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3,434,479

PERMANGANATE TOBACCO SMOKE FILTER
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7 Claims

ABSTRACT OF THE DISCLOSURE

A cigarette filter comprising a non-oxidizable, particulate support impregnated with at least one permanganate salt having a water solubility of not less than 100 grams per liter at room temperature in amounts of from about 5 to about 20 weight percent removes substantial quantities of nitrogen oxides from tobacco smoke without adverse effect on the taste of the smoke.

This invention relates to filters for cigarettes and other smoking articles.

Tobacco smoke, as is well known, consists of a gaseous or vapor phase in which are suspended liquid or semi-liquid droplets or solid particles (herein referred to generally as "droplets") which form the visible smoke stream. Many cigarette filters of commerce consisting of a bundle of cellulose fibers and convoluted crepe paper formed into a cylindrical plug, are designed to and do remove varying proportions of these droplets passing through them. They do not effectively remove gaseous molecules, except for components soluble in the filtering material, with the result that the gaseous or vapor phase normally passes through such a filter substantially unaffected by it.

The vapor phase of smoke obtained from tobacco contains small quantities of oxides of nitrogen, more particularly nitric oxide and nitrogen dioxide. Nitrogen oxides are known to be toxic to humans in relatively small concentrations and therefore their removal is desirable.

In recent years considerable attention has been devoted to the development of new cigarette filters which will remove substantial quantities of toxic constituents of tobacco smoke while exerting only a minimal effect on the taste of the cigarette. Among the filters which have been proposed are various filters comprising a solid adsorbent contained in a cylindrical chamber formed by a wrapper and a pair of filter plugs, usually of cellulose acetate, at either end. Among the adsorbent materials which have been proposed are activated charcoal, alumina, natural and synthetic clays, and silica gel. Filters containing such adsorbents have usually been of limited effectiveness, and have been notably ineffective in removing certain harmful and irritating constituents of tobacco smoke. Impregnation of the adsorbent with various materials has been proposed in order to improve the adsorption of specific constituents of tobacco smoke. However, prior to this invention there has been no filter which is capable of removing substantial quantities of oxides of nitrogen.

An object of this invention is to provide a filter for cigarettes and other smoking articles which is capable of removing substantial quantities of nitrogen oxides without adversely affecting the taste of the smoke.

According to this invention a cigarette or other smoking article has a filter which contains a non-oxidizable solid adsorbent impregnated with at least one water-soluble permanganate salt having a water solubility not less than 100 grams per liter at room temperature (25° C.). The impregnant can be either a single permanganate salt

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or a mixture of permanganates. Generally the impregnant is an inorganic permanganate salt. The total weight of impregnant is in the range of about 5 to 20 percent of the total weight of dry impregnated adsorbent. Most effective action is obtained when the impregnant is present in amounts of about 10 to 15 percent of the weight of the dry impregnated adsorbent. Amounts of permanganate either less than 5 percent or greater than 20 percent are less effective.

The permanganate impregnant may be any water-soluble permanganate salts or mixtures of such salts. The water solubility of the permanganate salt must be at least about 100 grams per liter, and the term, "water-soluble permanganate" as used herein, denotes a salt having at least this water solubility. Usually the impregnant consists of one or more permanganates of light metals in Group I and Group II of the Periodic Table. Calcium permanganate, magnesium permanganate, lithium permanganate, sodium permanganate, and zinc permanganate are examples of suitable impregnants. Mixtures of water-soluble permanganates may also be used as the impregnant.

The support may be any of the common adsorbent materials which are not capable of further oxidation. For example, bauxite, activated alumina, clay, kaolin, and silica gel may be used as an adsorbent material. Charcoal has not been found to be suitable for impregnation with a permanganate according to this invention, and it is believed that this lack of suitability is probably due to the fact that charcoal and permanganate react during impregnation, reducing the permanganate and oxidizing the charcoal, thereby reducing the effectiveness of the impregnant.

The physical form of the adsorbent has been found to be crucial to its effectiveness. The surface area of the adsorbent is critical and must be in the range of about 5 to about 200 square meters per gram in order to obtain efficient nitrogen oxide removal. The high surface area in solid adsorbents is attributable to a multiplicity of pores, usually of varying diameters. Pores of very large diameter, i.e., in excess of about 10,000 angstrom units (1 micron) result in a sacrifice of surface area and hence a less efficient filter. Pores may have a diameter of as little as about 5 angstroms and yet contribute to the effectiveness of the solid material as an adsorbent. Generally the average pore diameter of effective adsorbents according to this invention is in the range of about 50 to about 10,000 angstroms. The total pore volume should be in the range of about 0.1 to about 2.0 cc. per gram. Adsorbents having higher pore volumes are generally fragile structures of limited practical application. Lower pore volumes necessitate a sacrifice of surface area in pores of useful diameter.

The particle size of the adsorbent is generally in the range of 20 to 200 mesh (U.S. Standard screen size). Particles coarser than 20 mesh are avoided because they cannot be packed closely, with the result that channeling occurs and the removal of nitrogen oxides is less than that obtained when the particles are in the 20 to 200 mesh range. Particles finer than 200 mesh are avoided because of excessive draw resistance and difficulty in handling.

The adsorbent may be impregnated with a water-soluble permanganate according to conventional impregnation techniques. The adsorbent to be impregnated is soaked in a solution of the permanganate for a time sufficient to reach substantial equilibrium. For example, soaking in a permanganate solution for about ½ hour at room temperature has been found to give effective impregnation. As already noted, any of the water-soluble permanganates, particularly the permanganates of metals of Groups I and II of the Periodic Table, are useful impregnants.

The permanganate solution generally has a concentration of at least 20 percent by weight, the concentration of

the salt increasing as the desired loading of impregnant on the adsorbent increases. Thus, for example, a 35 percent solution of calcium, magnesium, lithium, or zinc permanganate, will generally give an impregnated adsorbent containing about 11 to 13 percent by weight of the permanganate, based on the weight of dry impregnated adsorbent. The solution may contain either a single permanganate or a mixture of permanganates as afore-described.

After the adsorbent material has been soaked in the impregnating solution long enough for the pores to fill up with the impregnating solution, the adsorbent material and the liquid phase may be separated by any conventional means such as filtration. The adsorbent is then dried. Vacuum drying has been found to be especially useful. Drying may be carried out expeditiously at room temperature, although no deleterious effect results from the use of moderate heat, i.e., drying temperatures up to about 60° C.

A cigarette of this invention comprises a tobacco column wrapped in cigarette paper having attached thereto, by means of a paper wrapper, a filter assembly which includes a permanganate-impregnated adsorbent as described and claimed herein. This permanganate-impregnated adsorbent may be incorporated in known filter assembly structures, such as those described in U.S. Patents 2,881,770, 2,915,069, and 3,251,365, in place of the adsorbents described therein. In a preferred embodiment of this invention, permanganate-impregnated adsorbent is incorporated in the filter structure of Patent 3,251,365, which includes a pair of filter plugs of cellulose acetate or other filter material secured in coaxial alignment by a paper wrapper, and an adsorbent-filled chamber enclosed by the plugs and the wrapper. Relatively coarse adsorbent particles, e.g. 20-40 mesh, are preferred in this type of filter. Alternatively, the permanganate-impregnated adsorbent may constitute a surface coating on convoluted crepe paper or on a fibrous material such as cellulose acetate or other material described in Patent 2,881,770. Fine adsorbent particles, preferably in the range of 100 to 200 mesh, may be blown on to the fibrous material to form this type of filter. The permanganate-impregnated adsorbent may also be incorporated in a cigarette filter paper as described in Patent 2,915,069. Another useful filter assembly is a three-part structure including a pair of cellulose acetate filter plugs at either end and a core of permanganate-impregnated adsorbent granules bonded together with a polymeric adhesive such as polyethylene. Still other filter structures containing permanganate-impregnated adsorbent as described herein are within the purview of this invention. The filter assembly may be of any convenient length, e.g. about 20 mm.

This invention will now be described in further detail with reference to specific embodiments thereof. All weight percentages of impregnant given in the examples are based on the total dry weight of adsorbent plus impregnant.

EXAMPLE 1

Activated alumina pellets (Harshaw Chemical Company, Grade A1-0104) were crushed and screened, and the particles having a size in the range of 20 to 40 mesh (U.S. Standard screen size) were retained. These particles had a surface area of 77 square meters per gram, an average pore diameter of 210 angstrom units, and a pore volume of 0.41 cc. per gram.

Twenty gram samples of the alumina particles were immersed in 50-gram portions of impregnating solutions containing various concentrations of calcium permanganate, $\text{Ca}(\text{MnO}_4)_2 \cdot 5\text{H}_2\text{O}$. The particles were allowed to soak in the impregnating solutions at room temperature and pressure for 30 minutes. The liquid was filtered off, and the impregnated particles were vacuum dried at room temperature overnight. The dried impregnated samples were then again screened to remove fines and agglomerates formed during the drying step, retaining the particles in

the size range of 20 to 40 mesh. The quantity of permanganate in each impregnated sample was determined by taking a small aliquot of the impregnated adsorbent, washing out the permanganate with water, and titrating the solution.

Portions of each of the dried impregnated adsorbents were packed into cigarette filter chambers 6 mm. in length and 8 mm. in diameter, formed by an 8 mm. ID glass tube and a pair of porous cellulose acetate plugs, each 6 mm. long and spaced apart by 6 mm. Each filter unit was then attached to an unfiltered cigarette 65 mm. in length and 8 mm. in diameter. Cigarettes of the same length, diameter, and tobacco blend were used in all tests reported in this specification. The sample cigarettes were smoked by a standard smoking technique described in an article by J. R. Newsome, V. Norman and C. H. Keith, Tobacco Sci. 9, 102-110, 1965, which takes a puff of 40 ml. volume (measured at standard temperature and pressure) of 2 seconds duration every 60 seconds. Each cigarette was smoked in 8 puffs, leaving a butt approximately 30 mm. long. For control purposes an unfiltered cigarette was smoked without any filter unit attached.

The smoke from each cigarette was collected and analyzed for oxides of nitrogen (NO and NO_2) according to the analytical procedure of Saltzman, J. Anal. Chem., 26, 1949 (1951).

Table I below indicates the weight percentage of calcium permanganate in each impregnating solution, the weight percent of calcium permanganate impregnant in each adsorbent sample, and the percentage of nitrogen oxides removed in each case.

TABLE I

Wt. percent $\text{Ca}(\text{MnO}_4)_2$ on alumina.	2.4	5.1	9.6	14.1	18.7	30.1
Wt. percent $\text{Ca}(\text{MnO}_4)_2$ in solution.	5	10	20	30	38	70
Percentage nitrogen oxides removed.	84	66	77	83	63	11

The effect on ciliary motility was determined using excised rabbit trachea and following the procedure of Kensler and Battista, New England Journal of Medicine, 269, 1161-1166 (1963). A sample cigarette attached to a filter containing alumina impregnated with 14 percent by weight of calcium permanganate was smoked in the above described smoking machine. For comparison purposes an unfiltered cigarette was also smoked in the machine. The filter cigarette showed no inhibition of ciliary motility after 8 puffs, while the unfiltered control showed 50 percent inhibition after 4 puffs.

Reduction in components that inhibit the growth of the KB line of human cells was determined according to the method of Thayer and Kensler, Science, 146, 3644, p. 642 (1964). A sample cigarette attached to a filter unit containing alumina impregnated with 14 percent by weight of calcium permanganate and an unfiltered control cigarette were used in this test. The reduction in cytotoxicity in the test cigarette was about 50 percent, compared to the control cigarette.

EXAMPLE 2

Twenty gram samples of alumina particles of 20 to 40 mesh size, obtained as described in Example 1, were impregnated with lithium permanganate, magnesium permanganate, and zinc permanganate respectively. In each case a 35 percent permanganate solution was prepared by dissolving 35 grams of the permanganate in 65 grams of water. Each sample was immersed in one of the impregnating solutions for 30 minutes at room temperature and pressure, was recovered by filtration, and vacuum dried overnight. A portion of each sample was then introduced into the chamber of a filter unit and test cigarettes were smoked as described in Example 1. The weight percentage of permanganate impregnant in each adsorbent sample, the content of nitrogen oxides in microliters (STP), and the percentage removal of nitrogen oxides (NO and NO_2) for each of the filter materials, as compared to an

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unfiltered cigarette, were measured. Results are given in Table II below:

TABLE II

	Weight percent permanganate	Percent (NO and NO ₂) removed
Zn(MnO ₄) ₂ -----	12.7	79
LiMnO ₄ -----	12.8	70
Mg(MnO ₄) ₂ -----	11.0	79

EXAMPLE 3

Activated alumina, 20 to 40 mesh, obtained as described in Example 1, was impregnated with 14 percent by weight of sodium permanganate, based on the weight of dry unimpregnated adsorbent. Impregnation was accomplished by immersing the alumina in a 35 percent aqueous solution of sodium permanganate for 30 minutes at room temperature and pressure. A portion of the impregnated adsorbent was then packed into a cigarette filter chamber 6 mm. in length and 8 mm. in inside diameter as described in Example 1. A second filter, also 6 mm. long and 8 mm. in inside diameter, was filled with a filter material prepared by combining equal volumes of the above-described impregnated alumina and unimpregnated charcoal. Test cigarettes using each of the two filters were smoked in the smoking machine as described in Example 1. An unfiltered control cigarette and a second control cigarette using a charcoal filter having a chamber 6 mm. long and 8 mm. in diameter were also smoked according to the same procedure. The amounts of nitrogen oxides in micrograms per puff were measured on each of the two test cigarettes and the two control cigarettes. Results (average of 2 cigarettes in each test) are given in Table III below.

TABLE III

Cigarette filter material:	NO/NO ₂ , μg./puff (av.)
Na permanganate-alumina -----	7.0
Na permanganate-alumina/charcoal -----	19.4
Charcoal -----	31
No filter -----	31

These results indicate that the permanganate-impregnated alumina filter of this invention reduces the amount of nitrogen oxides by about 75 percent. The combination filter containing both charcoal and permanganate-impregnated alumina takes advantage of the superior adsorptive power of charcoal for organic irritants such as acetaldehyde and isoprene, although it is less effective than the filter containing permanganate-impregnated alumina alone for the removal of nitrogen oxides.

EXAMPLE 4

Twenty gram samples of activated alumina, 20 to 40 mesh, having a surface area of 180 square meters per gram, an average pore size of 96 angstroms, and an average pore volume of 0.43 cc./gm. (Girdler Catalyst Department of Chemetron Chemicals, Type T126), were impregnated in calcium permanganate solutions of various concentrations following the procedures of Example 1. The dried impregnated adsorbents were incorporated into filters which were tested in the smoking machine as described in Example 1. Results are given in Table IV below.

TABLE IV

Wt. percent Ca(MnO ₄) ₂ in alumina..	1.2	4.0	7.8	11.8	17.0	22.2
Wt. percent Ca(MnO ₄) ₂ in solution..	3	10	20	30	40	50
Percent NO and NO ₂ removal.....	16	29	57	64	66	28

EXAMPLE 5

Activated kaolin ("Kaosorb," Minerals and Chemicals Phillip Corporation), having a surface area of 95 square meters per gram, was impregnated in a 29 percent sodium permanganate solution as described in Example 1. This yielded impregnated kaolin containing 16.1 percent by weight of sodium permanganate, based on the weight of dry impregnated adsorbent. This material was packed into a cigarette filter chamber and evaluated in the smok-

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ing machine test as described in Example 1. Analysis of the smoke for nitrogen oxides showed that the filter removed 62 percent of the nitrogen oxides in the smoke.

EXAMPLE 6

Activated bauxite ("Porocel," Minerals & Chemicals Phillip Corporation), having a surface area of 96 square meters per gram, and a particle size of 20 to 40 mesh, and an average pore diameter of 310 angstroms, was impregnated in a 30% aqueous sodium permanganate solution as described in Example 1. The impregnated bauxite contained 13.7% by weight of sodium permanganate, based on the weight of the dry impregnated adsorbent.

A portion of the impregnated adsorbent weighing 0.312 grams was packed into a cigarette filter chamber and evaluated in the smoking machine as described in Example 1. Analysis of the smoke showed that the filter removed 72% of the nitrogen oxides.

What is claimed is:

1. A cigarette filter comprising a wrapper, a tobacco charge, and a filter assembly, said filter assembly including filter material comprising a solid non-oxidizable particulate adsorbent having a multiplicity of pores with an average pore diameter of about 50 to about 10,000 angstrom units, a total pore volume of about 0.1 to about 2.0 cubic centimeters per gram, a surface area in the range of about 5 to about 200 square meters per gram, and a particle size predominantly in the range of 20 to 200 mesh, said filter material being impregnated with at least one permanganate salt having a water solubility of at least 100 grams per liter at 25° C., the total amount of impregnant being in the range of about 5 to 20 percent by weight, based on the weight of impregnated adsorbent.

2. A cigarette filter according to claim 1 in which the amount of impregnant is in the range of about 10 to about 15 percent by weight, based on the weight of impregnated adsorbent.

3. A cigarette filter according to claim 1 in which said adsorbent is activated bauxite.

4. A cigarette filter according to claim 1 in which said adsorbent is activated alumina.

5. A cigarette filter according to claim 1 in which said chamber includes said solid non-oxidizable adsorbent and activated charcoal.

6. A cigarette filter according to claim 5 in which said solid non-oxidizable adsorbent is impregnated with sodium permanganate.

7. A filter assembly for smoking articles comprising a wrapper and a solid non-oxidizable adsorbent having a multiplicity of pores with an average pore diameter of about 50 to about 10,000 angstroms units, a total pore volume of about 0.1 to about 2.0 cubic centimeters per gram, and a surface area in the range of about 5 to about 200 square meters per gram, impregnated with at least one water-soluble permanganate, the amount of impregnant being in the range of about 5 to 20 percent by weight, based on the weight of impregnated adsorbent.

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