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BONDING PLASTICIZERS FOR CIGARETTE FILTERS  
OF CELLULOSE ACETATE FIBERS  
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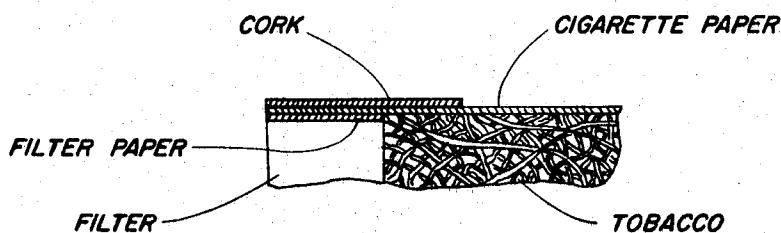


FIG. 1

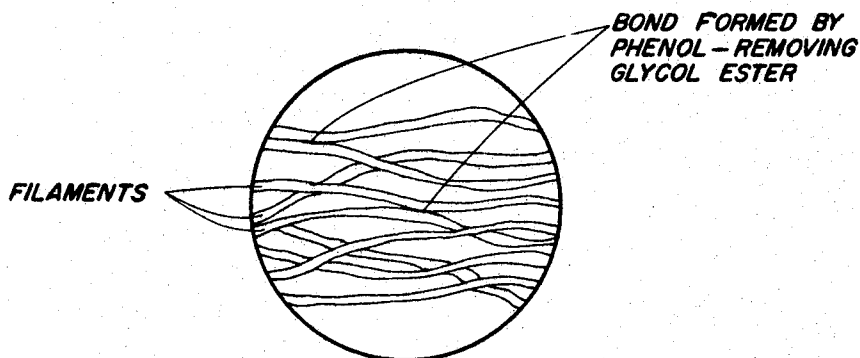


FIG. 2

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## BONDING PLASTICIZERS FOR CIGARETTE FILTERS OF CELLULOSE ACETATE FIBERS

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Continuation-in-part of application Ser. No. 246,362, Dec. 21, 1962. This application Aug. 26, 1965, Ser. No. 482,882

5 Claims. (Cl. 131—267)

### ABSTRACT OF THE DISCLOSURE

A tobacco smoke filter element having an improved plasticizer type hardening and phenol removing agent which cures very rapidly and has improved hydrolytic stability. The hardening and phenol removing agents are the completely esterified propionic acid esters of tri-, tetra-, and pentaethylene glycol.

This is a continuation-in-part of our copending application Ser. No. 246,362, filed Dec. 21, 1962, now Patent No. 3,229,699.

This invention relates to a tobacco smoke filter element having as an additive thereto an improved plasticizer type hardening agent which cures very rapidly and has improved hydrolytic stability. More particularly, this invention relates to the use of substantially completely esterified propionic acid esters of tri-, tetra-, and pentaethylene glycol as improved hardening agents for tobacco smoke filter elements prepared from continuous filaments of either cellulose acetate or cellulose triacetate.

The now universally accepted technique of preparing a rigid filter rod or element from a cord of continuous cellulose acetate filaments, which is commercially known as a "filter tow," involves adding from 5 to 15 percent by weight of glycerol triacetate to the opened or spread out tow at some point during its passage through a filter rod fabricating machine. The treated tow is then compacted into a paper-wrapped rod which has substantially the same diameter as a cigarette. The glycerol triacetate plasticizer on the tow functions as a slow solubilizing agent for the filaments thereby slowly dissolving a portion of the fibers with which it comes in contact. This causes a fusing action of the fibers at random points of contact throughout the filter rod matrix 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 nonporous 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 cellulose acetate filter tow is 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 hardening of the plasticizer treated 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 but are either nonhardening agents for the cellulose acetate rod regardless of the curing steps taken, or are so sluggish in their hardening action that heat is required at

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some point in the fabrication of the filters for accelerating the bonding reaction.

Another unique advantage of glycerol triacetate as a hardening agent for cellulose acetate filter tow rods is its non-tacky nature. As mentioned hereinabove, glycerol triacetate is an oily substance which gradually hardens the filter rods at room temperature after they are fabricated. This is in marked contrast to the use of so called "adhesive" types of hardening agents which make the tow tacky as soon as they are applied. The use of such adhesive hardening agents in the manufacture of tobacco smoke filters is very objectionable since they cause the tow to adhere to the guide rolls and other parts of the filter fabricating equipment through which it must pass after the application of the hardening 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 hardening cellulose acetate tow filter rods, and is vastly superior to adhesives, glues, or other solvent based resins as a hardening agent, it still leaves much to be desired. For example, the freshly prepared glycerol triacetate containing rods must be stored for about two hours at room temperature before they have sufficient rigidity to be cut into smaller segments and attach 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 fibers 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 fiber and no longer on its surface it cannot cause the fibers to fuse to adjacent fiber 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 fibers would be a more efficient bonding agent than triacetin. In addition, a plasticizer such as triacetin which diffuses into the fibers is no longer available to selectively remove 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, January 1963) that a cellulose acetate filter containing 6-12% 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 fibers and, as a result, the aged but still rigid filter shows very little improvement in phenol removal over an unplasticized control filter.

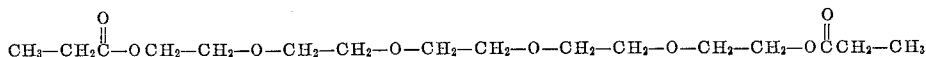
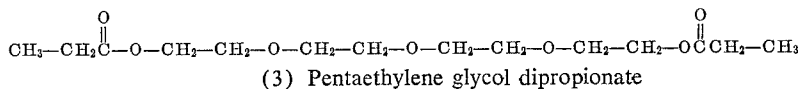
A third disadvantage of glycerol triacetate, and for that matter most other plasticizer hardening agents heretofore recommended for cellulose acetate tow filters, is its very bitter taste. Obviously, there is always the possibility that this taste might be detected by the smoker.

A fourth disadvantage of glycerol triacetate is its relatively low boiling point (258° C. at 760 mm.). Although it is substantially nonvolatile 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

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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 nonbonding plasticizers which do not produce a rigid filter of cellulose acetate, or they require heat to function as a bonding or hardening agent.

Still another disadvantage of glycerol triacetate as a hardening agent for cellulose acetate tow filters is its ineffectiveness for hardening cellulose acetate tow filters



when the acetyl content of the fibers is above about 41%. 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%, it is a poor hardening or bonding agent for a tow of cellulose triacetate filaments (acetone insoluble but soluble in methylene chloride) which have acetyl contents ranging from above 41% to 44.7%, the theoretical maximum for a cellulose triacetate.

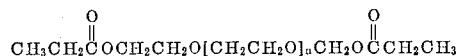
In our copending application Ser. No. 246,362, of which this application is a continuation-in-part, we have disclosed various diacetate esters of certain water immiscible poly(ethylene glycols) which have been proven to be better bonding agents for plasticizable filaments than the agents heretofore used. These new diacetate esters are superior to these prior known bonding agents in that they harden the plasticizable filters at room temperature in a shorter length of time and, since they are polymeric, they are considerably less volatile than, for example, glycerol triacetate. Also, it has been found that when these poly(ethylene glycol) esters are added to a cellulose acetate tow filter they make the filter more effective for the removal of phenol since, unlike triacetin, they are not gradually diffused into or absorbed by the cellulose acetate fibers from which the filter is made.

However, even though these poly(ethylene glycol) esters disclosed and claimed in our copending application Ser. No. 246,362 represent a substantial advancement in the types of bonding or hardening agents available to the tobacco smoke filter industry, they nevertheless have certain features which could be improved. For example, it is desirable that the hydrolytic stability of the tobacco smoke filter hardening agents be improved. Furthermore, there is a real need for a hardening agent for use in the filter manufacturing industry which is not only able to produce a rigid filter when conventional tow of acetate fibers (39–40 percent acetyl) is used, but is also able to produce a rigid filter from a tow of cellulose acetate fibers with acetyl contents approaching that of certain cellulose triacetate (43 to 44.7 percent acetyl). This improved hardening agent must also have no bitter taste as is characteristic of glycerol triacetate and other like heretofore used agents. Obviously, any new bonding agents which are to be used in producing cigarette filters must be non-tacky and, ideally, capable of hardening the filter at room temperature in less time than heretofore required.

According to the present invention it has been found that a superior group of bonding or hardening agents for tobacco smoke filters can be produced which have superior phenol removal capabilities yet at the same time will

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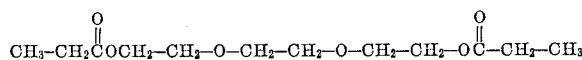
fulfill the characteristics hereinabove set forth. These new hardening agents are produced from a glycol base and are characteristic as being completely esterified propionate esters of tri-, tetra-, and pentaethylene glycol. The generic molecular formula of these agents is:



wherein  $n=1$  to 3.

The specific molecular formulas are as follows:

(1) Triethylene glycol dipropionate



(2) Tetraethylene glycol dipropionate

(3) Pentaethylene glycol dipropionate

Therefore, an object of this invention is to disclose a certain group of tri- and poly(ethylene glycol) esters which have improved hydrolytic stability over heretofore known like agents including their corresponding diacetate esters.

Another object is to disclose selected tri- and poly(ethylene glycol) esters particularly adapted for use as bonding agents in cigarette smoke filter elements made of cellulose acetate and cellulose triacetate.

Yet another object of this invention is to disclose various tobacco smoke filter element hardening agents of the tri- and poly(ethylene glycol) ester classes which harden at room temperature and in a shorter length of time than was heretofore considered possible.

A further object of the invention is to describe a class of completely esterified propionate esters of tri-, tetra-, and pentaethylene glycol filter hardening agents which have no extremely bitter taste.

A still further object of this invention is to disclose a method for producing a plasticizer-hardened tobacco smoke filter made from a crimped tow of either cellulose acetate or cellulose triacetate which is both economical and readily adaptable for use with existing filter forming equipment.

Still another object of this invention is to disclose a method for producing a plasticizer-hardened tobacco smoke filter which selectively removes a high percentage of phenol from cigarette smoke and which maintains this high capacity for phenol absorption after months of storage.

Yet another object of this invention is to provide a cigarette filter which is essentially tasteless and odorless.

These and other objects and advantages of this invention will be more apparent upon reference to the accompanying specification, specific working examples, appended claims and drawings wherein:

FIGURE 1 is a cross-sectional side view of a portion of a cigarette provided with a filter made in accordance with this invention; and

FIGURE 2 is an enlargement of a portion of the filter section of FIGURE 1 showing certain filaments bonded at random points with a phenol-removing glycol ester according to this invention.

As briefly set out hereinabove, this invention involves the use of completely esterified propionate esters of tri-, tetra-, and pentaethylene glycol as the hardening agent in cigarette filters made from cellulose acetate or cellulose triacetate tow material. These dipropionate esters of tri-, tetra-, and pentaethylene glycol can be prepared by any convenient method. One such method which has been found to be acceptable involves 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 is added the reaction is allowed to continue for about one hour at 80–100° 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 hardening 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 hardening 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 hardening 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. However, regardless of the method or apparatus used to evenly disperse the plasticizer hardening agent throughout the tow, it has been found that the amount of agent used can vary from 4 to 20 percent by weight with the preferred range being from 6 to 12 percent.

A further understanding of the invention will be had from a consideration of the following examples that may be used in actual commercial practice of the invention and which are set forth to illustrate certain preferred embodiments and features thereof.

#### EXAMPLE 1

A filter tow of 16,000 crimped fibers 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 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 plasticizer 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 plasticizers it was also processed into paper wrapped filter rods. In all cases the filter rods were 25.2 mm. in circumference and were fabricated on a machine similar to the one described in the Crawford-Stevens U.S. Patents 2,794,239 and 3,017,309. Table 1 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 1

Filter Rod Hardening Agent Used in Filter	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 min. 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, all of the poly(ethylene glycol) propionate treated rods after 15 min. 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 poly-(ethylene glycol) dipropionate esters of this invention are more rapid filter hardening agents than their corresponding diacetate esters. It is also readily apparent that both the diacetate and the dipropionate esters of these poly-(ethylene glycols) are more rapid hardening agents than glycerol triacetate, which is the conventional plasticizer used by the cellulose acetate tow filter industry.

#### EXAMPLE 2

A tow of 16,000 crimped continuous fibers of cellulose triacetate (43.6 percent acetyl) was divided into seven 500 ft. 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 2 below shows the plasticizer used and the observed hardness of the rods after they had been stored at room temperature (75° F.) for various lengths of time.

TABLE 2

Filter Rod Hardening Agent Used In Filter	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	-----

This example clearly illustrates that the poly (ethylene glycol) dipropionates are hardening agents for filter rods prepared from a tow of crimped cellulose triacetate (42+percent acetyl) fibers whereas the poly(ethylene glycol) diacetates and glycerol triacetate exhibited a very slow bonding action with this type of material.

#### EXAMPLE 3

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 plasticizers 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 odor was observed in all of the diacetate solutions, but after 168 hours there was still no acid odor observed for the dipropionate samples. The complete results of this test are given in Table 3 below.

TABLE 3

Sample	Plasticizer	Percent Free Acid Found		
		24 hr.	72 hr.	168 hr.
1.....	Triethylene glycol diacetate.....	0	0.8	3.2
2.....	Triethylene glycol dipropionate.....	0	0	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

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. Obviously, a

less hydrolyzable poly(ethylene glycol) ester is the preferred type of plasticizer hardening agent for a cellulose acetate filter since there is always the possibility of the development of an odor in a filter containing a more readily hydrolyzed plasticizer. Also, a plasticizer which liberates an acid on exposure to moisture could be detrimental in a cellulose acetate filter containing activated carbon since it would deactivate the carbon rendering it less effective for the removal of such smoke vapors as acetaldehyde and acroleins.

From the foregoing it will be obvious that the use of these new filter hardening agents offer numerous advantages over any other such agents heretofore used by the tobacco industry. For example, they are more resistant to hydrolysis and they can produce a rigid filter from a tow of cellulose triacetate fibers. Furthermore, they cure or harden more rapidly than any other plasticizer of the non-tacky, high boiling liquid type. The fact that they also contribute to the phenol removal capacity of the filter, and are odorless, tasteless and adapted for use in existing commercial filter forming equipment is of prime importance.

What is claimed and desired to be secured by the United States Letters Patent is:

1. As a new article of manufacture a filter rod adapted for use in filtering tobacco smoke, said rod being comprised principally of a bundle of continuous substantially horizontally aligned plasticizable cellulose acetate filaments some of which are intermingled and carrying thereon from 4 to 20 percent by weight of said filaments of a dipropionate ester of a poly(ethylene glycol) selected from the group consisting of triethylene glycol, tetraethylene glycol or pentaethylene glycol, said ester resulting in minimal diffusion of said ester into the filaments upon storage while at the same time improving the phenol-removal capabilities of said filter rod by maintaining a high capacity for phenol absorption after months of storage, said rod being typified by high resistance to hydrolysis and a more rapid hardening after formation thereof.

2. As an article of manufacture a filter rod adapted for use in filtering tobacco smoke, said rod being comprised principally of a bundle of continuous substantially horizontally aligned plasticizable cellulose triacetate filaments some of which are intermingled and carrying

thereon from 4 to 20 percent by weight of said filaments of a dipropionate ester of a poly(ethylene glycol) selected from the group consisting of triethylene glycol, tetraethylene glycol, or pentaethylene glycol, said rod being characterized by both a high capacity for phenol absorption after months of storage and a high resistance to hydrolysis coupled with a faster bonding by said ester to a firmness maintained after months of storage.

3. A tobacco smoke filter tow adapted to be formed into a tobacco smoke filter element comprising plasticizable filaments of cellulose acetate having coated thereon an additive including a dipropionate ester of a poly(ethylene glycol) selected from the group consisting of triethylene glycol, tetraethylene glycol, and pentaethylene glycol for bonding said filaments together at random points to thereby form a firm filter element.

4. A tobacco smoke filter tow according to claim 3 wherein said plasticizable filaments are formed of cellulose triacetate.

5. A tobacco smoke filter comprising a porous mass of cellulose acetate material having therein interconnected interstices through which the tobacco smoke is drawn, and said material carrying an additive of dipropionate ester of a poly(ethylene glycol) selected from the group consisting of triethylene glycol, tetraethylene glycol, and pentaethylene glycol located within said interstices so as to contact the tobacco smoke being drawn therethrough, said additive being selected so as to react with said cellulose acetate to form a firm filter and to remove the phenol constituent contained within said tobacco smoke.

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