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COMPLETE SPECIFICATION

Filter Material

5 We, LIGGETT & MYERS TOBACCO COMPANY, a corporation organised under the laws of the State of New Jersey, United States of America, of 630 Fifth Avenue, New York, State of New York, United States of America, 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

10 by the following statement:—

15 This invention relates to a filtering material and filter construction for removing deleterious materials from tobacco smoke while maintaining a pleasant tasting smoke. It is intended for use either attached to cigarettes and cigars, or as a separate cartridge filter for pipes and cigarette or cigar holders.

20 Tobacco smoke, as is well known, consists of a gaseous or vapour 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. The cigarette filters of commerce, consisting of a bundle of cellulosic fibres or convoluted creped 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 molecule, except for components, soluble in cellulose acetate, with the result that the gaseous or vapour phase normally passes through such a filter substantially unaffected by it.

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35 There exists in the vapour phase of smoke obtained from tobacco and other natural leafy materials variable and generally small quantities of the acidic gaseous compounds hydrogen cyanide and hydrogen sulphide, which exhibit a specific toxic action on the human tissues with which they come into contact. These materials are also found to contribute to the inhibition of the action of the whiplike appendages or cells called cilia which line the trachea and bronchioles. These cells rhythmically beat to and fro, and by this action carry

foreign bodies up and out of the respiratory tract. Toxic materials such as those mentioned are found to inhibit and in higher concentrations destroy this beating action in excised test specimens. It is postulated that a similar retardation occurs in the smoker so that the presence of these toxic materials in tobacco smoke impairs the capacity of the human lung to eliminate undesirable foreign material.

55 Hydrogen cyanide and hydrogen sulphide have a considerable vapour pressure at room temperature and above. They may be classified as gases or highly volatile liquids. During the processes of imperfect combustion such as occur in cigarettes, pipes, and cigars they are liberated from the tobacco or are synthesized in a wholly vaporized state. In the brief period of time during which they are carried from the combustion zone to the smoker's mouth, there is relatively little opportunity for these volatile materials to condense into the semi-liquid and solid droplets which form the visible smoke stream. These materials are consequently almost entirely in a vaporized state as they leave the smoking article and enter the smoker's mouth.

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90 The commonly utilized cigarette filter of commerce removes from tobacco smoke a proportion of the droplets passing through it. This is accomplished by a combination of diffusional, impactive, and direct collision of the droplets with the filter fibres. Upon collision the droplets are retained on the fibres by the surface attraction between the extremely small particles and the relatively large fibre. Such fibrous filters are, however, not particularly effective for removing vaporized components from the smoke stream by the processes of physical and chemical adsorption. The smooth and non-porous nature of the commonly used fibrous filtering materials, while effective in capturing tobacco smoke droplets, does not present a sufficient surface area to effectively adsorb gaseous molecules.

[Price 4s. 6d.]

cellulose

It is calculated that an ordinary cellulose acetate cigarette filter plug has a surface area ranging from 1,000 to 10,000 square centimetres per gram of material. This affords insufficient surface area for effective adsorption of gaseous molecules, and has no significant selectivity. In some instances, where a vaporized material is sufficiently soluble in the fibrous material so that its surface concentration is rapidly depleted, a significant removal can be achieved by the process of absorption. An example of such material present in tobacco smoke is phenol, which has a pronounced solubility in cellulose acetate filtering material. Cellulose acetate filters allow both hydrogen cyanide and hydrogen sulphide to pass through in undesirably high concentrations.

In attempts to improve the adsorptive properties of tobacco smoke filters, various treatments of ordinary filtering material, various new fibrous filtering materials, and various adsorbents added to ordinary filtering materials have been proposed. Among the materials and treatments proposed a number of well-known adsorbents such as activated charcoal, alumina, natural and synthetic clays and silica gel have been proposed as additives to tobacco smoke filters. These materials are classified as adsorbents and are used in gas-stream treatment because they possess in common the characteristic that their specific surface area exceeds a million square centimetres per gram of material. A good grade of gas adsorbent quality activated carbon, for example, has a specific surface area in excess of 5 million square centimetres per gram. In general, the preferred method heretofore used of including these adsorbents in tobacco smoke filters has been by dusting, spraying, tumbling, slurring, or otherwise incorporating the finely-divided adsorbent into the fibrous material which forms the filter or a part thereof.

Such adsorbent-containing tobacco smoke filters are only partially effective for several reasons. One is that the adsorbent is often rendered ineffective by the incorporation process and subsequent handling in the cigarette manufacturing and distribution process, in that water, plasticizing agents, glues, adhesives and volatile flavouring materials, in prolonged close contact with the finely-divided adsorbent, partially or completely utilize the adsorbent surface, thus decreasing its capacity to adsorb gaseous molecules from the smoke stream.

Another reason is that when adsorbent and fibrous filtering materials are intimately mixed, condensed droplets tend to be deposited in such a filter on or near an adsorbent particle, with the result that relatively non-volatile smoke constituents quickly permeate the adsorbent and thus reduce its capacity for adsorption of gaseous molecules.

Further disadvantages of such known adsorbent filters are that the inclusion of considerable quantities of adsorbent in a tobacco smoke filter has both a marked effect upon the draw resistance of the smoking article, and upon the taste of the smoke stream. A powdered or finely divided adsorbent dispersed in a matrix of fibrous filtering elements impedes the flow of smoke through the filter and requires that the smoker apply additional suction to withdraw his normal amount of smoke. If enough adsorbent is included to remove considerable quantities of deleterious materials, the draw resistance is well above a desirable and comfortable level.

On the other hand, as our studies indicate, segregation of the adsorbent into a portion of the filter separated from the fibrous portion thereof, has pronounced deleterious effects on the taste of the smoke. When adsorbents such as charcoal, alumina, or silica gel are incorporated in a cigarette filter (segregated from the cellulose acetate filter) in sufficient quantities to considerably reduce the levels of gaseous materials, it is found that the taste of the smoke stream is far from pleasing to experienced smoke tasters. Although some irritating factors are reduced, the smoke is found to have an astringent, bitter, drying taste. Other mineral adsorbents have a similar overall effect, with minor modifications in taste and aroma depending on the particular adsorbent. The general result is that a pleasing smoke is obtained only when the amount of adsorbent is reduced to the point where it is well in minor proportion to the fibrous filtering agent. When present at such diminished levels it is insufficiently effective in removing undesirable smoke constituents.

The principal object of this invention is to provide a filtering material and a tobacco smoke filter capable of extracting from tobacco smoke a significantly large proportion of the acidic gaseous compounds hydrogen cyanide and hydrogen sulphide, and at the same time so operating upon all components of the smoke stream that the taste of the smoke is unimpaired or is improved.

According to one aspect of the invention our filtering material, for use in connection with smoking articles of any kind, comprises adsorbent granules of any of the known gas-adsorbent materials having a specific surface area exceeding a million square centimetres per gram, preferably but not necessarily activated charcoal, these granules having a particle size between 8 and 50 mesh (all mesh sizes herein are U.S. Standard Screen) and being impregnated with the finely-divided oxides of both iron and zinc, each oxide being present in an amount not less than 1% nor more than 13% by weight on the adsorbent and the two oxides together not exceeding 14% by weight thereon, preferably one or both of the oxides being present in an amount

between 4% and 6% by weight on the adsorbent. Stated another way, the filter material is impregnated with 1% to 13% by weight thereof of an oxide selected from the group consisting of iron and zinc oxides, plus at least 1% of the other (non-selected) oxide in said group, said oxides being present in finely divided forms and together present in an amount not exceeding 14% of the weight of the adsorbent granules; preferably, the filter material is impregnated with between 4% and 6% of the selected oxide.

According to another aspect of the invention we provide a tobacco smoke filter, for use either in a cigarette or in a cigar or cigarette holder, consisting of two spaced-apart filter plugs of conventional and known type, for example, of perforated paper, plastic, metal, a bundle of cellulosic fibres or convoluted crepe papers which are secured in coaxial alignment by means of a wrapper or tube which also secures them separated a short distance from each other thus forming a chamber between them defined by their opposing end faces and by said wrapper or tube, the chamber containing a suitable amount of the filtering material above described.

According to still another aspect of the invention, we prepare the filtering material above described by soaking the adsorbent material, for example activated charcoal, either before or after screening to appropriate particle size, in an aqueous mixed solution of (a) a substance selected from the group consisting of zinc carbonate, zinc oxide and zinc acetate, (b) a substance selected from the group consisting of ferric ammonium citrate, ferric citrate, ferrous citrate, ferrous ammonium citrate, ferrous acetate and ferrous ammonium carbonate, and (c) ammonia, a preferred mixture being zinc carbonate, ferric ammonium citrate and ammonia, for 5 to 20 minutes, and then heating the wetted adsorbent material under conditions and for a time long enough to decompose the adsorbed salts to their respective metal oxides and to drive off liberated ammonia, carbon dioxide and other gases without oxidizing the adsorbent material. The relative amounts of ingredients (a) and (b) are selected in proportion to the desired ratio of zinc and iron oxides which it is desired to deposit upon the adsorbent.

In the drawing annexed to and forming a part of this specification Figure 1 is a perspective view of a cut away cigarette equipped with a filter tip of our invention.

Figure 2 is a longitudinal section of a filter cartridge suitable for use in the stems of pipes and cigar or cigarette holders and containing an embodiment of our invention.

Referring to Figure 1, 10 is a cigarette column of the dimensions ordinarily found in filter cigarettes, which is comprised of a

mass of shredded tobacco, 11, wrapped in cigarette paper 12. Attached to this column 10, by means of a paper wrapper 13, is a filter assembly 14. This assembly 14 is originally prepared in a rod containing multiple filter units. This is sectioned and attached to the tobacco column 11 by methods commonly used in filter cigarette manufacture. The filter assembly 14 consists of three parts — the plugs 15 and 16 and our filtering material packed in space 17 between the plugs. The plugs 15 and 16, one located next to the tobacco column 10 and the other at the end of the filter assembly remote from the tobacco, consist of fibrous tobacco smoke filtering material of the kind generally used in filter cigarette manufacture. It may, for instance, be a plasticized bundle of cellulose acetate fibres of denier per filament between 1.5 and 25, and with a total denier between 30,000 and 90,000. Alternatively a short filter plug composed of convoluted creped paper may be used. In practice each fibrous or creped filter plug 15 and 16 is respectively wrapped in an additional paper wrapper 18, 19 to facilitate handling during the filter making process. The length of each of plugs 15 and 16 may be between 5 and 10 millimetres and its diameter such that the finished assembly will match the diameter of the tobacco column 11. The two plugs 15 and 16 are enclosed within and secured in coaxial alignment by a tubular wrapper 20 of paper which holds them in spaced-apart relationship so as to form a chamber 17 between them whose walls are defined by the opposed ends of plugs 15 and 16 and by the exposed inner annular surface of wrapper 20 between the plugs.

Chamber 17 is loosely packed with our filtering material as described below. This chamber may be from 2 to 15 millimetres in length, and may contain from 40 to 400 milligrams of granular impregnated filtering material.

Referring to Figure 2, another embodiment of this invention is pictured therein. For insertion into the stems of pipes and suitable plastic or metallic cigarette and cigar holders, a cartridge filter assembly 24 is provided. This assembly consists of a tube 25 of paper, plastic material or metal. This tube may be fitted at each end with plugs 26 and 27, of porous material through which tobacco smoke can pass. Suitable plugs of perforated paper, plastic or metal, or fibrous filter plugs can serve this purpose. These plugs may be of such dimensions and porosity as to remove practically none, or else considerable quantities, of the passing smoke droplets. Alternatively either or both of the plugs 26 and 27, may be replaced by perforated end caps made of thin paper, plastic or metal. The plugs and/or caps may be guided, welded or solvent sealed to the cartridge tube 25. The chamber

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27 created by the cartridge tube 25 and the end plugs and/or caps 26 and 27 is loosely packed with our filtering material described below, the amount depending upon the volume of the chamber.

Various adsorbent substances are suitable for impregnation and use according to this invention. Examples are activated charcoal, alumina, natural and synthetic clays, and silica gel, each of which has a specific surface area exceeding one million square centimetres per gram. The preferred adsorbent is a high density activated charcoal with good mechanical strength. Such material of gas adsorbent grade has a specific surface area in excess of 5 million square centimetres per gram. Suitable carbons for this purpose are obtained from nut shells or can be manufactured from bituminous coal.

The adsorbent, when used in a tobacco smoke filter, should be in the form of a granules or particles of a size between about 8 and 50 mesh, that is, of such size that they will pass through a U.S. Series number 8 sieve but not through a U.S. Series number 50 sieve. Particles larger than 8 mesh are difficult to handle and to incorporate in the chamber section of the filter assembly; particles smaller than 50 mesh adversely affect the draw resistance.

The impregnated adsorbent, for example activated carbon, may be prepared by soaking a highly activated carbon in a mixed aqueous solution of zinc carbonate, ammonia, and ferric ammonium citrate. Such a solution can be prepared by separately dissolving zinc carbonate in ammonia water and ferric ammonium citrate in water. The two solutions are mixed in the desired amounts to obtain a treatment solution. Alternatively and preferably zinc carbonate, ferric ammonium citrate, and water are placed in a reaction vessel and ammonia is introduced until a solution saturated with ammonia at 28°C. is achieved. This solution can be used as it is or can be appropriately diluted for soaking the carbon.

Following a 5 to 20 minute soaking, during which considerable quantities of air are replaced by the treatment solution in the porous carbon, the excess solution is removed by suction filtration. The wetted carbon granules are then roasted to decompose the adsorbed salts to the respective metal oxides. The adsorbed zinc ammonium carbonate component decomposes with the liberation of ammonia and carbon dioxide leaving a residue which is chiefly zinc oxide. This residue is uniformly distributed throughout the porous carbon granules. Similarly the ferric ammonium citrate component of the solution decomposes with the evolution of ammonia and the thermal decomposition products of the citrate ion. The residual material left from the decomposition of this component of the solu-

tion is a mixture of ferrous, ferroso-ferric, and ferric oxides, the lower oxidation states being obtained through reduction of the original ferric ion by the carbon adsorbent. This mixture of iron oxides is referred to as "iron oxide" throughout the specification and claims. It is found that this decomposition is essentially complete after heating for one hour or more at temperatures between 175 and 350°C. in a sufficient flow of air to carry off the gaseous decomposition products. Complete removal of these gaseous decomposition products is achieved if the carbon is heated to temperatures between 300 and 500°C. in an inert atmosphere for periods in excess of 45 minutes. Steam, nitrogen, and carbon dioxide have been found to be effective as an inert atmosphere.

In the treatment solution, other salts of the desired metals may be utilized in place of zinc carbonate and ferric ammonium citrate. For example, zinc oxide or zinc acetate may be substituted for zinc carbonate. Ferric citrate, ferrous citrate, ferrous ammonium citrate, ferrous acetate, or ferrous ammonium carbonate may be satisfactorily substituted for ferric ammonium citrate. Inorganic ferric or ferrous salts are excluded as ferrous and ferric hydroxides precipitate from them when they are mixed into the ammoniacal zinc carbonate solution.

The percentages by weight of zinc oxide and iron oxide can be best controlled by adjustment of the concentration of the zinc compound and iron compound, respectively, in the treatment solution. For example, treatment of 10 grams of Pittsburgh Chemical Co. gas adsorbent carbon, grade BPL, 12 to 30 mesh, with 24 millilitres of a solution containing 18.6 milligrams per millilitre of zinc ion and 21.9 milligrams per millilitre of ferric ion yielded after the prescribed heat treatment a carbon containing 2.30% zinc oxide and 1.76% iron oxide computed as Fe_2O_3 . treatment of another 10 gram carbon sample with 24 millilitres of a solution containing 109.0 mg./ml. of zinc ion and 77.5 mg./ml. of ferric ion gave upon roasting an impregnated adsorbent containing 7.96% zinc oxide and 5.31% iron oxide, again computed as Fe_2O_3 . These examples and that described later illustrate the establishment of the oxide level by the concentration of metal salts in the treatment solution.

Alternatively, the oxide levels may be controlled by repeated treatments with solutions containing salts of one or both of the desired metals. In such treatments the carbon is soaked in the desired solution and the wetted carbon is heated at 110°C until dry, and then the process is repeated until the desired level of treatment is attained. Such a method is desirable when difficultly soluble iron salts such as ferrous ammonium carbonate are utilized in the treatment solution.

It has been found that treatment of adsorbents with mixtures of oxides at a total oxide level of greater than 1% and less than 14% of the weight of the adsorbent is effective to accomplish the objects of this invention. With impregnations of less than 1%, the treated adsorbent exhibits the undesirable taste properties of the untreated adsorbent. At oxide level of greater than 14%, the adsorption capacity of the adsorbent is adversely affected. Treated activated carbon containing from 1 to 13% by weight of carbon of zinc oxide and 1 to 13% by weight of iron oxide are found to be effective, with the preferred level being 4 to 6% of each oxide.

The following illustrates in detail the best manner of carrying out the invention known to us, and sets forth the result of tests indicating the utility of the invention.

A mixture of 447 grams of zinc carbonate, 1584 grams of ferric ammonium citrate (brown) and 2160 millilitres of water was dissolved by bubbling ammonia gas through the mixture until saturation was achieved at 28°C. 750 millilitres of this solution were contacted with 500 grams of Pittsburgh Chemical Co. carbon, grade BPL, 12 to 30 mesh for ten minutes with stirring. The excess solution was removed by vacuum filtration and the wetted carbon was roasted for one hour in a slow stream of steam at temperatures between 400° and 500°C. It was found that the resultant carbon contained 5.8% iron oxide computed as Fe_2O_3 and 4.3% zinc oxide. 85 to 100 milligrams of this impregnated carbon was placed in a 5 millimetre chamber between two 7.5 mm plasticized cellulose acetate filter plugs with a denier per filament of 2.8 and a total denier of 50,000. These 20 mm plugs were attached to 65 mm cigarettes containing a standard commercial tobacco blend to make a finished 85 mm cigarette with a circumference of 24.75 millimetres. These cigarettes were designated by the code number 7A.

For comparison purposes several other sample cigarettes were prepared. These all had the same dimensions, tobacco blend, and cellulose acetate filter plugs as those described for the Sample 7A cigarettes. They differed only in the material in the central chamber. These materials and the cigarette code number designations are as follows:

Sample 5A: Chamber empty.

Sample 6A: Chamber filled with untreated BPL carbon as obtained from the manufacturer.

Sample 7A: Chamber filled with BPL carbon impregnated as described above with 5.8% iron oxide (computed as Fe_2O_3) and 4.3% zinc oxide.

Sample 8A: Chamber filled with BPL

carbon impregnated with 7.3% iron oxide (computed as Fe_2O_3) and no added zinc oxide.

Sample 9A: Chamber filled with BPL carbon impregnated with 6.6% zinc oxide and no added iron oxides.

The impregnating solution used in making Sample 8A cigarettes contained 600 grams of ferric citrate in 1 litre of saturated ammoniacal solution. The impregnating solution in the case of Sample 9A consisted of 187.5 grams of zinc carbonate and 40.0 grams of citric acid per 1 litre of saturated ammoniacal solution. The carbon used and the impregnation and roasting procedures for Samples 8A and 9A were the same as that used in preparing Sample 7A.

The five above sample cigarettes, consisting of a control (5A), an untreated carbon (6A), a carbon treated with both zinc and iron oxides (7A), a carbon treated with iron oxide only (8A), and a carbon treated with zinc oxide only (9A) were subjected to the tests shown below.

The five sample cigarettes were tested for the content of hydrogen cyanide in the effluent smoke stream. Samples of 5 of each of the five sample cigarettes were smoked on an automatic smoking machine to a 30 mm butt by taking 40 ml. puffs of 2 seconds duration once every minute. The smoking machine and smoke collection system were that described by Keith and Newsome in *Tobacco Science*, 1, 51 (1957). In general, the cigarettes were consumed in 7 puffs. Following the smoking cycle for all five cigarettes, the collection traps, which were cooled to minus 70°C. during the smoking operation, were allowed to warm up to 0°C. in an ice bath, and were maintained at that temperature for 10 minutes to allow interfering volatile materials to escape. The collection traps were then extracted repeatedly with small volumes of 0.1 N sodium hydroxide solution until slightly less than 250 ml. of solution was obtained. This solution was made up to 250 ml. with 0.1N NaOH for the cyanide measurement.

The cyanide content of the smoke solutions was measured by an adaptation of the spontaneous electrolysis technique of Baker and Morrison as published in *Analytical Chemistry*, 27, 1306 (1955). A solution containing cyanide ion when placed between a silver electrode and a platinum electrode generates an electrolytic current over a period of several minutes. By reading this current at fixed times with specified resistances in the circuit and comparing it with that obtained from known cyanide solution, a measure of the cyanide content is obtained. The measurement of the standard cyanide solution is made directly after the measurement of the smoke solution, and is made in exactly the same manner and



volatile

with the same resistances in the circuit. Since the current generated is directly proportional to the cyanide concentration, a simple ratio of the current readings for the unknown smoke solution and known cyanide solution gives a measure of the hydrogen cyanide content of the smoke solution. These values were computed in the units of micrograms of hydrogen cyanide per 40 ml. puff of smoke. The samples of five cigarettes of each of Sample cigarettes 5A, 6A, 7A, 8A and 9A were measured and their average values and the standard deviation of those averages are listed in Table I.

The hydrogen sulphide content of the smoke obtained from Sample cigarettes 5A, 6A, 7A, 8A and 9A was estimated by a color reaction involving the formation of methylene blue dye. Specifically the method described by M. B. Jacobs in the "Analytical Chemistry of Industrial Poisons, Hazards and Solvents" 2nd edition, page 326, was utilized. 13 millilitres of 1% aqueous zinc acetate and 0.5 ml. of 10% aqueous sodium hydroxide are placed in an evacuated flask of approximately 55 millilitre volume. The flask is then connected through a flow-limiting orifice and a "Cambridge" (registered Trade Mark) CM-113 filter pad to a lighted cigarette, thus forming a smoking apparatus. The vacuum in the flask which is adjusted to a level which will give a 40 ml. puff on the cigarette, draws smoke from the cigarette through the filter pad and orifice. The filter pad separates out the condensed smoke particles, and the orifice limits the rate at which smoke gases are drawn from the cigarette, thus providing a normally shaped puff which lasts for two seconds similar to that taken by automatic smoking machines. In this experiment the fourth puff was taken on all cigarettes, as this should represent most nearly the average of all puffs taken on each cigarette. Previous puffs were taken on the automatic smoking machine previously mentioned, and the cigarette was transferred to the flask smoking apparatus between the third and fourth puffs. After drawing the smoke gases into the evacuated bulb, the bulb was closed off and shaken to absorb the hydrogen sulphide in the reagent solution. Following this, 2.5 mls. of a solution containing 0.1 gram of N,N-dimethyl-p-phenylene diamine sulphate in 100 mls. of 1:1 HCl in H₂O is added. 0.5 ml. of a 0.02 molar solution of ferric chloride in a 1:9 hydrogen chloride water mixture is also added. The smoke gas solution with these additions is further shaken and allowed to stand overnight for complete colour development, at which time its optical density is measured at a wavelength of 665 millimicrons. By comparison of this optical density with that of dye solutions containing known amounts of hydrogen sulphide, the concentration of hydrogen sulphide in the smoke gases can be estimated. Such measure-

ments were made on 10 cigarettes of each of the samples, 5A, 6A, 7A, 8A and 9A. The average and standard deviation of the average of these measurements are presented in Table I.

The five sample cigarettes were tested for their inhibitory effect on the motility of the ciliated cells of rabbit trachea. The technique utilized was an adaptation of that described by Battista in the June 1962 issue of the *ADL Review* published by Arthur D. Little, Inc., of Cambridge, Mass. In this measurement, seven cigarettes of each of the samples 5A, 6A, 7A, 8A and 9A were smoked in an apparatus which drew a 40ml puff once a minute, and the smoke was led directly over excised specimen of rabbit trachea. The ciliated specimen was mounted at a inclined angle in an exposure chamber and was continuously fed with Tyrode's physiological salt solution at its lower extremity. The action of the hair-like cilia carried a film of this solution up the inclined surface of the specimen and let it drop off the upper end into the chamber. The concentrated smoke cloud from each puff was allowed to remain in contact with the trachea for 10 seconds at which time the exposure chamber was flushed with air saturated with water vapour, until the smoke from the next puff was admitted.

The normal action of the cilia removing small solid particles of foreign matter was observed by dusting a small number of 50 to 100 micron carbon particles on the ciliated tissues and observing the motion of these particles along the trachea by means of a microscope. It was observed that the cilia would move the particles at a constant rate of 20 to 30 millimetres per minute when the exposure chamber was filled with saturated air. The ciliated specimens were exposed to successive puffs from each cigarette until all ciliary action ceased or until the cigarette was expended after eight puffs.

In Samples 6A, 7A, 8A and 9A where ciliary action was slowed down but not completely inhibited, the percentage inhibition after 8 puffs is given in Table I. Sample cigarette 5A caused a complete inhibition of ciliary action in 3 to 6 puffs. Commercial unfiltered cigarettes frequently cause complete cessation of ciliary action after one puff in this test and generally cause complete cessation after two puffs.

The five sample cigarettes were submitted to a taste panel of 3 members who were experienced in the art of describing and evaluating the taste and aroma of cigarette smoke. The operation of panels of this type is explained in *Perfumery and Essential Oil Record*, 49, 130 (1958) and in an article by E. I. Salzman in *Bulletin CORSETA*, No. 1961-1, page 120 (1961). The cigarettes were coded and unidentified during this evaluation. Each panelist rated each cigarette on a scale

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of 0 to 5 for desirable taste elements, i.e., sweet fragrance and smoothness, and for undesirable taste elements, i.e., bitter taste and throat irritation. On this scale 0 indicates absence or a very low level of the quality, while 5 indicates a high level. These results are given in Table I.

Each of the five sample cigarettes was then submitted to a 9-member taste panel composed of men who had considerable experience in the art of describing and evaluating

the taste and aroma of cigarette smoke. The taste characteristics were the same as those evaluated in the 3-man panel. The cigarettes were coded and unidentified, as in the 3-man test. Each panelist made his evaluation independently; no notes were compared between panelists during the test. The same rating scale of 0 to 5 which was used in the 3-man evaluation was also used in the 9-man evaluation

TABLE I

Sample	5A	6A	7A	8A	9A
Activated charcoal	(none)	C	C	C	C
Oxide impregnant		(none)	Fe+Zn	Fe	Zn
Content of HCN, micrograms/puff average	37.3	18.2	15.2	21.0	18.5
Content of HCN, standard deviation	(± 1.4)	(± 1.8)	(± 1.2)	(± 1.0)	(± 0.9)
Content of H ₂ S, micrograms/puff average	4.39	2.40	1.86	2.09	1.63
Content of H ₂ S, standard deviation	(± 0.23)	(± 0.19)	(± 0.20)	(± 0.20)	(± 0.10)
Ciliary Inhibition, % after 8 puffs	*	16%	15%	23%	30%
Desired taste elements					
Scale 0 to 5)					
Sweet fragrance (3-man panel)	0	0	3	1	1
Sweet fragrance (9-man panel)	1.8	2.2	2.7	2.3	2.2
Smoothness rating (3-man panel)	1	3	4	3	2
Smoothness rating (9-man panel)	2.0	3.2	3.4	2.9	2.7
Undesired taste elements					
(Scale 0 to 5)					
Bitter taste (3-man panel)	3	2	1	2	3
Bitter taste (9-man panel)	2.5	2.1	1.7	2.2	2.3
Throat irritation (3-man panel)	4	2	1	3	2
Throat irritation (9-man panel)	2.8	1.9	2.1	2.6	2.3

* There was 100% ciliary inhibition after 3 to 6 puffs in each test made upon a Sample 5A cigarette.

The cigarette filter of this invention, containing both iron and zinc oxides impregnated on charcoal (Sample No. 7A) removed considerably more hydrogen cyanide from tobacco smoke than did a filter of activated charcoal impregnated with either iron oxide or zinc oxide alone (Samples 8A and 9A respectively), or an unimpregnated charcoal filter (Sample 6A). The smoke from Sample cigarette 7A of this invention contained more hydrogen sulphide than the smoke from Sample cigarette 9A, but less than the smoke from any of the other cigarettes. Cigarettes containing the filters of this invention caused the least ciliary inhibition of any of the samples tested, 15% after 8 puffs. The ciliary inhibition obtained with cigarettes containing activated charcoal filters impregnated with either iron oxide or zinc oxide alone (Samples 8A and 9A respectively) was much higher. Cigarettes of this invention are markedly superior in taste to the other cigarettes tested, both in the presence of desired taste elements and the absence of undesired taste elements, as found by both the 3-member and 9-member taste panels.

Other grades of gas adsorbent carbon can be used in place of the grade illustrated in the example with equivalent results.

WHAT WE CLAIM IS:

1. Filter material comprising adsorbent granules having specific surface area exceeding a million square centimetres per gram, a particle size between 8 and 50 mesh, and impregnated with 1% to 13% by weight thereof of an oxide selected from iron and zinc oxides, plus at least 1% of the other (non-selected) oxide in said group, said oxides being in finely-divided form and together present in an amount not exceeding 14% of the weight of the adsorbent granules.
2. Filter material according to claim 1, in which the adsorbent granules are activated charcoal.
3. Filter material according to any one of the preceding claims, in which one or both

of the oxides are present in amount between 4% and 6%.

4. A tobacco smoke filter consisting of a first filter plug, a second filter plug coaxial with the first, a wrapper securing said plugs in coaxial alignment and separated from each other to form a chamber between them defined by their opposing end faces and by said wrapper, said chamber containing filter material according to any one of the preceding claims.

5. A cartridge tobacco smoke filter assembly consisting of a tube with a perforated end cap secured to said tube at each end thereof characterized by the fact that the space within said tube and between said end caps contains filter material according to any of claims 1 to 3.

6. A process of making a filter material according to any one of claims 1 to 3, which comprises soaking the adsorbent material in an aqueous mixed solution of (a) zinc carbonate, zinc oxide or zinc acetate, (b) a ferric ammonium citrate, ferric citrate, ferrous ammonium citrate, ferrous citrate, ferrous ammonium acetate, ferrous acetate or ferrous ammonium carbonate, and (c) ammonia, and heating said adsorbent material to decompose the adsorbed salts.

7. A process according to claim 6, in which said heating is carried out in air at temperatures between 175° and 350°C.

8. A process according to claim 6, in which said heating is carried out in an inert (non-oxidizing) atmosphere at temperatures between 300° and 500°C.

9. Filter material substantially as hereinbefore described.

10. A tobacco smoke filter substantially as hereinbefore described and as illustrated in the accompanying drawings.

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Chartered Patent Agents.
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The cigarette filter of this invention, containing both iron and zinc oxides impregnated on charcoal (Sample No. 7A) removed considerably more hydrogen cyanide from tobacco smoke than did a filter of activated charcoal impregnated with either iron oxide or zinc oxide alone (Samples 8A and 9A respectively), or an unimpregnated charcoal filter (Sample 6A). The smoke from Sample cigarette 7A of this invention contained more hydrogen sulphide than the smoke from Sample cigarette 9A, but less than the smoke from any of the other cigarettes. Cigarettes containing the filters of this invention caused the least ciliary inhibition of any of the samples tested, 15% after 8 puffs. The ciliary inhibition obtained with cigarettes containing activated charcoal filters impregnated with either iron oxide or zinc oxide alone (Samples 8A and 9A respectively) was much higher. Cigarettes of this invention are markedly superior in taste to the other cigarettes tested, both in the presence of desired taste elements and the absence of undesired taste elements, as found by both the 3-member and 9-member taste panels.

Other grades of gas adsorbent carbon can be used in place of the grade illustrated in the example with equivalent results.

WHAT WE CLAIM IS:

1. Filter material comprising adsorbent granules having specific surface area exceeding a million square centimetres per gram, a particle size between 8 and 50 mesh, and impregnated with 1% to 13% by weight thereof of an oxide selected from iron and zinc oxides, plus at least 1% of the other (non-selected) oxide in said group, said oxides being in finely-divided form and together present in an amount not exceeding 14% of the weight of the adsorbent granules.

2. Filter material according to claim 1, in which the adsorbent granules are activated charcoal.

3. Filter material according to any one of the preceding claims, in which one or both

of the oxides are present in amount between 4% and 6%.

4. A tobacco smoke filter consisting of a first filter plug, a second filter plug coaxial with the first, a wrapper securing said plugs in coaxial alignment and separated from each other to form a chamber between them defined by their opposing end faces and by said wrapper, said chamber containing filter material according to any one of the preceding claims.

5. A cartridge tobacco smoke filter assembly consisting of a tube with a perforated end cap secured to said tube at each end thereof characterized by the fact that the space within said tube and between said end caps contains filter material according to any of claims 1 to 3.

6. A process of making a filter material according to any one of claims 1 to 3, which comprises soaking the adsorbent material in an aqueous mixed solution of (a) zinc carbonate, zinc oxide or zinc acetate, (b) a ferric ammonium citrate, ferric citrate, ferrous ammonium citrate, ferrous citrate, ferrous ammonium acetate, ferrous acetate or ferrous ammonium carbonate, and (c) ammonia, and heating said adsorbent material to decompose the adsorbed salts.

7. A process according to claim 6, in which said heating is carried out in air at temperatures between 175° and 350°C.

8. A process according to claim 6, in which said heating is carried out in an inert (non-oxidizing) atmosphere at temperatures between 300° and 500°C.

9. Filter material substantially as hereinbefore described.

10. A tobacco smoke filter substantially as hereinbefore described and as illustrated in the accompanying drawings.

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