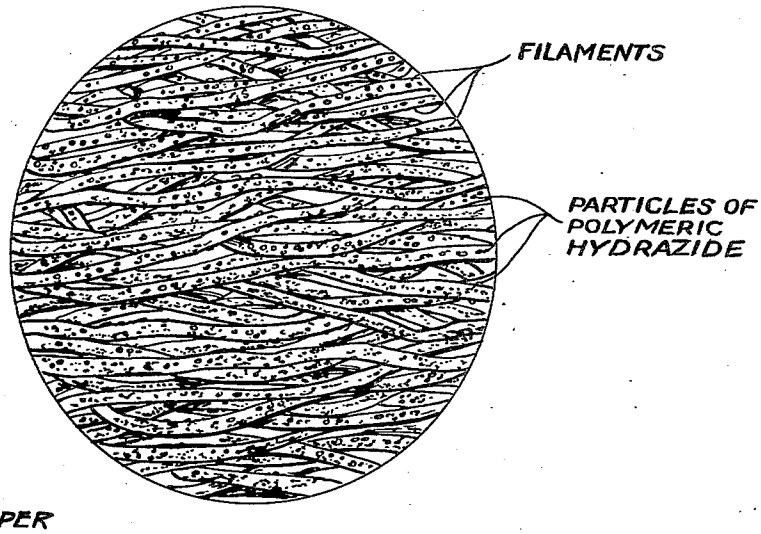
Dec. 10, 1957 N. H. SHEARER, JR 2,815,761

FIBROUS TOBACCO SMOKE FILTER

Filed Feb. 29, 1956

FIG. 1.



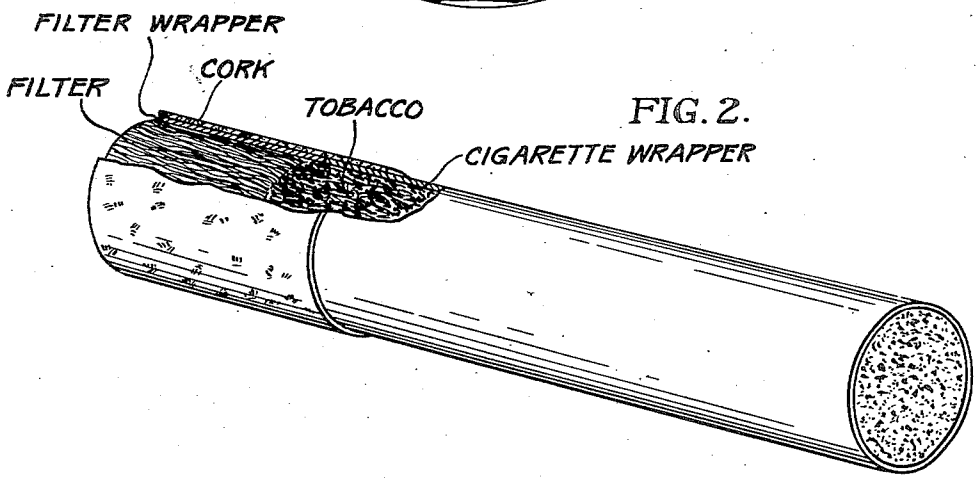


FIG. 2.

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FIBROUS TOBACCO SMOKE FILTER

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Application February 29, 1956, Serial No. 568,563

12 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 a cylindrical, elongated, structurally unitary, rod-like mass of filaments and an annular wrapper encircling the mass, the filaments being in the aggregate substantially parallel to the longitudinal axis of the mass and to each other but substantially all of the individual filaments each having a plurality of short portions crimped into diverging and converging relationship to the main filament axis, and each filament of the mass being substantially coextensive therewith, and 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 some of the particulate liquid and solid components of the smoke which are filtered out may contain within them a small portion of the gaseous constituents in occluded or dissolved form, and while some gaseous components to a limited extent may be condensed on the fibers of the filter, 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. Another object is to provide a fibrous filter capable of removing particulate solids and liquids and also certain gases from tobacco smoke. It is another object of the invention to provide in a filter of longitudinally and parallelly 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 gaseous 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 the gaseous phase of tobacco smoke without destroying the taste or aroma of the smoke, that is, without removing certain vapors or aromas which contribute to the enjoyment of the smoking. 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.

I have discovered that certain polymeric hydrazides, e. g. polyacrylylhydrazide and polymethacrylylhydrazide are selective in removing undesirable aldehydes from tobacco smoke with which they are brought into contact. I have further found that when these polymeric hydrazides are incorporated in the form of finely divided solids in tobacco smoke filters, the salts do not exhibit detrimental aging in storage. What is more, when a deposit of finely divided solid polymeric hydrazide is uniformly dispersed throughout a filamentary filtering mass of the type disclosed by Crawford and Stevens, with the particles of the polymer 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 re-

moval 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 of particulate material from the liquid-solid phase of the smoke comprises a gas-pervious supporting mass and a deposit of a finely divided, water-insoluble, solid polymeric hydrazide. In a preferred embodiment of the invention, the polymeric hydrazide is selected from the group consisting of polyacrylylhydrazide and polymethacrylylhydrazide.

In what I have found to be a most advantageous embodiment, a tobacco smoke filter is made up of an elongated cylindrical mass of cellulose acetate filaments, a uniformly dispersed deposit of the finely divided polymeric hydrazide carried by and on the filaments, and an annular paper wrapper encircling the filament mass, the filaments being in the aggregate substantially parallel to the longitudinal axis of the mass and to each other, but substantially all of the individual filaments each being provided with short crimped portions disposed in diverging and converging relationship to the main filament axis, the filaments of the mass being coextensive therewith, and a plurality of the filaments 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. Preferably 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 polymeric hydrazide in the amount of about 5% to 60% by weight of the filter.

Polymeric hydrazides suitable for the invention are those having sufficient molecular size to provide water-insoluble material of low vapor pressure, that is to say, the polymers will always have a molecular weight of at least 1000. While I prefer that the polymers be in the form of dry solids, viscous low polymers may be more suitable in certain cases. The polymers should contain a large number of free hydrazide groups readily available for reaction with aldehyde gases. I believe that a suitable polymer should contain, theoretically at least, a minimum of for example, one hydrazide group for each two monomeric units of the polymer. However, some polymeric hydrazides containing as little as one hydrazide group per five monomeric units will still be operative. Any commercial grade polymeric hydrazide which meets these requirements should be satisfactory for the purpose of the invention. Any suitable alcohol ester of polyacrylic or polymethacrylic acid, preferably an ester of butyl or lower alcohol, may be used for preparation of polyacrylic or polymethacrylic hydrazides. The method by which the polymer is obtained is of no importance, and the polymers may be synthesized by any suitable conventional procedures such for instance as those described in the examples below.

As the pervious supporting mass I prefer to use a mass of fibers in which the fibers are disposed to provide minute channels for smoke through the mass. The invention finds greatest utility when the supporting mass of fibers is elongated and the fibers are in the aggregate substantially parallel to each other and to the longitudinal axis of the mass. Such will be the condition of the fibers when a segment of a continuous filament tow is used as the pervious support. It will be apparent, however, that the invention will be useful with other types of fibrous masses, e. g. conventional forms such as wads, or for example, bats interleaved with paper and rolled into a convoluted configuration. Cellulose acetate and other synthetic thermoplastic fibers will be particularly useful where the fiber mass comprises a segment of a crimped tow and where the fibers are bonded at spaced intervals to contiguous fibers. It is preferred to use for filter preparation in accordance with the present invention a crimped tow of 4,000 to 35,000 plasticizable thermoplastic filaments, the filaments being of 16 to 3 denier and having about 4 to 10 crimps per inch. 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. However, fibers of regenerated cellulose, asbestos, cotton, nylon, polyamides, polyesters, and other known fibrous materials may be employed as well as suitable non-fibrous pervious masses. For instance, the polymeric hydrazides disclosed herein may be added in solid finely divided form to filtering masses formed either of paper (e. g. paper pulp, crepe paper, or filter paper), of granular material, or of other conventional pervious substances. In fact the invention will find utility where the supporting mass comprises, for instance, only an annular wrapper within which the additive is contained.

Filters of the invention are advantageously prepared by dispersing finely divided polymeric hydrazide on the material of the support while the latter is in a spread or open condition and subsequently forming a pervious mass by shaping the supporting material carrying the deposit. For example, the finely divided solid is added to the surfaces of fibers prior to fabrication of the fibers into a filter cartridge, e. g. a tip for a cigarette. Various methods are suitable for carrying out the addition. When the fibers are in the form of a continuous strand, e. g. a tow, the polymeric hydrazide, may be sprayed on as a liquid suspension or it may be dusted on as a solid powder. The liquid should be a non-solvent for the polymer but may be a softener or plasticizer for the material of the support. However, other suitable methods may involve dissolving the polymeric hydrazide in a volatile solvent, applying the solution to the support, and evaporating the solvent.

Application of either spray or dust 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. The spray is directed onto the fibers and adjusted to form droplets somewhat larger than in a mist so that each fiber theroetically will carry small sprayed deposits of the polymeric hydrazide suspension or solution. The liquid vehicle subsequently is removed by evaporation.

When the liquid suspension technique is employed, it has been found that inclusion of a hygroscopic agent such as for example glycerine, sorbitol, propylene glycol, and other hygroscopic materials in the suspension aids in preventing the finely divided solid material from dusting out of the finished filler. In other words, the hygroscopic agent does not allow the 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 polymeric hydrazide, the hygroscopic agent can be sprayed on the fibrous material either before or after dusting and in either case will help 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. Actually 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, another method involves applying the polymer as a slurry in a liquid comprising a non-volatile plasticizer for the fiber plus an inert diluent. Another method is to apply the material to the fibers electrostically, 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 polymeric hydrazide. 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 dry powder 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 polymer 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 a dispenser adjacent which the tow passes. The polymeric hydrazide may be added before, simultaneously with, or after the plasticizer, preferably after.

The polymer of course 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. The exact size of the particle does not appear to be critical. While it is generally better that the material should be capable of passing through a 200 mesh screen, a more coarse deposit may be effective. I belive that generally most of the particles should have diameters within the range of 1.0 to 30 microns. 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. Where fibers of diameters in the range of 30 to 60 microns are used, no substantial number of particles should be as large as twice the filament diameter or as small as one-tenth the filament diameter. A good particle size range is one within the limit of 1.0 micron to 10 microns, but this may differ for different size fibers and different types of supporting masses.

The amount of polymeric hydrazide required in a cigarette filter or other tobacco smoke filter to remove the gaseous aldehydes in the smoke will depend mainly on the particular polymer employed, its physical form, and the amount of aldehyde which must be removed in order to make the smoke less irritating to the smoker. As reported by Toney ("Gaseous Phase of Cigarette Smoke, Isolation and Analysis of Total Aldehydes," Anal. Chem. 27, 1788, 1955) most unfiltered cigarettes manufactured in the U. S. have been found to produce about 1 mg. of acetaldehyde per cigarette during normal smoking. Tests have been made with these cigarettes containing filters of cotton and of cellulose acetate tow to which had been added various concentrations of various polymer hydrazides. These tests have shown that at least a 5 molar excess of these polymers 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 polymer 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 80%, preferably about 10% to about 50% by weight of the entire filter mass, particularly when based on the weight of a 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.

In the most advantageous form of the present invention wherein polymeric hydrazide is carried on the surfaces of crimped, parallel, filaments comprising a segment of a continuous filament tow, the polymer provides for removal of gaseous aldehydes and for increased tar and nicotine removed by infringement without a corresponding pressured drop increase. The more important structural factors found in this 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 polymer. Obviously no plasticizer should be employed which has a detrimental action on the activity of the particles.

(3) That substantially all the polymeric hydrazide particles be carried on the surfaces of the filaments, supported by the filaments, and substantially immobile with respect thereto. When the polymer is to be added as a dry solid, e. g. a dust, this structure is best accomplished by first softening 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 textile type filaments of e. g. 20–60 microns filament diameter are employed, and 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 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.—Preparation of polymethacrylyl hydrazide

75 g. of polymerized methylmethacrylate and 375 g. of 95% hydrazine (aqueous solution) were placed in a 2 liter flask. The mixture was heated at about 95° C. for 11 hours, at the end of which time, solution of the polymethylmethacrylate was substantially complete. Hydrazine was distilled from the mixture first at atmospheric pressure and then under slightly reduced pressure. The polymethacrylyl hydrazide residue was then pulled from the flask and cut into small pieces. The pieces were placed in a clean flask and heated for a short time under a vacuum of about 1 mm. of mercury until a brittle material resulted. The brittle polymer was removed from the flask and ground to 20 mesh size in a mechanical grinder. The finely divided polymeric material which resulted was dried for 1.5 hours in a vacuum oven at 40–50° C. The final product appeared to be water insoluble. It weighed 84.5 g. Analysis for nitrogen indicated 22.42% present corresponding to 80% conversion of ester groups to hydrazide groups.

Example 2.—Preparation of polymethacrylyl hydrazide

In a 200 ml. flask a mixture was prepared by adding 10 g. of polymethylmethacrylate and 100 g. of 95% hydrazine (aqueous solution). The flask was fitted with a reflux condenser protected with a tube containing anhy-

drous calcium sulfate and the mixture refluxed for a total of 7 hours. After about 2 hours heating, the mixture appeared homogeneous. Excess hydrazine, water, and methanol were removed from the reaction mixture under reduced pressure. The polymeric product was cut into small pieces and dried in a vacuum desiccator over phosphorous pentoxide under reduced pressure. The dried pieces were ground into a fine powder. Analysis showed the conversion of approximately two-thirds of the ester groups to hydrazine groups, the product containing about 18.9% nitrogen. The proportion of ester groups probably could have been decreased by using a longer reflux period or by heating in an autoclave to higher reaction temperatures.

Example 3.—Preparation of polymethacrylyl hydrazide

The procedure of Example 2 was repeated using polyethylmethacrylate instead of polymethylmethacrylate. Upon refluxing off of excess hydrazine, polymethacrylyl hydrazide was obtained.

Example 4.—Polymethacrylyl hydrazide powder supported on cellulose acetate tow

A cellulose acetate tow of 8 denier per filament, and a total of 8,880 filaments was slowly pulled over a series of rollers which spread out the filaments of the tow to a total width of about 12 inches. While the tow was in this spread condition, it was dusted with the powdered hydrazide polymer prepared as described in Example 1. After the spreading and dusting treatment, the tow was pulled back to its original shape and fed through a conventional cigarette make-up machine, i. e. a garniture which wrapped the tow with paper and cut the wrapped tow into cylindrical rods of about 8.1 mm. diameter and 71 mm. length. The rods contained 22 parts of hydrazide and 78 parts cellulose acetate. The rods were severed into 13 mm. length filter tips. These were attached by means of adhesive tape to king-size cigarettes of a standard brand retailed in the U. S. which had been shortened by 13 mm. Five 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, vol. 28, pages 836–9 (1936). The gaseous phase of the smoke was collected and analyzed for acetaldehyde. Five cigarettes without filters, but having the same total length as the filtered cigarettes, were smoked and the gaseous phase analyzed in the same manner. Five additional cigarettes of the same kind were shortened by 13 mm. and fitted with 13 mm. filter tips of the same tow of cellulose acetate fibers without the hydrazide polymer. The last cigarettes were also smoked and the gaseous phase resulting was analyzed for aldehydes in the same way. The experimental data recorded was as follows:

TABLE I

	Milligrams of aldehydes found in smoke
Smoke collected from 5 unfiltered cigarettes (50 mm. of the cigarette smoked)	10
Smoke collected from 5 filtered cigarettes, filter of cellulose acetate (50 mm. of the cigarette smoked)	10
Smoke collected from 5 filtered cigarettes, filter of 78 parts cellulose acetate and 22 parts hydrazide polymer (50 mm. of the cigarette smoked)	7

The values listed above indicate that the filter of cellulose acetate fibers containing no hydrazide polymer removed none of the aldehydes from the smoke stream while the filter containing 22% hydrazide polymer removed 30% of the aldehydes from the smoke stream. The filters containing 22 parts hydrazide had an increased pressure drop (compared with the plain acetate filters) of only about 5% and removed substantial quantities of nicotine and tar.

Example 5.—Preparation of polyacrylyl hydrazide

In a 200 ml. flask a mixture was prepared by adding 10 g. of polymethacrylate and 100 g. of 95% hydrazine (aqueous solution). The flask was fitted with a reflux condenser protected with a tube containing anhydrous calcium sulfate and the mixture was refluxed for a total of 7 hours at about 95° C. Excess hydrazine, water and methanol were removed from the reaction mixture under reduced pressure to give the polymeric product. The product was cut into small pieces and freed of the last traces of hydrazine by drying in a vacuum desiccator over phosphorous pentoxide. The small pieces of the product were ground into a granular material which passed through a 20 mesh screen.

Example 6.—Polyacrylyl hydrazide supported on cellulose acetate tow

Filters containing polyacrylyl hydrazide were prepared by the method described in Example 4 using the finely divided polyacrylyl hydrazide prepared as described in Example 5. Tests were conducted to determine the filtration efficiency of these filters by the method described in Example 4. The resulting data showed that polyacrylyl hydrazide was equally as effective in removing aldehydes from the smoke screen as the polymethacrylyl hydrazide.

I claim:

1. A tobacco smoke filter comprising a supporting mass and a deposit carried by said mass of a water-insoluble polymeric hydrazide.

2. A fibrous tobacco smoke filter capable of removing gaseous aldehydes from tobacco smoke comprising a supporting mass of fibers, the fibers being disposed to provide minute passages for smoke through the mass, and a dispersed deposit of a water-insoluble, finely divided, polymeric hydrazide.

3. A filter as defined in claim 2 wherein the polymeric hydrazide is in the form of a dry finely divided solid.

4. A tobacco smoke filter as defined in claim 2 wherein the polymeric hydrazide is polymethacrylyl hydrazide.

5. A tobacco smoke filter as defined in claim 2 wherein the polymeric hydrazide is polyacrylyl hydrazide.

6. A tobacco smoke filter as defined in claim 7 wherein the polymeric hydrazide contains an average of at least 1 hydrazide group to every ester group.

7. A tobacco smoke filter as defined in claim 2 wherein the deposit comprises from 10 to 60% by weight of the filter.

8. A tobacco smoke filter as defined in claim 2 wherein the supporting mass comprises an elongated cylindrical mass of crimped thermoplastic fibers which are coextensive and, in the aggregate, substantially parallel to each other and to the longitudinal axis of the mass.

9. A tobacco smoke filter as defined in claim 8 wherein the fibers are bonded to adjacent fibers at spaced intervals.

10. A filter as defined in claim 9 wherein the fibers are thermoplastic textile fibers of a size within the range of 2 to 20 denier and the bonds are surface solvation bonds.

11. A filter as defined in claim 10 wherein the fibers are cellulose acetate and the polymeric hydrazide is polymethacrylyl hydrazide.

12. A filter as defined in claim 10 wherein the fibers are cellulose acetate and the polymeric hydrazide is polyacrylyl hydrazide.

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