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TOBACCO SMOKE FILTER

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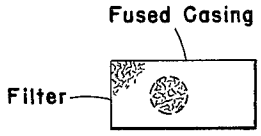


Fig. 1.

Fig. 2.

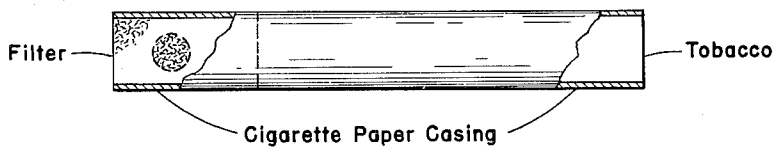


Fig. 3.

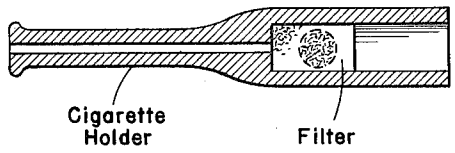
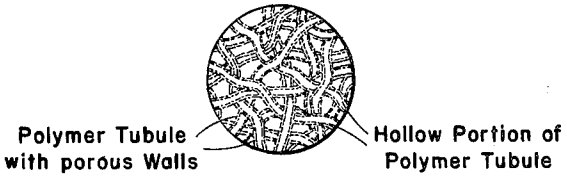


Fig. 4.



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TOBACCO SMOKE FILTER

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This invention relates to a filter and, more particularly, to a filter for purifying fluids such as tobacco smoke.

While the device of this invention is susceptible of a wide variety of filtering applications, as will be readily apparent to those skilled in the art, it will be described principally with reference to its application to a cigarette filter, because that particular use is particularly illustrative of the nature and of the utility of the device.

The construction of cigarette filters and the selection of filter materials therefore has been subject to a considerable amount of study. In general, using conventional filter materials, the construction of such filters has necessarily been a compromise among several mutually antagonistic properties. Thus an ideal filter should remove a large proportion of the tars and nicotine naturally occurring in tobacco smoke. On the other hand, filters that are effective in this respect tend to be dense and in use, become progressively resistant to the passage of gases therethrough, resulting in a cigarette that can be "puffed" only with difficulty. Also, filters that are effective to remove a high percentage of tar and nicotine also tend to be effective in removing other components of the smoke-bearing vapor stream, particularly by absorption or adsorption of water vapor. This, in turn, makes the smoke dry and harsh, adversely affecting the flavor of the smoke so that the more effective filters are unacceptable to the consumer. Filter effectiveness is, therefore, sacrificed in order to make a cigarette of acceptable smoking qualities.

An object of this invention is to provide an improved tobacco smoke filter. Another object is to provide a filter medium having low resistance to the passage of vapors. Still another object is to provide a filtration medium for vapor and gas streams which results in a minimum of moisture loss from the filtered gases. Other objects and advantages will become apparent from the following more complete description and claims and attached drawing diagrammatically illustrating on an enlarged scale the invention and in which:

FIG. 1 is a longitudinal view of a filter of the instant invention, the casing of the filter consisting of a surface area of a mass of hollow and porous polymer tubules which have been fused to seal the pores in accordance with one embodiment of the invention;

FIG. 2 is a partially sectional, longitudinal view of a cigarette containing a filter of the instant invention. The casing of the filter and the tobacco portion of the cigarette are enclosed in a cigarette paper casing in accordance with a further embodiment of the invention;

FIG. 3 is a longitudinal sectional view of a cigarette holder containing and encasing a filter of the instant invention in accordance with another embodiment of the invention; and

FIG. 4 is an enlarged view of that portion of the filter in the areas circularly enclosed with the dashed lines of FIGS. 1, 2 and 3, and showing, diagrammatically, hollow polymer tubules having porous walls in accordance with the instant invention.

Broadly, this invention contemplates a novel filter suitable for the purification of tobacco smoke or the like, said filter being composed of a self-supporting micro-porous mass of hollow tubules of a polymer of a monomer selected from the group consisting of aliphatic 1-olefins having less than 6 carbon atoms, said tubules being fused together at their points of contact.

This invention also contemplates a filtering medium for purifying tobacco smoke which comprises a self-sustaining micro-porous mass consisting essentially of minute, porous tubules of a polymer of a monomer selected from the group consisting of aliphatic 1-olefins having less than 6 carbon atoms, said tubules being fused together at their points of contact.

This invention further contemplates a filter tip cigarette comprising a housing open at its opposite ends, tobacco in one end of said housing and a filter in the opposite end of said housing, said filter comprising a mass of hollow tubules of a polymer, said tubules being joined together at their points of contact to form, intermediate said points of contact, tortuous paths for the passage of tobacco smoke axially of said housing, said hollow tubules having porous walls, the pores in said walls connecting the interiors of said tubules with said tortuous paths, said housing adjacent said compacted mass being substantially impervious to air.

Methods for making porous tubes of polyolefins by encasing individual cellulosic fibers in polyolefin to form a tube or sleeve around individual fibers and subsequently leaching to remove the cellulose fiber, are more fully described and claimed in copending application Serial No. 852,844, filed November 13, 1959, now Patent 3,121,698.

In accordance with the teaching of the above mentioned copending application, fibers or filaments of cellulosic material are encased in tubes, sleeves or shells of polyolefin plastic polymerized in situ, preferably by the use of what is known as an organometallic-transition metal catalyst system. The components of such a catalyst system, as will be understood by those skilled in the polymer art, react when mixed together to produce a substance or substances highly active as a polymerization initiator for the low molecular weight aliphatic 1-olefins.

Any of the aliphatic 1-olefins having less than 6 carbon atoms may be employed in the manufacture of filters according to the present invention. These include the simplest 1-olefins such as ethylene, propylene, butene-1 and the like and also di-olefins such as butadiene-1,3 and isoprene. These 1-olefins may be used in the form of homopolymers, or mixtures of them may be polymerized together to form various copolymers. In addition, other compounds which are known to copolymerize with these 1-olefins to form useful products, may be employed in combination therewith.

For purposes of the instant invention we prefer to use ethylene or propylene which have the outstanding advantages of being gases at ordinary temperatures, of being relatively inexpensive and available in large quantities, and of producing polymers of high molecular weight having very desirable properties for filtration purposes.

As disclosed in the aforesaid application, it is important to treat the cellulosic material with one of the components of the catalyst system before the components have been mixed together long enough to complete their reaction with each other. Some reaction appears to take place between this catalyst component and the cellulosic material. The exact nature of this reaction is not known but it is thought to involve either the active hydroxyl groups, or the ether type linkages of the cellulose. Usually, the other component of the catalyst system is then added and the treated cellulosic material is brought into contact with the olefin under proper conditions to form a shell or sleeve of the polymer directly on the surface of the cellulosic material. When the cellulosic material is treated with the components of the catalyst system in

this manner, active catalyst sites are formed on the cellulose surfaces so that the polymer chains grow on and from these sites as the polymerization reaction proceeds. The use of catalyst in excess of the amount which will form active sites on the cellulosic material produces a different kind of product and should be avoided.

The cellulosic material may be treated with each of the components of the catalyst system in separate steps or the components may be mixed before treatment. However, if the components are mixed and the cellulosic material is treated in a single step, care must be exercised. If the catalyst components are mixed together for a sufficient time (for example, 5 minutes) and then added to the cellulosic material, the polymer that is formed is of a heterogeneous character and most or all of the polymer is in the form of separate pieces which can be readily separated from the cellulosic material by flotation techniques. On the other hand, if the cellulosic material is treated with any one of the catalyst components before this component is fully reacted with the other catalyst component, the polymerization takes place at and on the surface of the cellulosic material building up a shell of any desired thickness on the cellulosic material.

One simple and convenient way of carrying out the treatment is by the slurry method in which the cellulosic material is suspended in a suitable liquid medium such as an organic liquid which does not dissolve or react with either cellulose or the polymer to be formed. The cellulosic material may be treated with one of the catalyst components before or after it is placed in the suspending liquid. The other catalyst component is then brought into contact with the cellulose, or the two catalyst components may even be added to the suspending liquid simultaneously with the cellulosic material. The slurry of catalyst treated cellulosic material in the organic liquid, after the second component of the catalyst has been added, is treated in a closed reaction vessel with the monomer by feeding the monomer into the vessel at a suitable rate while agitating the slurry. Provisions should be made to control the temperature of the reaction vessel, and the reaction should be carried out under reasonably anhydrous conditions. As polymerization proceeds, the slurry becomes thicker and reaction is stopped at any desired stage depending upon how much of the polymer is to be formed. The slurry can then be removed from the reaction vessel and simply pressed or filtered to remove the free organic liquid and then washed in water, methanol or other materials.

This process may be applied to a variety of different cellulosic materials, including not only natural cellulose such as wood, wood fibers, sawdust, wood-flour, various kinds of paper pulp, bagasse, cotton, in the form of batting, linters or filaments, line, hemp and the like, but also regenerated cellulose such as viscose, cuprammonium or cellulose acetate rayons and cellulose compounds such as cellulose acetate and the like. For purposes of the instant invention, as will be pointed out hereinafter, it is preferred to employ natural cellulose fibers.

Catalyst systems which are useful include any two or more component systems which, mixed together, react to form a material that initiates the polymerization of the 1-olefins, and which have at least one component that reacts with or becomes fixed in some way on cellulosic materials when brought in contact therewith. In general, we have found that two component systems which are particularly suitable are those in which one component is an organometallic reagent such as an aryl of one of the metals lithium, sodium, potassium, magnesium, calcium, zinc, cadmium, boron, or aluminum, and the other component is a transition metal compound such as a halide or ester of titanium, zirconium, vanadium or chronium. Other similar catalyst systems can be used as will be apparent to those skilled in the art of producing polyolefins.

It is important, when using the catalyst systems noted above, to conduct the polymerization under substantially oxygen free and water free conditions since the activity of the catalyst system is impaired by the presence of any substantial amount of oxygen or water. When treating cellulosic materials, however, more water than usual can be tolerated in the system. A small fraction of 1% of moisture retained within the cellulose does not appear to interfere with the reaction and may in fact have a beneficial effect.

The polymerization reaction may be carried out at atmospheric pressure, or higher pressures if desired, and over a wide range of temperature. Ordinarily, the polymerization proceeds rapidly at atmospheric pressure and at a temperature between about 20° C. and about 100° C. The amount of polymer formed will vary with the time of the polymerization reaction, the particular catalyst used and the particular monomer or monomers being polymerized. For purposes of the instant invention, the amount of polymer formed on the cellulose fibers should be sufficient so that, after the cellulose fibers are removed, a self-sustaining, porous shell of polymer will remain. A polymer content of not substantially less than 5% and not substantially greater than 75%, based on the total weight of the cellulose fibers and polymer, has been found to be acceptable. A polymer content of not substantially less than 10% and not substantially greater than 50% is preferred.

The cellulose is treated, for purposes of the present invention, in the form of fibers preferably ranging from about 30 microns to 7,000 or 8,000 microns in length and around 7 to 55 microns in diameter. The individual fibers can be substantially encased in individual shells of the polymer without appreciable agglomeration of the fibers. At the end of the polymerization reaction, the product is composed of fibers of about the original size, which are free flowing. This free-flowing property facilitates the molding of the polymer-encased fiber into the shape required for the finished filter. Simple heating without pressure fuses the particles together to form a porous, self-sustaining article. To increase the density and reduce the pore size, heating to fuse the particles may be accompanied by moderate pressure. Temperatures as high as or somewhat above the crystalline melting point of the polymer coating may be employed. In the case of cellulose fibers coated with polyethylene, a heating temperature as high as 310° F. or even higher may be employed, while with products coated with polypropylene, other polyolefins or copolymers, the temperature of heating may be somewhat higher or lower depending on the crystalline melting point of the polymer coating.

After the polymer-coated cellulose fiber is molded to the desired shape it is subjected to a liquid, such as strong sulfuric acid solution (preferably about 70% H_2SO_4) which dissolves out the cellulose, or most of it, leaving porous, hollow shells or tubules of the polyolefin fused together in the cast or molded state. Based on microscopic and other observations of the manner in which the leaching out of the cellulose proceeds while leaving the shell intact, we believe that the acid penetrates the walls of the tubules, sleeves or shells. It therefore appears that the tubule sleeve or shell is not a completely continuous film, but rather possesses discontinuities through which the acid is capable of penetrating. When the cellulose has been removed, these discontinuities presumably appear as pores in the walls of the remaining hollow tubes, sleeves or shells.

Thus, it is believed that two pore structures are present in the formed filter, namely the pores formed between the fused shells or tubes and the pores of the shell walls. This pore structure, which for purposes of convenience, may be referred to as a pore structure within a pore structure, is believed to account for the increased filtering effectiveness, coupled with lowered resistance to passage of gases and vapors through the filter, that we have observed when comparing the filters of this invention with con-

ventional tobacco smoke filters. The reduction of resistance to passage of gases and vapors is of considerable importance in cigarette filters since it improves the "draw" of the cigarette.

Relatively porous cast or molded articles of substantially pure polyolefin can also be produced by dissolving out some or all of the cellulose before fusing. In this case the molding powder is composed of a mass of hollow shells or tubes of polymer which are capable of forming cast or molded articles of varying degrees of porosity depending upon the amount of heat and pressure applied during fusing. In this mode of operation, however, there is a tendency for the tubules to collapse during the molding operation. It is, therefore, generally preferred to first mold the polymer-encased cellulose to a self-sustaining shape before extracting the cellulose. Strong sulfuric acid, caustic soda, cuprammonium solution, or other substances that are known to dissolve or solubilize cellulose may be used to remove cellulose from the product either before or after molding.

The molded product is enclosed in a tube or housing having walls substantially impervious to air. The tube or housing is open at its opposite ends. In use the smoke to be filtered is drawn into one end of the filter and is discharged from the opposite end. The tube or housing may be formed from paper, cork sheet, or any other material impervious to air which is suitable for the particular filter use.

In selecting a material for the housing consideration should, of course, be given to the manner in which the filter is to be used. If the end of the filter is to be placed in the mouth as in most filter cigarettes, the housing material should be, among other things, nontoxic, tasteless and resistant to moisture. Irrespective of the material employed, the housing should envelop the molded filtering medium in such a manner that axial air passages are not formed between the housing and the filtering medium. Rather than forming the housing or cover from a separate material, the sides of the filter may be coated with a material which is substantially air impervious or the surface may be treated to close the surface pores for example by fusing the surface to seal the pores. In one embodiment of the invention, the housing or cover may consist of a closely-fitting chamber recessed in a cigarette holder, pipe stem, or the like.

It has been found that filters produced in accordance with the instant invention have outstanding and unusual properties as filter media. These properties are no doubt at least partially attributable to the physical structure of the material. The microtubular form of the polymer provides a multiplicity of very fine passages, with a high proportion of void space. It is not difficult, under the instant invention, to form a filter having a 95% void content which has sufficient rigidity to withstand handling and is capable of supporting reasonable loads such as the loads normally encountered in machine production. As has been noted above, the vast number of fine passages, coupled with the high void content, provides a filter material which is highly effective and yet not unduly resistant to the passage of gases or vapors. Also, the surface area of the polymer in this form is so great that surface phenomena play a significant role. As compared to conventional filter material made of cellulose fibers, the material according to the present invention is composed of fiber-shaped, tubules, each of which is approximately of the dimensions of a cellulose fiber but, instead of being solid, is a hollow tube having porous walls. This configuration increases the surface area and void space enormously as compared to filters made of bundled cellulose fibers. Thus, adsorption takes place to a very considerable extent, where impurities in the material to be filtered are of such a nature as to be adsorbable on an olefin polymer surface. The porous walled tubules form numerous traps for materials to be removed. The filter of the instant invention is impervious to water. However, while impervious to water, it is not impervious to water vapor. Thus, the water vapor content of the cigarette smoke is not substantially reduced in passing through the filter. This is of considerable advantage since it permits the filter to be used without making the smoke dry and harsh.

The inertness of the polyolefin materials to water leads to still another important advantage. When a conventional cellulosic filter becomes moistened by contact with saliva, as occasionally happens, the moistened fibers swell, impeding the passage of smoke through the filter and causing the cigarette to draw with difficulty. In addition to making smoking more difficult, when the draw is increased channels tend to form through the filter which reduce the filter's effectiveness. The filter of the present invention neither wets nor swells, and difficulties of this nature are not encountered.

In order to illustrate more fully the nature of this invention and the manner of practicing the same, the following example is presented.

Example

A polyethylene-encapsulated cellulose composition was prepared as follows:

Twenty-four grams of wood cellulose floc were dispersed in 1400 cc. of toluene under dry conditions. The air in the vessel was replaced with nitrogen and 0.3016 mol of $TiCl_4$ were added to the dispersion. This mixture was allowed to react one-half hour at room temperature to bring about the titanation of the cellulose, after which 0.075 mol of methylmagnesium bromide were added. The temperature was raised to and maintained at 50–60° C., while a stream of gaseous ethylene was passed through the mixture. The color changed from orange through dark green to almost black. The flow of ethylene was continued for six hours, until the rate of absorption became negligible. The amount of ethylene absorbed was approximately equal to the amount of cellulose floc in the reaction vessel.

The solution was cooled and diluted by adding an equal volume of methanol, and the cooled solution was filtered and washed with additional methanol. The filter cake, after drying, was a white, powdery cellulose-polyethylene composition containing approximately 50% polyethylene.

This composition was fabricated into a rod by heat-fusing in a glass mold. A glass tubing approximately six inches long was closed at one end and filled with the cellulose-polyethylene composition, with light tamping. The glass tube was then immersed for three minutes in an oil bath maintained at 150° C., and then withdrawn and cooled. The fused rod of cellulose-polethylene composition thus formed shrank slightly in the fusing, and could easily be removed from the tube. A tube of 8–9 mm. inside diameter was found to give a sintered rod of approximately the proper diameter for use as a cigarette filter. The rod was then treated twice with 70% sulfuric acid to extract the cellulose and washed repeatedly with water to remove the acid. The rod at this stage consisted of a mass of hollow, porous tubules of polyethylene, sintered together at the points where they touched. After drying, the rod was cut into lengths corresponding to the length of a typical commercial cigarette filter (17 mm.).

The efficacy of the filters so produced was tested by substituting such filters for the original filters in commercial filter cigarettes and running comparative smoking tests. The smoking apparatus was made from glass tubing and protected from air drafts by a glass funnel clipped over the cigarette receiver, which was a short piece of glass tubing. The receiver was connected with rubber tubing to a glass stopcock and thence to an aspirator flask. The test was carried out by inserting a cigarette in the receiver, lighting it, and allowing it to burn down close to the holder, the necessary suction being provided by the aspirator, which was kept running at a constant rate. When the cigarette was consumed, the aspirator was turned off, the cigarette butt was removed from the re-

ceiver and the filter was removed from the butt. The filter was then dropped into a test tube containing 15 ml. of benzene and the test tube was stoppered.

After twenty-four hours extraction in the test tube, during which the tube was shaken several times to speed extraction of tars, the solution was shaken again to ensure thorough mixing and the color intensity of the solution was measured with a spectrophotometer at various wave lengths.

The entire procedure was carried out repeatedly, and the color intensity (indicated by greater light absorption) was invariably about 25% higher in extracts of the filters of this invention, as opposed to those of the commercial filters. This indicates a substantial improvement in the efficiency of the filters of this invention over commercial filters in the removal of tars from the smoke stream. It was also noted that after extraction as described, the commercial filters were almost white, while the originally white filter according to this invention remained distinctly brown, indicating the stubborn retention by the filter according to the invention of additional amounts of tar over and above that removed by the solution. Seven commercial brands of filter cigarettes were compared with the filters according to this invention, with substantially the same results in all cases; the filter according to this invention trapped about 25% more tars as indicated by solution color intensity, plus a further increment of indeterminate magnitude, indicated by the residual color in the extracted filter. Organoleptic tests of the filters of the instant invention revealed that the smoking qualities of the cigarettes made with filters of this invention were, in general, as good as those of commercial cigarettes, and frequently better.

The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention, in the use of such terms and expressions, of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed.

What is claimed is:

1. A filter suitable for filtering tobacco smoke comprising a mass of hollow tubules of a polymer of a monomer selected from the group consisting of aliphatic 1-olefins having less than 6 carbon atoms, said tubules being randomly oriented and in contact and forming intermediate their points of contact, tortuous paths for the passage of smoke through said mass, said hollow tubules having porous walls, the pores in said walls connecting the interiors of said tubules with said tortuous paths, and a casing open at its opposite ends surrounding said mass, said casing intermediate said opposite ends being substantially impervious to air.

2. A filter suitable for filtering tobacco smoke comprising a self-supporting mass of hollow tubules of a polymer of a monomer selected from the group consisting of aliphatic 1-olefins having less than 6 carbon atoms, said tubules being randomly oriented and fused together at their points of contact to form intermediate said points of contact a pore structure through said mass, said hollow tubules having porous walls, the pores in said walls connecting the interiors of said tubules with said pore structure and a casing open at its opposite ends surrounding said mass, said casing intermediate said opposite ends being substantially impervious to air.

3. A filter as recited in claim **2** in which said monomer is ethylene.

4. A filter as recited in claim **2** in which said monomer is propylene.

5. A filter as recited in claim **2**, wherein said casing consists essentially of an open-ended tube of impervious sheet material enveloping said mass of tubules.

6. A filter as recited in claim **2**, wherein said casing consists essentially of an outer layer of pore-sealing material on the sides of said filter.

7. A filter as recited in claim **2**, wherein said casing consists essentially of a surface area of said mass of tubules, said surface area being fused to seal the pores thereof.

8. A filter as recited in claim **2**, wherein said casing consists essentially of a hollow, nonporous tube adapted to fit snugly around said mass of hollow, porous tubules.

9. A filter tip cigarette comprising a housing open at its opposite ends, tobacco in one end of said housing and a filter in the opposite end of said housing, said filter comprising a mass of hollow tubules of a polymer, said tubules being randomly oriented and joined together at their points of contact to form, intermediate said points of contact, tortuous paths for the passage of smoke through said mass axially of said housing, said hollow tubules having porous walls, the pores in said walls connecting the interiors of said tubules with said tortuous paths, said housing adjacent said compacted mass being substantially impervious to air.

10. A filter tip cigarette as recited in claim **9** in which said polymer is a polymer of a monomer selected from the group consisting of aliphatic 1-olefins having less than 6 carbon atoms.

11. A filter tip cigarette as recited in claim **10** in which said monomer is ethylene.

12. A filter tip cigarette as recited in claim **10** in which said monomer is propylene.

13. A filter for use with a filter casing having open ends and walls that are substantially impervious to air, said filter comprising a mass of hollow tubules of a polymer, said tubules being randomly oriented and joined together at their points of contact to form, intermediate said points of contact, tortuous paths for the passage of smoke through said mass axially of said casing, said hollow tubules having porous walls, the pores in said walls connecting the interiors of said tubules with said tortuous paths.

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