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3,285,255

POLYOLEFIN FILTER

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This application is a continuation-in-part of Serial No. 185,825, filed April 9, 1962, now abandoned, in turn a continuation-in-part of Serial No. 65,941, filed October 31, 1960, and Serial No. 143,604, filed October 9, 1961, now U.S. Patent 3,173,426.

This invention relates to a new and improved tobacco smoke filter. In particular, this invention relates to polyolefin tobacco smoke filters containing an aromatic hydroxy-removing agent thereon.

In said Serial Nos. 65,941 and 143,604, we disclosed polyolefin tobacco smoke filters of high tar-removal efficiency as well as simplicity of structure and manufacture thereof. However, in many instances these filters have not been entirely satisfactory in their ability to remove aromatic hydroxy containing compounds such as phenols from tobacco smoke. Therefore, it is believed apparent that it is highly desirable to provide a filter additive for such polyolefin filters which will hold aromatic hydroxy compounds and prevent the inhaling thereof with tobacco smoke. After further investigation we have found such an agent which may be added to polyolefin filters to substantially remove aromatic hydroxy compounds from tobacco smoke.

One object of this invention is to provide a tobacco smoke filter additive for polyolefin filters for removing aromatic hydroxy components from tobacco smoke. Another object is to provide a polyolefin tobacco smoke filter containing therein an agent capable of removing aromatic hydroxy compounds from tobacco smoke. Still another object is to provide an improved polyolefin filter. Other objects will appear hereinafter.

In the broader aspects of our invention these objects are obtained by adding to or incorporating with polyolefin filter material such as that of our U.S. Patent 2,966,157 and the above-mentioned Serial Nos. 65,941 and 143,604 a glycol or like acylate which acts as a solvent for aromatic hydroxy compounds which may be contained in the tobacco smoke. It is known that certain organic ester-type materials may be used in cellulose ester filters as plasticizers and bonding agents. Polyolefin filters because of their heat-sealable nature do not ordinarily require such additives. We have found, however, quite unexpectedly that according to our invention as will be set forth hereinafter high-boiling, non-volatile, non-odorous, water-insoluble organic ester-type materials and certain other materials are highly efficient as the agent for removing aromatic hydroxy compounds from tobacco smoke when added to polyolefin filters. These materials would have been expected to be inefficient on polyolefin tow due to their tendency to not be absorbed by or to exude therefrom. Although we do not wish to be bound by any particular theory as to why these materials function so efficiently in this respect according to our invention, one explanation may be that our ester-type or acylate additives when applied to polyolefin tow exist on the surface of the filaments in a layer or exudate which is at least monomolecular in thickness. Thus, they are not absorbed by the polyolefin filaments to an appreciable degree such as might be expected to inhibit the already good filtration characteristics of the polyolefin tow but are still there once deposited, i.e., remain substantially permanently deposited on and between said filaments. In other words the ester-type materials used according to our in-

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vention function effectively as phenol-removing ingredients by remaining for the most part on or between the surfaces of the filaments of the polyolefin tow.

The substantially completely, that is, almost entirely, water-insoluble organic ester or acylates of our invention have boiling points above and about 200° C. such that they may be easily sprayed at temperatures between 25 and 100° C. They may be divided into the following three classes, viz., (1) monomeric esters prepared by reacting a di-, tri-, or polyhydroxy alcohol with a monocarboxylic acid having from 2 to 12 carbon atoms, (2) monomeric esters prepared by reacting a monohydroxy alcohol with a di-, tri-, or polycarboxylic acid having from 3 to 12 carbon atoms and (3) polymeric esters prepared by reacting a dihydric alcohol with a dicarboxylic monocarboxylic acid having from 3 to 12 carbon atoms.

Illustrative of the di-, tri-, and polyhydroxy compounds of class (1) above are ethylene glycol, di- and poly(ethylene glycols), propylene glycol, di- and poly(propylene glycols), butylene glycol, di- and poly(butylene glycols), glycerol, pentaerythritol, butanediol, hexanetriol, neopentyl glycol, sorbitol, mannitol, glucose, sucrose, alkyl glucosides, inositol and the like. Representative of monocarboxylic acids used in preparing the compounds of group (1) are acetic, propionic, butyric, isobutyric, valeric, hexanoic, heptanoic, 2-ethyl-hexanoic, octanoic and the like. The preferred esters from these compounds are the liquid water-insoluble monocarboxylic acid esters of glycerol, ethylene, and propylene glycol, sucrose and sorbitol containing acyl groups of from 2 to 12 carbon atoms, especially the water-insoluble acetates, propionates, butyrates, isobutyrate, valerates, hexanoates, heptanoates and octanoates of glycerol, ethylene glycol, diethylene glycol, propylene glycol, dipropylene glycol, sucrose and sorbitol. Preferred sucrose esters include the octabutyrate and the mixed sucrose esters containing two types of acyl groups, specifically, sucrose acetate isobutyrate.

Representative of monohydroxy alcohols used in preparing the monomeric esters of class (2) above are the aliphatic monohydroxy alcohols such as methyl, ethyl, propyl and butyl alcohols and the like. Included within these groups of alcohols are di- and polyhydroxy alcohol derivatives which contain only one remaining esterifiable hydroxy group, for example, such compounds as ethylene glycol monomethyl ether, ethylene chlorohydrin, ethylene glycol monoacetate, ethylene cyanohydrin and the like. Aromatic alcohols such as benzyl alcohol and benzyl alcohols containing substituent groups on the benzene ring may also be used to prepare the monomeric esters of said class (2). Representative of di-, tri-, and polycarboxylic acids which may be used in preparing the monomeric esters of said group (2) are malonic, succinic, glutaric, adipic, sebacic, itaconic, diglycollic, maleic, phthalic, isophthalic, citric, trimellitic, pyromellitic and the like, especially aliphatic alcohol esters of phthalic, adipic and citric acid wherein the number of carbon atoms in the alcohol ranges from 1 to 8 such as diethyl phthalate, dibutyl phthalate, dioctyl phthalate, triethyl citrate, tributyl citrate and dioctyl adipate.

Illustrative of the dihydric alcohols which may be used in preparing the polymeric esters of class (3) above are simple and polymeric ethylene, propylene and butylene glycol. Typical of the dicarboxylic acids which may be used in preparing said polymeric esters are malonic, succinic, glutaric, adipic, sebacic, itaconic, diglycollic, maleic, phthalic and isophthalic acids. Preferred polymeric esters of said class (3) are esters prepared from ethylene and propylene glycol and phthalic or adipic acid. The molecular weight of these polymeric esters of said class (3) should be of sufficient magnitude that the final product is non-volatile, non-odorous, water-insoluble and

sprayable at temperatures ranging from about room temperature to about 100° C.

Although it is preferred that the solvent glycol acylate additives of this invention be sprayed on the filter material, other suitable methods of applying additives to the polyolefin filters may be used. A description of spray methods may be found in Touey and Kiefer Serial No. 807,003, now U.S. Patent 3,033,212.

The amount of ester-type organic compound which may be added to the polyolefin filter material according to our invention should not be less than 4 percent and not greater than 10 percent by weight of the total weight of polyolefin material and additive, preferably about 8 percent.

The liquid ester can be added to the polyolefin material at any convenient stage in the manufacture of the filter. Thus, the spread-out filter material can be dipped into a bath of the ester or a bath of the ester dissolved in a volatile solvent, dried and compacted back together again into the form of a rod or other filter shape. Another method is to apply the ester to the opened-out material at a calender roll in the manner a paper sheet is treated with a sizing agent on a paper machine. A very convenient method is to spray or wick the ester onto the opened-out polyolefin material just prior to its compaction into the form of a filter rod. Still another method is to incorporate the ester in the polyolefin material before it is melt spun.

Since the structure of polyolefin tobacco smoke filters is known to the art, for example, as in the above-mentioned U.S. Patent 2,966,157 and in Serial No. 65,941 and 143,604 and since the filters of the present invention may be of the same or usual shapes and configurations, it is unnecessary to include with the present specification a drawing of such structure.

For a further understanding of my invention reference will now be made to the following examples for illustrating certain preferred embodiments. In these examples the method used for determining phenol in tobacco smoke was that described by C. H. Rayburn, W. R. Harlan and H. R. Hanmer in *Analytical Chemistry*, 25, 1419 (1953). Percent refers to percent by weight except where otherwise indicated.

Example I

A continuous crimped textile tow of polypropylene fibers of 1 denier per filament and containing approximately 28 crimps per inch was spread out to a width of 12 in. and then cut into 10-ft. lengths. By means of a spray gun both sides of each of these spread-out samples were uniformly sprayed with one of the materials listed in Table 1 which follows until the weight increase of the samples indicated between 7 percent and 9 percent of the material had been added. During this operation the temperature of the spray gun was held at 100° C. to maintain a highly fluid sprayable liquid in all of the cases. After addition of the organic liquid, the sample was compacted into the form of a bundle of continuous filaments 10 ft. long. It was then fed into the garniture of a cigarette filter rod-making assembly which paper wrapped it into the form of a cylinder rod 10 ft. in length and 25.4 mm. in circumference. The paper wrapping was 0.045 in. thick. The rod was then cut into filter tip lengths of 15 mm. and these were placed on standard 85 mm. (king-size) non-filter cigarettes which had been shortened by 15 mm. to compensate for the length of the filter. The cigarettes were smoked on an automatic smoking machine similar in design and operation to the one described by Bradford, Harlan, and Hanmer in *Ind. Eng. Chemistry*, vol. 28, pp. 836-839 (1936). The smoke was collected in an empty 300-ml. Kjeldahl flask maintained at -20° C. Two small traps above the collection flask and containing glass wool wet with methanol collected the residual smoke which did not settle in the flasks. Forty filter

cigarettes were smoked for each type of ester listed. In addition, 40 non-filter cigarettes which were not shortened by 15 mm. and 40 cigarettes containing the polyolefin filter without a plasticizer were smoked to represent the control cigarettes. In each run a 35-ml. puff of 2 seconds' duration was taken at the rate of 1 puff per minute until a 55-mm. portion of the cigarette was consumed leaving a 30-mm. butt.

After each run of 40 cigarettes was completed, the smoke was allowed to settle in the flask for 30 minutes. Then the contents of the small traps were rinsed into the collection flask using a mixture of 95 percent methylene chloride and 5 percent methanol (v./v.). The resulting solution (100 ml.) of smoke was divided into two equal portions. One half was analyzed to ascertain the amount of dissolved smoke ("tars") in the sample. This was accomplished by evaporating off the solvent (40° C.) in a petri dish and drying the dish at room temperature over P₂O₅ until it had reached a constant weight. Usually this drying operation required 48-72 hours. The other half of the solution was analyzed for phenol.

The percentage phenol in the smoke based on the weight of smoke solids which passed through the plasticizer-treated filters is shown in the table below. In each instance the additive was applied in at least a monomolecular layer. Also shown is the percentage phenol in the smoke which passed through the untreated filters and through the tobacco filters (non-filter cigarettes, 85 mm. in length). In the case of the treated filters in every instance there was a marked reduction in the amount of the phenol in the smoke compared with both the untreated polyolefin filter and the tobacco filter (a non-filter cigarette 85 mm. in length being the equivalent of a 70-mm. cigarette containing 15 mm. of tobacco filter). In the table the percent of the various ester additives is by weight.

TABLE

Run No.	Additive in the Crimped Polyolefin Tow Filters Attached to Cigarettes	Percent Phenol Content of the Smoke
1	Glycerol triacetate (8%)	0.37
2	Glycerol tripropionate (8.2%)	0.39
3	Glycerol triisobutyrate (7.7%)	0.40
4	Diethylene glycol dipropionate (7.8%)	0.38
5	Dipropylene glycol dipropionate (8.0%)	0.39
6	Sucrose octabutyrate (8.2%)	0.34
7	Sucrose acetate isobutyrate (8.2%) (18.6% acetyl, 39% isobutyryl)	0.30
8	Di(methoxy ethyl) phthalate (8.1%)	0.36
9	Diethyl phthalate (7.4%)	0.46
10	Tributyl citrate (7.0%)	0.44
11	Diethyl adipate (7.2%)	0.45
12	Ethylene glycol-adipic acid polyester-molecular weight 1000-(8.1%)	0.47
13	Ethylene glycol-phthalic acid polyester-molecular weight 1500-(7.7%)	0.42
14	Propylene glycol-succinic acid polyester-molecular weight 800 (8.0%)	0.42
15	Sorbitol hexapropionate (7.2%)	0.40
16	No additive control filters (0%)	0.66
17	Non-filter cigarettes (tobacco filter) (0%)	0.73

Example II

A continuous crimped textile tow of polypropylene fibers of 1 denier per filament and containing approximately 28 crimps per inch was spread out to a width of 12 inches and cut into 10-ft. lengths. Several of these 10-ft. lengths of polypropylene tow were spread out and sprayed with glycerol triacetate (triacetin) by means of a spray gun. Samples containing respectively 2.1%, 3.8%, 5.6% and 8.0% (by weight) were prepared.

Each sample was compacted and converted into filters by feeding into the garniture of a cigarette filter rod-making assembly which paper wrapped it into the form of a cylindrical rod which was cut into filter tip lengths of 15 mm. The filter tips were placed on standard 85 mm. (king-size) non-filter cigarettes which had been shortened by 15 mm. to compensate for the length of the filter. The

cigarettes were smoked on an automatic smoking machine similar in design and operation to the one described by Bradford et al. in Ind. Eng. Chem., vol. 28, pages 836-839 (1936). The smoke was collected in an empty 300-ml. Kjeldahl flask maintained at -20° C. Two small traps above the collection flask containing glass wool wet with methanol collected the residual smoke which did not settle in the flasks. 35-ml. puffs of 2 seconds' duration were taken at the rate of 1 puff per minute until a 55 mm. portion of the cigarette was consumed, leaving a 30 mm. butt.

For each level of triacetin added to the tow the smoke was allowed to settle in the flask for 30 minutes, and then the contents of the smoke traps were rinsed into the collection flask using a mixture of 95 percent methylene chloride and 5 percent methanol (volume per volume). A portion of the resulting solution of smoke was analyzed for phenol content. The percent phenol in the smoke, based on the weight of the smoke solids which passed through the triacetin-treated filters, is shown in the following table. Also shown is the percent phenol in the smoke which passed through an untreated polypropylene filter and through a non-filter cigarette 85 mm. in length.

TABLE

Run No.	Percent Glycerol Triacetate on Tow	Percent Phenol Content of the Smoke
1-----	0	0.66
2-----	2.1	0.64
3-----	3.8	0.52
4-----	5.6	0.44
5-----	8.0	0.37
6-----	(1)	0.73

¹ Non-filter Cigarette.

Example III

The glycerol triacetate used in this example represents a highly fluid type of ester at normal temperatures which may be added in considerable amounts with no harmful results. A 10-ft. length of the spread-out tow of Example I was sprayed on one side with glycerol triacetate (triacetin). The treated tow contained 4 percent plasticizer on its surface. It was converted into filters and tested in the manner described in Example I using the same type cigarettes. The collected smoke which passed through the filter contained 0.52 percent phenol. Using the value for the polyolefin control filter of Example I, this amounts to a reduction of 21 percent in the phenol content of the smoke.

The polyolefin material most useful according to our invention has a molecular weight above 10,000 and below 1,000,000. For best results polyolefin material is used which has a molecular weight between 30,000 and 200,000 and a denier per filament of less than 5 in the case of a filamentary material. Although in the foregoing examples we have used a 45,000-filament, 28 crimps-per-inch tow of spun polypropylene fibers of 1 denier per filament which exhibits outstanding capability in removing aromatic hydroxy components from tobacco smoke when the additives of the present invention are used therewith, other polyolefins and copolymers thereof may also be used as the basic filter material as may polyolefins in a form other than filamentous.

Example IV

(1) A cellulose acetate tow consisting of 12,000 fibers of 5 den./fil. was spread out and sprayed with triacetin until the tow had increased 7 percent in weight. The tow was then processed into cigarette filter rods by a commercial filter making machine.

(2) A second set of filter rods were prepared as in 1, except that no triacetin was added to the fibers.

(3) A polypropylene tow consisting of 12,000 fibers of 5 den./fil. was spread out and sprayed with triacetin

until the tow had increased 7 percent in weight. The tow was then processed into filter rods by a commercial filter making machine.

(4) Another set of filter rods were prepared as in 3, except that no triacetin was added to the fibers.

(5) The filter rods described in 1 through 4 were cut into 17-mm. filter tips and attached to king size (85 mm.) commercial cigarettes which had previously been shortened by 17 mm. All of the filter cigarettes were sealed in aluminum foil wrappers for a period of 4 weeks in order to simulate the conditioning a filter cigarette normally encounters between manufacture and consumption.

The filter cigarettes as well as some non-filter cigarettes were smoked with an automatic smoking machine, and the smoke was collected and analyzed for phenol content by a procedure similar to the one described by Hoffman and Wynder in J. National Cancer Institute, pp. 67-84, January 1963. The results of these tests were as follows:

Type of filter:	Phenol in trapped smoke, percent
1. Cellulose acetate plus 7% triacetin-----	0.26
2. Cellulose acetate (no additive)-----	0.29
3. Polypropylene plus 7% triacetin-----	0.24
4. Polypropylene (no additive)-----	0.71
5. Control (no filter)-----	0.75

The above data demonstrate that the addition of triacetin or like sprayable water-insoluble acylate brings polyolefin filters from a less desirable category in the industry as far as phenol removal is concerned to a more desirable level comparable to that of the widely used commercial cellulose acetate filters.

From the foregoing description and examples it will be apparent that we have provided a novel polyolefin tobacco smoke filter adapted for the removal of aromatic hydroxy compounds from tobacco smoke. In general we prefer to use aromatic hydroxy-removing additives those which have glycerol or alkylene glycol units in their structure.

Although the invention has been described in considerable detail with particular reference to certain preferred embodiments thereof, variations and modifications can be effected within the spirit and scope of the invention as described hereinabove and as defined in the appended claims.

We claim:

1. A tobacco smoke filter consisting of a rod-shaped bundle of crimped continuous polyolefin filaments having deposited on and between the surfaces of said filaments in substantially permanent form a substantially non-penetrating surface layer capable of dissolving phenol vapors and at least monomolecular in thickness of 4 percent to 10 percent by weight of said filter of a water-insoluble acylate ester of 2 to 12 carbon atoms having a phenol removal capability which lasts for at least about eight weeks, said acylate ester being easily sprayable at 25-100 C.° and having a boiling point above about 200° C.

2. The tobacco smoke filter of claim 1 wherein the acylate ester is selected from the group consisting of a glyceryl acylate, a glycol acylate and an alcohol acylate.

3. The tobacco smoke filter of claim 1 wherein the acylate ester is triacetin.

4. A process for improving phenol removal capability of substantially 100 percent polyolefin filament tobacco smoke filters which comprises spraying in a layer at least monomolecular in thickness in an amount of 4 to 10 percent by weight on the surface of and between substantially horizontally aligned crimped continuous filaments of a polyolefin of a molecular weight of 30,000 to 200,000 said filaments having a denier per filament of 5 or less, a water-insoluble acylate ester having 2 to 12 carbon atoms which is easily sprayable at 25 to 100° C. and has a boiling point above about 200° C., and shaping said filaments into compact rod-shaped elements adapted for

reduction in phenol content of tobacco smoke from a smoked polyolefin filter cigarette of at least about 20 percent after storage for at least 4 weeks, said acylate characterized by remaining in a substantially permanently deposited non-penetrating form on said filaments without losing any substantial amount of phenol vapor-dissolving capability until after at least about 8 weeks.

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