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PATENT SPECIFICATION

NO DRAWINGS

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Inventors: GEORGE PATRICK TOUEY
and JOHN EDWARD KIEFER.

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COMPLETE SPECIFICATION

Tobacco Smoke Filters

We, EASTMAN KODAK COMPANY, a Company organized under the Laws of the State of New Jersey, United States of America of 343 State Street, Rochester, New York 14650, United States of America (Assignees of GEORGE PATRICK TOUEY and JOHN EDWARD KIEFER) do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to tobacco smoke filters. The now universally accepted technique of preparing a cigarette filter from continuous cellulose acetate filaments, which is commercially known as a "filter tow", involves adding from 5 to 15 percent by weight of glycerol triacetate, that is triacetin, to the opened or spread out tow at some stage during its passage through a filter rod making machine. The treated tow is then compacted into a paper-wrapped rod which has substantially the same diameter as a cigarette. The glycerol triacetate on the tow functions as a slow acting plasticizing agent for the filaments thereby slowly dissolving a portion of the filaments with which it comes in contact. This causes a fusing action of the filaments at random points of contact throughout the filter rod giving the rod the rigid structure so necessary for subsequent cutting into segments suitable for use as tobacco smoke filter elements. Obviously the amount of plasticizer added to the tow must be controlled within certain limits since too small an amount would not give sufficient rigidity to the finished filter rod while too large an amount would fuse too many filaments together thereby producing a substantially non-porous filter. Therefore, most commercial cellulose acetate tow filters contain from 5 to 12 percent glycerol triacetate which is the range of concentration most ideally suited to give the proper rigidity to the filter rod without impairing its air permeability.

The action by which the filaments of the

cellulose acetate filter tow are fused together by the glycerol triacetate plasticizer is very important since it is accomplished without the application of heat. As is well known, this gradual fusing of the plasticizer-treated filaments of the filter rod takes place at room temperature thus eliminating the need for heating either the plasticizer or the tow during the plasticizer addition, or heating the final filter rod. Other types of conventional cellulose ester plasticizers do not possess this asset or are so sluggish in their action that heat is required at some point in the fabrication of the filters for accelerating the bonding reaction.

Another significant advantage of glycerol triacetate as a bonding or hardening agent for cellulose acetate filter tow rods is its non-tacky nature. As mentioned hereinabove, glycerol triacetate is an oily substance which gradually fuses the filaments of the filter rods at room temperature after they are fabricated. This is in marked contrast to the use of so called "adhesive" types of bonding agents which make the tow tacky as soon as they are applied. The use of such adhesive bonding agents in the manufacture of tobacco smoke filters is very objectionable since they cause the tow to adhere to the guide rollers and other parts of the filter fabricating equipment through which it must pass after the application of the bonding agent. Also, the use of adhesives usually implies the need for removal of either water or an organic solvent which adds both to the equipment necessary and the expense involved in producing the final product.

Even though glycerol triacetate is the most efficient of the plasticizers which has been used in the tobacco smoke filter trade for bonding the filaments in cellulose acetate tow filter rods, and is vastly superior to adhesives, glues, or other solvent-based resins as a bonding agent, it still leaves much to be desired. For example, the freshly prepared glycerol triacetate-containing rods must be stored for

[Price 4s. 6d.]



about two hours at room temperature before they have sufficient rigidity to be cut into smaller segments and attached to cigarettes. This slow curing time often causes "oval" shaped rods to form in the filter rod collection trays at the end of the filter rod making machine. This is because, for expediency, the trays must be placed in a vertical position so that the filter rods can be stacked on top of each other in layers. Thus, the pressure of the weight of the rods in a full tray can cause some of the rods in the bottom section of the tray to become distorted before they develop sufficient rigidity to resist distortion.

Another disadvantage of the triacetin is that it diffuses into the fibres fairly rapidly after the filter rod is prepared. This, in turn, represents a loss in its bonding capacity since once the triacetin is within the fibre and no longer on its surface it cannot cause the fibres to fuse to adjacent fibres and thereby create a more rigid filter structure. Thus, a room temperature-bonding type of plasticizer which would remain longer on the surface of the fibres would be a more efficient bonding agent than triacetin. In addition, a plasticizer such as triacetin which diffuses into the fibres is no longer effective for selective removal of certain undesirable constituents from the smoke. For example, it has been reported (D. Hoffmann and E. L. Wynder, J. Nat. Cancer Institute, pp. 67-84, Jan. 1963) that a cellulose acetate filter containing 6-12 percent triacetin removes more phenol from cigarette smoke than a similar filter without triacetin. However, it is pointed out in this report that when the filter has aged for several weeks the triacetin is absorbed within the fibres and, as a result, the aged but still rigid filter shows very little improvement in phenol removal over an unplasticized control filter.

A third disadvantage of glycerol triacetate, and for that matter most other plasticizer bonding agents heretofore recommended for cellulose acetate tow filter, is its very bitter taste. Obviously, there is always the possibility that this taste might be detected by the smoker.

A fourth disadvantage of glycerol triacetate is its relatively low boiling point (258°C. at 760 mm). Although it is substantially non-volatile at room temperature, a significant amount of triacetin can be eluted from the filter during the smoking of the filter cigarette. This is because during the last few puffs on a cigarette the temperature of the smoke entering the filter can be as high as 95°C. although the smoke exit temperature may be only a maximum of 45°C. This could result in enough triacetin being eluted in the smoke during the last few puffs to impart a bitter taste to the smoke. Therefore, it would be more desirable to use a room temperature bonding plasticizer which has a much higher boiling point than triacetin. However, as mentioned hereinabove, even though there are many high boiling

organic plasticizers which have boiling points considerably higher than that of triacetin, they are either non-bonding plasticizers which do not produce a rigid filter of cellulose acetate, or they require heat to function as a bonding agent.

Still another advantage of glycerol triacetate is its ineffectiveness in bonding cellulose acetate tow fibres when the acetyl content of the fibres is above about 41 percent. For example, although it is satisfactory for the commercial grades of cellulose acetate filter tow which are prepared from filaments spun from acetone and which have an acetyl content of 39-40 percent, it is a poor bonding agent for tows of cellulose filaments which are insoluble in acetone but soluble in methylene chloride and have acetyl contents ranging from 41 percent to 44.8 percent.

According to the present invention, a tobacco smoke filter comprises a plasticizable fibrous filter medium bonded together at random points by a diacetate, dipropionate or dibutyrate ester of a polyethylene glycol.

Suitable diacetate, dipropionate or dibutyrate esters include those of triethylene glycol, tetraethylene glycol and pentaethylene glycol.

Conveniently, the fibrous filter medium contains from 4-20 percent, preferably from 5-12 percent by weight of the polyethylene glycol ester.

The fibrous filter mediums which are preferred are those composed of a cellulose acetate.

The polyethylene glycol esters and more especially those derived from polyethylene glycols having molecular weight of up to 2,000, serve as non-tacky bonding agents for the cellulose ester tows. While all the esters have proved suitable for producing rigid filters from a conventional tow of acetate fibres having an acetyl content of from 39-40 percent, the polyethylene glycol dipropionates have been found to be more effective than the diacetate esters with those cellulose acetate tows having an acetyl content approaching the range of 43-44.8 percent.

What is more, the hydrolytic stability of a dipropionate ester is greater than that of a diacetate ester. A less hydrolyzable polyethylene glycol ester is a preferred bonding agent for a cellulose acetate filter since there is always the possibility of the development of an odour in a filter containing a more readily hydrolyzable agent. Moreover, a bonding agent which liberates an acid on exposure to moisture could be detrimental in a cellulose acetate filter containing activated carbon since the acid would tend to deactivate the carbon thereby rendering the latter less effective for the removal of smoke vapours such as acetaldehyde and acroleins.

It has been found that the glycol esters of the present invention are generally superior to

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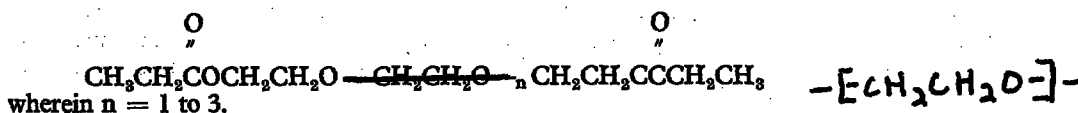
130

the bonding agents which have been previously employed. For one thing, they fuse together the plasticizable fibres at room temperature in less time than the known agents and, in view of their polymeric structure, they are appreciably less volatile than, for example, triacetin and hence impart little or no bitter taste to the smoke during the last few puffs.

Furthermore, the present esters, unlike triacetin, are more effective in their ability to remove phenol since they are not gradually diffused into or absorbed by cellulose acetate fibres to anywhere near the same extent. Unlike glycerol triacetate, the polyethylene glycol esters are also miscible in water thus enabling

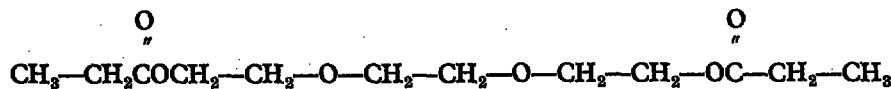
them to be diluted to provide more economical bonding agents. When they contain an appreciable amount of water, for example, 10—30 percent, their ability to spread over the filament surfaces of the tow can be enhanced by incorporating small amounts of conventional ionic-type surfactants such as the alkyl, aryl and alkylaryl sulphates and sulphonates.

The ~~general~~ molecular formula of the bonding agents of the present invention can be represented, by way of example, with reference to the completely esterified propionate esters of tri-, tetra- and penta-ethylene glycol as follows:

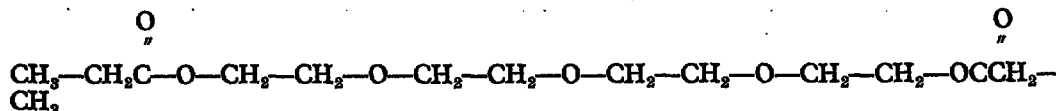


The specific molecular formulae of the various dipropionate esters are as follows:

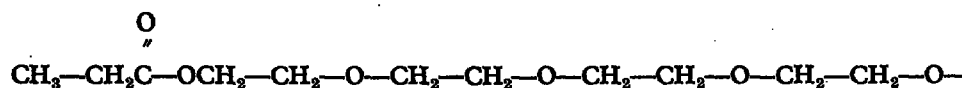
1. Triethylene glycol dipropionate



2. Tetraethylene glycol dipropionate



3. Pentaethylene glycol dipropionate



The diacetate, dipropionate and dibutyrate esters of tri-, tetra-, and pentaethylene glycol can be prepared by any convenient method. For example, the dipropionate esters can be conveniently prepared by heating a mole of the glycol at between 80 and 100°C., with proper agitation, while 2.2 moles of propionic anhydride are slowly dripped into the reaction flask which is equipped with a condenser. No catalyst for this reaction is required. After all the anhydride has been added, the reaction is allowed to continue for about one hour at 80 and 100°C. Finally, a mole of water is added to the mixture within the condenser for converting any excess anhydride therein to propionic acid. The resulting product is then purified by distillation under reduced pressure.

These new plasticizer type bonding agents may be applied to the filter tow being used by any convenient manner while the tow is being fabricated into filter rods. For example, the plasticizer bonding agents can be sprayed on the bloomed-out (opened) tow just prior to the point where the tow is recompacted and drawn through the paper wrapping assembly of the filter rod making machine. Another way of adding these high boiling liquid bonding agents to the tow is to employ a wicking device which "wipes" the desired amount of the liquid on the bloomed-out tow at some point during its travel through the filter tow assembly machine.

The invention will now be illustrated with reference to the following Examples:—



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generic

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EXAMPLE 1

A tow consisting of 12,000 cellulose acetate filaments of 5 denier per filament and crimped to 12 crimps per inch was spread out and sprayed with a polyethylene glycol diacetate having a molecular weight of 484. The tow which contained 0.8 percent of the ester was then processed into filter rods on a standard cigarette filter rod-making machine.

After 30 minutes, the rods were firm and suitable for cutting into 17 mm. lengths for attaching to a brand of cigarettes. The cigarettes were smoked on an automatic smoking machine and the smoke was collected and analyzed for its phenol content.

The smoking experiment was repeated after the filter rods had been aged at room temperature for four weeks. For the purpose of comparison, (a) the unsprayed tow which served as a control and (b) the tow when sprayed with 6.7 percent and 10 percent glycerol triacetate were also subjected to the

aforementioned procedure.

The results from these experiments are to be found in Table A below.

EXAMPLE 2

The procedure of Example 1 was repeated except that only 6.2% of the polyethylene glycol diacetate was applied to the tow. As in Example 1, the filters were firm after 30 minutes storage at room temperature.

EXAMPLE 3

The procedure of Example 1 was repeated except that 9.5% of polyethylene glycol dipropionate was applied to the tow. As in Example 1 the filters were firm after 30 minutes.

The ability of the filters of Examples 1-3 to remove phenol from cigarette smoke is illustrated by the results shown in Table A below.

TABLE A

Bonding Agent	Amount of phenol in Mg. Found in Smoke from 100 Filter Cigarettes	
	Aged 1 Day	Aged 4 Weeks
Control	7.0	7.1
Polyethylene glycol diacetate (9.8%)	4.4	4.6
Polyethylene glycol diacetate (6.2%)	5.3	5.8
Polyethylene glycol dipropionate (9.5%)	4.2	4.5
Glycerol triacetate (triacetin) (10.3%)	4.7	6.7
Glycerol triacetate (6.7%)	5.9	6.9

Aging time refers to time from application of the bonding agent to smoking test.

It will be noted that while the filters incorporating glycerol triacetate were quite efficient when freshly prepared, they were little better than the control filters after four weeks storage.

EXAMPLE 4

A filter tow of 16,000 crimped filaments of cellulose acetate (39.8 percent acetyl) was divided into eight 500 foot sections. The first section was processed and wrapped with a paper of 1.2 mils thickness to form filter rods without any plasticizer bonding agent being added thereto for purposes of establishing a control sample. Each of the remaining seven sections was coated with one of the following

plasticizers until 9 to 9.5 percent by weight of the bonding agent had been added to the tow: (1) triacetin; (2) triethylene glycol diacetate; (3) tetraethylene glycol diacetate; (4) pentaethylene glycol diacetate; (5) triethylene glycol dipropionate; (6) tetraethylene glycol dipropionate; (7) pentaethylene glycol dipropionate. After each 500 foot section was coated with one of these bonding agents it was also processed into paper wrapped filter rods. In all cases the filter rods were 25.2 mm. in circumference and were made on a conventional filter rod-fabricating machine. Table B below shows both the plasticizer used and the observed hardness of all the filter rods after they had been stored at room temperature (75°F.) for various lengths of time.

TABLE B

Bonding Agent	Observed Rod Hardness on Storage				
	15 min.	30 min.	45 min.	60 min.	2 hr.
control, no plasticizer	12	12	12	12	12
triacetin	12	9	9	6	3
triethylene glycol diacetate	10	6	3	—	—
tetraethylene glycol diacetate	10	6	3	—	—
pentaethylene glycol diacetate	12	9	5	3	—
triethylene glycol dipropionate	9	3	—	—	—
tetraethylene glycol dipropionate	6	3	—	—	—
pentaethylene glycol dipropionate	9	6	3	—	—

wherein:

12 = soft rod, could not be cut into filter segments.

9 = semi firm rod.

6 = firm rod, could be cut into filter segments but difficulty encountered; some of the filaments pulled from the filter segments during the cutting.

3 = rigid rod, could be easily cut into filter segments, no problem with frayed filter ends.

It was also observed that when the thin paper (filter plug wrap similar in thickness to cigarette paper—1.2 mils) was removed from the rods 15 minutes after they were prepared, the control and the triacetin treated rods fluffed out. This indicated no bonding action had taken place. On the other hand, the polyethylene glycol dipropionate treated rods after 15 minutes storage did not fluff out when the paper was removed, thus indicating that the plasticizer had started to function as a bonding agent.

From these examples it is readily seen that the polyethylene glycol dipropionate esters of this invention act more rapidly as bonding agents than their corresponding diacetate esters. It is also readily apparent that both the diacetate and the dipropionate esters of

these polyethylene glycols act more rapidly as bonding agents than glycerol triacetate, which is the conventional plasticizer used by the cellulose acetate tow filter industry.

EXAMPLE 5

A tow of 16,000 crimped continuous filaments of cellulose acetate having an acetyl content of 43.6 percent was divided into seven 500 foot sections. Each section was processed into plasticizer treated (9—9.5%) paper wrapped rods, each of which was 25.2 mm. in circumference, by means of a production type filter rod making machine.

Table C shows the plasticizer bonding agents used and the observed hardness of the rods after they had been stored at room temperature (75°F.) for various lengths of time,

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TABLE C

Observed Rod Hardness on Storage

Bonding Agent	30 min.	1 hr.	3 hr.	6 hr.	24 hr.
triacetin	12	12	12	10	10
triethylene glycol diacetate	12	12	12	9	6
tetraethylene glycol diacetate	12	12	12	9	6
pentaethylene glycol diacetate	12	12	12	10	9
triethylene glycol dipropionate	12	9	3	—	—
tetraethylene glycol dipropionate	12	10	3	—	—
pentaethylene glycol dipropionate	12	10	6	3	—

The key to the rod hardness figures is the same as in Example 4.

5 This Example clearly illustrates that the polyethylene glycol dipropionates are bonding agents for filter rods prepared from a tow of crimped cellulose triacetate filaments having an acetyl content above 42 percent whereas the polyethylene glycol diacetates and glycerol triacetate exhibited a very slow bonding action with this type of material.

10 **EXAMPLE 6**
Purified samples of the diacetates and the dipropionates of tri-, tetra-, and pentaethylene glycol were obtained. Blends of 50 cc. of

water and 150 cc. of each of the water-miscible plasticizer bonding agents were prepared and stored in sealed glass containers in a 50°C. bath for one week. At intervals the containers were opened and aliquots were removed and analyzed for the presence of free acid. After 72 hours a faint acid odour was observed in all of the diacetate solutions, but after 168 hours there was still no acid odour observed for the dipropionate samples. The complete results of this test are given in Table D below.



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and aliquots

TABLE D

Sample	Bonding Agent	% Free Acid Found		
		24 hr.	72 hr.	168 hr.
1	triethylene glycol diacetate	0	0.8	3.2
2	triethylene glycol dipropionate	0	0.6	0.1
3	tetraethylene glycol diacetate	0	0.6	3.0
4	tetraethylene glycol dipropionate	0	0	0.1
5	pentaethylene glycol diacetate	0	0.8	2.8
6	pentaethylene glycol dipropionate	0	0	0.2

25 As will be apparent, this Example illustrates the improved hydrolytic stability of the propionate esters of the tri-, tetra-, and pentaethylene glycols over the corresponding acetate esters of these glycols.

WHAT WE CLAIM IS:—

1. A tobacco smoke filter comprising a plasticizable fibrous filter medium bonded together at random points by a diacetate, dipropionate or dibutyrate ester of a polyethylene

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TABLE C

Bonding Agent	Observed Rod Hardness on Storage				
	30 min.	1 hr.	3 hr.	6 hr.	24 hr.
triacetin	12	12	12	10	10
triethylene glycol diacetate	12	12	12	9	6
tetraethylene glycol diacetate	12	12	12	9	6
pentaethylene glycol diacetate	12	12	12	10	9
triethylene glycol dipropionate	12	9	3	—	—
tetraethylene glycol dipropionate	12	10	3	—	—
pentaethylene glycol dipropionate	12	10	6	3	—

The key to the rod hardness figures is the same as in Example 4.

5 This Example clearly illustrates that the polyethylene glycol dipropionates are bonding agents for filter rods prepared from a tow of crimped cellulose triacetate filaments having an acetyl content above 42 percent whereas the polyethylene glycol diacetates and glycerol triacetate exhibited a very slow bonding action with this type of material.

EXAMPLE 6

10 Purified samples of the diacetates and the dipropionates of tri-, tetra-, and pentaethylene glycol were obtained. Blends of 50 cc. of

water and 150 cc. of each of the water-miscible plasticizer bonding agents were prepared and stored in sealed glass containers in a 50°C. bath for one week. At intervals the containers were opened and aliquots were removed and analyzed for the presence of free acid. After 72 hours a faint acid odour was observed in all of the diacetate solutions, but after 168 hours there was still no acid odour observed for the dipropionate samples. The complete results of this test are given in Table D below.



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2	triethylene glycol dipropionate	0	0.6	0.1
3	tetraethylene glycol diacetate	0	0.6	3.0
4	tetraethylene glycol dipropionate	0	0	0.1
5	pentaethylene glycol diacetate	0	0.8	2.8
6	pentaethylene glycol dipropionate	0	0	0.2



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25 As will be apparent, this Example illustrates the improved hydrolytic stability of the propionate esters of the tri-, tetra-, and pentaethylene glycols over the corresponding acetate esters of these glycols.

WHAT WE CLAIM IS:—

1. A tobacco smoke filter comprising a plasticizable fibrous filter medium bonded together at random points by a diacetate, dipropionate or dibutyrate ester of a polyethylene

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glycol.

2. A filter according to Claim 1, wherein the ester is of a polyethylene glycol having a molecular weight of up to 2,000.
- 5 3. A filter according to Claim 1 or 2, wherein the ester is of triethylene glycol, tetraethylene glycol or pentaethylene glycol.
- 10 4. A filter according to Claim 1, 2 or 3, wherein the ester is present in an amount of from 4—20% by weight of the fibrous filter medium.
- 15 5. A filter according to Claim 4, wherein the ester is present in an amount of from 5—12% by weight of the fibrous filter medium.
6. A filter according to any one of the preceding Claims 1 to 5, wherein the fibrous filter medium consists of a bundle of continuous and substantially horizontally aligned

plasticizable filaments some of which are intermingled.

7. A filter according to any one of the preceding Claims 1 to 6, wherein the fibrous filter medium is composed of a cellulose acetate.

8. A filter according to Claim 7, wherein the cellulose acetate has an acetyl content of from 39—40%.

9. A filter according to Claim 1, wherein the fibrous filter medium is composed of a cellulose acetate having an acetyl content ranging from 41—44.8% and the ester is a dipropionate of a polyethylene glycol.

10. Tobacco smoke filters as described in the Examples herein.

L. E. T. BRANCH, B.Sc., F.R.I.C.,
Patent Agent.

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