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SELECTIVE FILTER MEDIUM

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ABSTRACT OF THE DISCLOSURE

Tobacco smoke filtering media containing at least one polyol-amine or polyol-amine salt additive for selectively reducing the noxious gases found in the tobacco smoke.

This invention relates to a new and improved filter for the selective removal of noxious gases from tobacco smoke, and to a method for producing such a filter. More particularly, this invention relates to a new tobacco smoke filter element containing a polyol-amine blend, and the method of producing such filters, which will remove hydrogen cyanide from an effluenting stream tobacco smoke.

It has been known for some time that tobacco smoke contains certain harmful components which contribute nothing beneficial to the pleasant taste or aroma of the smoke and, therefore, for obvious reasons should be removed. It is well known, for example, that a limited amount of hydrogen cyanide is found in tobacco smoke and that this hydrogen cyanide is an extremely harmful ciliatoxic compound. It has therefore been the desire of the tobacco industry to provide an effective and practical tobacco smoke filter which is capable of selectively removing hydrogen cyanide from cigarette smoke without at the same time adversely affecting the pleasant taste and aroma found in the smoke.

The search for a suitable yet inexpensive filtering medium which could be used with any tobacco product, and especially with cigarettes, lead to the development of the so-called "fibrous" filter unit. These fibrous filters, and particularly those made of cellulose acetate tow, have been found to be very effective for removing solid particulate matter commonly referred to as "tar" from tobacco smoke. However, it is difficult, if not impossible, to remove certain undesirable gaseous components, such as hydrogen cyanide, which are found in tobacco smoke by use of such filters.

In an effort to improve the gas phase removal efficiency of fibrous filter units it has been proposed that certain gas adsorbing additives in the form of finely divided particles be dispersed within the fibrous filter. These particles of solid materials, which were usually of the type that adsorbed the gases, were generally placed on the surface of a fibrous material in either a dry or liquid state. Numerous solid adsorbing materials were tried with activated carbon and certain silica gels being the ones most often used.

However, there are certain limitations and disadvantages to using activated carbon in a cigarette filter for removing cigarette smoke vapors. For example, activated carbon does not remove cigarette smoke vapor selectively even though it has more affinity for some vapor components than others. In general the adsorption of vapors by carbon is dependent upon the boiling point of the vapor being adsorbed. That is, the least volatile vapors will be more readily adsorbed and retained by activated carbon additives as opposed to the more volatile vapors. This is a definite disadvantage since several of the least volatile vapors in cigarette smoke are those which give flavor and taste to the smoke and are neither

deleterious nor harmful to the smoker. Therefore, the removal of these vapors is highly undesirable and, if permitted to occur, can result in what has commonly been referred to as a "carbon" or "dry" taste.

Furthermore, the fact that the adsorption of vapors by carbon in a cigarette filter is a physical phenomenon depending upon temperature and pressure also presents a problem to the industry. That is, since the temperature of a cigarette filter increases as the burning zone of the cigarette approaches the filter during the smoking of a cigarette, the temperature of the carbon in the filter is raised causing the more volatile vapors adsorbed on the carbon to be eluted from the carbon. Thus, the carbon particles do not permanently nor effectively remove the more volatile deleterious vapors. In addition, as stated above, the less volatile gases which contribute to the taste and aroma of the smoke, and are generally neither deleterious nor harmful, are also removed by carbon filters. Furthermore, since the removal of solid particulate matter commonly called tar is also of prime importance, cigarette filters containing activated carbon additives for the removal of vapors do not fulfill the requirement for the removal of solid particulate matter such as tar. Thus the problem of the tobacco industry; namely, how to economically produce a filter which is capable of selectively removing vapors such as hydrogen cyanide from the vapor phase of tobacco smoke, has to-date remained unsolved.

It has been reported that certain amines when applied to tobacco smoke filters remove noxious gases from the smoke more selectively than carbon. However, there are several decisive disadvantages to their use in tobacco smoke filters. For example, amines are notorious for their offensive odors and this property alone eliminates most of them from consideration for this use. Another disconcerting property of amines is that significant quantities vaporize into the tobacco smoke stream which, due to their basicity, causes skin irritations. Tobacco smoke filters containing amines of the heretofore known type also tend to impart an "off-taste" to the smoke which may be due to the imbalance caused by adsorption of acids by the amine. Furthermore, they cannot be used as additives to cellulose acetate, the most widely used filter medium, because they tend to degrade it.

According to this invention it has been found that the aforementioned difficulties of the prior art tobacco smoke filters can be substantially eliminated or completely overcome by the use of certain amines and/or amine salts that have been dissolved in a polyol. Surprisingly, the amine or amine salt, once dissolved in the polyol, becomes nonvolatile which in effect at once eliminates the foul odor, bad taste, and any health hazards that would result from the entrance of the amine vapors into the stream of tobacco smoke. These polyol-amine blends are solutions when suitably inserted into a stream of tobacco smoke and arranged to provide interstices for the passage of smoke therethrough, serves to selectively remove hydrogen cyanide and other ciliatoxics from the smoke. In fact, the amine-polyol blends are solutions equal to the heretofore used amine salts in removing hydrogen cyanide and ciliatoxins from the tobacco smoke but have the important commercial advantage of being less expensive and easier to use.

Therefore, an object of this invention is to disclose a filter element containing an amine or amine salt-polyol blend.

Another object of this invention is to describe a method of producing an amine or amine salt-polyol containing filter element.

These and other objects and advantages of this invention will be more apparent upon reference to the accom-

panying specification, specific working examples, and appended claims.

As briefly set out hereinabove, this invention involves the use of a polyol-amine blend or solution for selectively removing hydrogen cyanide and other ciliatoxins from tobacco smoke. The polyol-amine blends of the invention are prepared by dissolving the selected amine or amine salt in the selected polyol.

The amine used in the blends or solutions may be any primary, secondary, or tertiary amine including polyamines. Some amines which were found to be especially effective are; diethylamine, dibutylamine, octylamine, diethanolamine, diethylene triamine, ethanolamine, ethylenediamine, triethanolamine, benzylamine, and arginine. Various carboxylic acid salts of the same amines have also been found to be equally effective. These included acetic, lactic, citric, itaconic, and pyromellitic acids.

Any polyol in which the amine or amine salt is soluble may be used. The following have been found to be especially useful: glycerol; 1,2-ethanediol; 1,2-propanediol; 1,3-propanediol; 1,4-butanediol; 1,3-butanediol; 1,2,4-butanetriol; diethylene glycol; triethylene glycol; 1,2,6-hexanetriol; polyethylene glycol; sorbitol.

These polyol-amine and/or amine salt blends or solutions can be applied to filter tow or other filter medium by any conventional manner while the medium is being fabricated into filter rods. For example, the blend or solution can be sprayed on a filter medium at any point prior to the point where the medium is compacted and formed into a filter rod. Another way of adding this polyol-amine or amine salt solution to a filter medium is to employ a wicking device which "wipes" the desired amount of liquid on the medium, which is normally bloomed out (opened), at some point during its travel through the filter rod assembly machine.

As will be appreciated, the polyol-amine or amine salt blends or solutions can be applied to some granular or like carrier medium, such as carbon, and this medium can be applied to the tobacco smoke filter by sifting, dusting, shaking or the like. The polyol-amine and/or amine salt can also be mixed with a suitable liquid, such as a plasticizer, and then dispersed onto a filter medium. Glyceryl triacetate has been found to be an especially good dispersing liquid although volatile liquids, such as methanol, can also be used with excellent results. Furthermore, more than one amine and/or amine salt can be dissolved together in a polyol and then used in a tobacco smoke filter element if this is necessary or desirable.

The fibrous media upon which the blends or solutions of this invention may be used can vary over a wide range but is preferably a crimped continuous filament cellulose acetate tow usually having a denier per filament of about 1.6–20. However, it will be appreciated that such polyol-amine solutions may be equally effectively employed upon filters which are made from other base materials such as paper, cotton, polyester, propylene and polyethylene fibers, or any other suitable material that can be formed into tobacco smoke filters.

The polyol-amine additive may be applied to the paper, tow or other carrier materials in the amount of from about 10–80 mg. (milligrams) per filter, the preferred amount being about 20 to 60 mg. By uniform application to the surface of the fibrous media the blend or solution is enabled to take advantage of the large surface area which provides the contact necessary for effective hydrogen cyanide removal.

It also has been found that it is possible to produce a fibrous filtering unit which is capable of selectively removing hydrogen cyanide from a gaseous medium by spinning the fibers of the filter from a dope of celluolse acetate which contains an additive of the polyol-amine or amine salt solutions. Since these polyol-amine blends are embodied in the cellulose acetate fibers as the fibers are being spun, the necessity of including additional processing steps, materials and equipment into the manufacturing operation is alleviated. The selected polyol-amine blend, if properly prepared, can be mixed with selective types of cellulose acetate dopes and spun to give a filament that readily neutralizes the hydrogen cyanide in tobacco smoke. It has been found, for example, rather unexpectedly that the amines are not masked by the acetate to a degree which would prevent their effective removal of hydrogen cyanide when employed in tobacco smoke filters.

The spinning solution or dope from which the filaments containing the organic salt are spun can be produced in any one of several manners. In one instance this can be accomplished by adding directly to the cellulose acetate solution one or more of the amine or amine salts dissolved in a polyol. More specifically, these polyol-amine blends are added to an acetone solution of cellulose acetate in the amount of from about 5 to 30 percent based on weight of the cellulose acetate. After the polyol-amine blends have been added to the acetone solution of cellulose acetate, the mix is uniformly dispersed. The spinning solution containing the polyol-amine blends is now ready to be spun into filaments on a conventional spinning machine after which it can be formed into a tobacco smoke filter by any suitable manner.

As will be apparent, filters incorporating these polyol-amine and/or amine salt blends provide a means for selectively removing hydrogen cyanide from cigarette smoke vapors without the use of activated carbons, silica gel, molecular sieve or other materials commonly used for the physical adsorption of vapor. It has been found that such polyol-amine blends are capable of chemically reacting on contact with the hydrogen cyanide vapor to neutralize the vapor thereby assuring that hydrogen cyanide is not later released or otherwise eluted from the filter due to the increase in temperature of the filter during the smoking of the cigarette. Furthermore, such means employed for selectively removing hydrogen cyanide from the vapor phase of tobacco smoke does so without decreasing the capacity of the filter for removing solid particulate matter such as "tar" from the tobacco smoke. Since the additive for the filter element is an odorless, nonvolatile, nonirritant which can be applied to such materials as cellulose acetate without subsequent degradation of the material, it can be used freely without fear of its affecting the taste of the tobacco smoke or entering the smoke stream.

The subject matter which is regarded as the invention is clearly pointed out and distinctly claimed in the concluding portion of the specification. The invention, however, as to its organization and operation, together with the further objects and advantages thereof will best be understood by reference to the following examples which are preferred embodiments of the invention, but they are included merely for purposes of illustration and not as a limitation thereof.

TABLE I.—AMINE VAPORIZED INTO SMOKE FROM SOME REPRESENTATIVE FILTERS

Example	Filter additive	Quantity amine in smoke, μg.
1	Diethanolamine	420
2	Diethylamine	790
3	Ethanolamine	480
4	Dibutylamine	630
5	Diethanol ammonium acetate	50
6	Diethyl ammonium citrate	72
7	Diethanol ammonium citrate	10
8	Ethanol ammonium pyromellitate	8
9	Dibutyl ammonium lactate	70
10	Triethanolamine-glycerol	<5
11	Diethanolamine-glycerol	<5
12	Diethylamine-glycerol	12
13	Ethanolamine-1,2,3-butanetriol	<5
14	Dibutylamine-glycerol	7
15	Triethanol ammonium acetate-glycerol	<5
16	Diethanol ammonium acetate-glycerol	<5
17	Diethyl ammonium citrate-1,2-ethanediol	<5
18	Dibutyl ammonium lactate-1,2,6-hexanetriol	<5

The Examples 1 through 18 are prepared by adding a solution of the polyol-amine, with methanol as a solvent, to commercial cellulose acetate filter. After the methanol has been evaporated, each 10 mm. filter will contain 30 mg. of the amine. The amount of amine salt, which is prepared in ratios of one amino group to one carboxyl group, on the filters is greater by the quantity of acid used to neutralize the salt.

The amount of amine which entered the smoke is determined by radioactive tracer techniques. By application of radioactive amines and amine salts to the filters on cigarettes and trapping the smoke which passed through the filters, the quantity of amine in the smoke is quite accurately determined.

In summary, Table I shows that several of the amine salt filters which are effective for removing HCN from cigarette smoke release some amine into the smoke. These particular amine salts, being somewhat unstable to heat, partially decompose due to the rising temperature of the last few puffs of smoke. The amine products of the decomposition then vaporize into the smoke.

Example 19

With methanol as solvent, a solution of polyol-amine blend is prepared by adding a ratio of 1 mole diethanol ammonium acetate to 1.2 moles of glycerol. The solution of 40 percent polyol-60 percent amine is added to commercial cellulose acetate filters and after evaporation of the methanol, the 10 mm. filters will each contain 18 mg. (12 percent by weight) of the polyolamine blend.

The 10 mm. filters are now attached to king size cigarettes and the cigarettes smoked by an automatic smoking device which removed particulate matter from the smoke by means of a Cambridge filter. By a colorimetric test the smoke vapors will be found to contain only 8 μg. of hydrogen cyanide vapors as compared to 155 μg. of hydrogen cyanide found in an unfiltered cigarette smoked in the same manner.

In addition ciliatoxicity of the vapor phase of smoke from these filtered cigarettes is determined by the method which was described by Spears, Tryfiates, and Schultz at the 18th Tobacco Chemists' Research Conference (1964) [see Science, 153, No. 3741, 1248 (1966)]. This method uses clam gill cilia as the test specimen. This test will show that the filter reduces ciliastasis of the gas phase of smoke to zero.

Examples 20–31

A filter tow consisting of 15,000 crimped (18 crimps per inch) cellulose acetate fibers of 5 denier per filament is spread out or bloomed to form a band of approximately 14 inches in width. The bloomed band of cellulose acetate tow is then treated with the various polyol-amine or polyol-amine salt blends shown under the heading "Filter Additive" in Table II. This treating of the tow with the polyol-amine formulations is accomplished by any suitable method such as by using a roller or spray booth. In each case the amount of formulation added to the opened tow during its progress through the filter plug making machine is held within the range of 5 to 30 percent by weight based on the total weight of the filter element. In general the most useful polyol-amine solutions are those containing 50 to 80 percent by weight amine or amine salt. Since approximately 10 mg. of the amine or amine salt is needed in the tobacco smoke filter element to be effective, lower concentrations require the application of so much solution to the filter that a wet appearance is imparted to it.

Immediately after the polyol-amine additive is placed on the tow, a plasticizer such as triacetin is added to the rapidly moving tow. The tow is then recompacted into a tight bundle, drawn through a device that wraps it in cigarette paper, and cut into 90 mm. rods with a circumference of 25.3 mm. The wrapped filter rods are now stored at about 75° F. until they are firm. After the rods become firm they are cut to a 10 mm. length and attached to a cigarette. Before testing an additional 10 mm. filter is added to the cigarette; this filter being identical to the other but without he amine-polyol solution. The results of the tests are given in Table II.

TABLE II.—HCN CONTENT AND CILIATOXICITY OF SMOKE FROM FILTER CIGARETTES

Example	Filter additive	HCN content, μg.	Percent inhibition of cilia motion
20	None	155	65
21	Diethanolamine (100%)	5	4
22	Diethyl ammonium citrate (70%)-1, 2-ethanediol (30%).	2	3
23	Ethanol ammonium pyromellitate (70%). 1, 4. butanediol (30%).	12	3
24	Dibutyl ammonium lactate (50%)-1, 2, 6-hexanetriol (50%).	7	0
25	Diethanolamine (70%). glycerol (30%).	0	0
26	Diethylamine (70%)-glycerol (30%)	5	0
27	Ethanolamine (70%)-1, 2, 4-butanetriol (30%).	8	5
28	Dibutylamine (70%)-glycerol (30%)	4	0
29	Ethylene diamine (60%)-1, 2-propanediol (40%).	10	4
30	Diethylene triamine (70%)-glycerol (30%).	5	4
31	Triethanolamine (70%)-glycerol (30%).	70	45

From the foregoing description and illustrative examples it is apparent that the inventive concept of blending or dissolving certain amine or amine salts of organic acids with a polyol and then adding this blend or solution to carrier media of a tobacco smoke filter offers numerous detoxicating advantages over those filters previously used in the tobacco industry. For example, a filter so produced is a highly selective one which is capable of removing substantial amounts of the solid particulate matter, such as tar, found in tobacco smoke as the smoke moves through the interstices of the filter, while at the same time selectively removing hydrogen cyanides from the vapor phase of the tobacco smoke by neutralizing or reducing it to a solid by-product which cannot later be eluted from the filter. Furthermore, the fact that the polyol-amine blends may also be embedded within the cellulose filaments of the filter eliminates numerous problems that have been heretofore present in filters containing such additives. Furthermore, these polyol-amine blends may be incorporated in any of the known filter fibrous media used in the making of tobacco smoke filters such as, for example, cellulose acetate or paper. However, the fact that these polyol-amine and/or polyol-amine salts are less expensive, odorless, tasteless and harmless due to their nonvolatile characteristic makes them especially attractive to the tobacco industry.

Thus, the hereinabove described method and materials described for the selective removal of hydrogen cyanide from the vaporous phase of tobacco smoke has been found to be both surprising and effective in its ability to remove this highly undesirable component from tobacco smoke and still provide the tobacco smoke with a taste and aroma most desirable for the ultimate smoker.

We claim:

1. A tobacco smoke filter element adapted for the removal of deleterious and noxious materials from tobacco smoke which comprises a filter carrier medium having as an additive thereto, a material selected from the group consisting of an amine that has been dissolved in a polyol or amine salt that has been dissolved in a polyol.

2. The filter element of claim 1 wherein the amine salt is produced by reacting primary, secondary, or tertiary alkyl and hydroxylalkylamines containing no more than 8 carbon atoms with an acid.

3. The filter element of claim 2 wherein the amine is selected from the group consisting of diethylamine, dibutylamine, octylamine, diethanolamine, diethylenetriamine, ethanolamine, ethylene diamine, triethanolamine, benzylamine, and arginine.

4. The filter element of claim 2 wherein the acid is

selected from the group consisting of acetic, lactic, citric, itaconic, and pyromellitic acids.

5. The filter element of claim 1 wherein the polyol is selected from the group consisting of glycerol; 1,2-ethanediol; 1,2-propanediol; 1,3-propanediol; 1,4-butanediol; 1,3-butanediol; 1,2,4-butanetriol; diethylene glycol; triethylene glycol; 1,2,6-hexanetriol; polyethylene glycol; and sorbitol.

6. The filter element of claim 1 wherein the additive material is carried by a carrier medium selected from the group consisting of paper, cotton, cellulose acetate, propylene, polyethylene, and polyesters.

7. The filter element of claim 1 wherein at least 10 mg. of the additive material is contained in the filter element.

8. The filter element of claim 1 wherein the amine is selected from the group consisting of diethylamine, dibutylamine, octylamine, diethanolamine, diethylenetriamine, ethanolamine, ethylenediamine, triethanolamine, benzylamine, and arginine.

9. A cellulose acetate tow material adapted for being formed into a tobacco smoke filter element, said tow material having embodied therein a material selected from the group consisting of an amine that has been dissolved in a polyol or an amine salt that has been dissolved in a polyol.

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