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CIGARETTE FILTER

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No Drawing. Continuation-in-part of application Ser. No. 262,653, Mar. 4, 1963, now Patent No. 3,251,365. This application Mar. 21, 1966, Ser. No. 535,739
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ABSTRACT OF THE DISCLOSURE

Compositions useful in cigarette filters are composed of a high surface area granular support, such as charcoal having a particle size of less than about 8 mesh and a specific surface area of one million square centimeters per gram, impregnated with 1 to 13% of an oxide of cobalt, copper or zinc and 1 to 13% of an oxide of cobalt, copper, zinc, silver or molybdenum, there being no more than 14 percent total oxides. Other useful compositions are composed of granules having particle sizes of not greater than 50 mesh and 1 to 14% of at least one oxide of cobalt, copper or zinc.

This application is a continuation-in-part of our copending application Ser. No. 262,653 filed Mar. 4, 1963 now Patent No. 3,351,365.

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.

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 cellulosic fibers 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 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.

There exists in the vapor 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 sulfide, 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 cilia which line the trachea and bronchioles. These cilia 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 human smoker so that the presence of these toxic materials in tobacco smoke impairs the capacity of the human lung to eliminate undesirable foreign material.

Hydrogen cyanide and hydrogen sulfide have a considerable vapor pressure at room temperature and above. This 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

state. In the brief period of time during which they are from the tobacco or are synthesized in a wholly vaporized 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.

The commonly utilized fibrous cigarette filter 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 fibers. Upon collision the droplets are retained on the fibers by the surface attraction between the extremely small particles and the relatively large fiber. 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. It is calculated that an ordinary cellulose acetate cigarette filter plug has a surface area ranging from 1,000 to 10,000 square centimeters 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 a 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 sulfide to pass through in undesirably high concentrations.

In attempts to improve the absorptive properties of tobacco smoke filters, various treatments or 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 centimeters 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 centimeters per gram. In general, the preferred method heretofore used for including these adsorbents in tobacco smoke filters has been by dusting, spraying, tumbling, slurrying, or otherwise incorporating the finely-divided adsorbent into the fibrous material which forms the filter or a part thereof.

A finely divided adsorbent can, for example, be added to a tow of cellulose acetate or other textile filaments of the kind ordinarily used in cigarette filter manufacture by sifting the adsorbent particles into the moving band of unplasticized or plasticized tow just before enclosure of the filaments in a paper wrapper in the filter making process. Alternatively the adsorbent particles can be blown into the mass of filaments by their inclusion in a jet of high pressure air which serves to fluff up and co-mingle the filaments in a confined space just preceding the actual formation of the filter rod. If desired, the adsorbent particles may be slurried with a suitable solvent and applied by painting the slurry onto the moving tow and subse-

quently removing the solvent by heat or other suitable means, leaving a tow of filaments essentially uniformly coated with adsorbent particles. Such methods of adding adsorbents to cellulose acetate filaments are described in U.S. Patent No. 2,881,770 and elsewhere.

Another method of incorporating adsorbents in filters which has been disclosed is that of embedding an adsorbent in a matrix of highly convoluted and partially torn cellulosic or non-cellulosic paper. Such incorporation can either be achieved by dusting dry or spraying slurried adsorbent onto the previously prepared paper filtering material, or as disclosed in U.S. Patents No. 2,801,638 and No. 2,915,069, it can be incorporated in the pulp from which such paper is formed.

Still another method of incorporating adsorbents into filters is to prepare a three-chamber filter having cellulose acetate filter plugs as the two end chambers and an open chamber filled with charcoal as the center chamber. Such a filter is described in our above mentioned Patent No. 3,351,365.

Known 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 flavoring 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. It is generally found that adsorbent filters, in which the adsorbent is co-mingled with the fibrous filtering material, are not as effective in the removal of hydrogen cyanide and hydrogen sulfide as might be expected or desired even when freshly made due to deactivation during manufacture. Such activity as they do possess is generally dissipated within the space of several weeks, so that the ultimate consumer quite frequently obtains cigarettes which essentially fail to perform their intended task in removing deleterious materials.

Another disadvantage of known adsorbent filters is that the inclusion of effective quantities of partially deactivated adsorbents in the tobacco smoke filter has a marked effect on the taste of the smoke stream. If enough adsorbent is included to remove considerable quantities of deleterious 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 generally found to have an astringent, bitter, or drying taste. Different charcoals or 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 components.

It is also found that inclusion of relatively large amounts of finely divided adsorbent in a tobacco smoke filter has an adverse effect on the draw resistance of the filter. The presence of such adsorbent in the 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 partially deactivated adsorbent is included to remove considerable quantities of deleterious materials, the draw resistance is above a desirable and comfortable level.

A primary object of this invention is to provide a cigarette or other smoking article having a filter which includes an improved impregnated adsorbent capable of removing substantial quantities of hydrogen cyanide and hydrogen sulfide without adversely affecting the taste of the smoke.

According to one embodiment of this invention a cigarette or other smoking article has a filter which contains an improved adsorbent material comprising a solid adsorbent having a particle size finer than 8 mesh and preferably in the range of 8 to 50 mesh, impregnated with about 1 to 13% by weight, based on the weight of unimpregnated adsorbent granules, of an oxide of cobalt, copper, or zinc, plus about 1 to 13% by weight, based on the weight of unimpregnated adsorbent granules, of at least one other oxide of cobalt, copper, zinc, silver, or molybdenum. The combined weight of metal oxide impregnants does not exceed 14% of the weight of unimpregnated adsorbent granules.

According to another embodiment of this invention, a cigarette or other smoking article is prepared having a filter which includes a finely divided solid adsorbent in which the particles are predominantly finer than 50 mesh, impregnated with at least one oxide of copper, cobalt, or zinc. The adsorbent according to this embodiment of the invention may also be impregnated with at least one other oxide, which is selected from the oxides of cobalt, copper, zinc, iron, silver and molybdenum. The amount of each metal oxide present is in the range of 1 to 13% by weight, based on the weight of dry unimpregnated adsorbent granules, and the combined weight of metal oxides does not exceed 14% of the weight of unimpregnated adsorbent granules.

Various adsorbent materials are suitable for impregnation and use according to this invention. Examples are activated charcoal, alumina, natural and synthetic clays and silica gels, each of which has a specific surface area exceeding one million square centimeters per gram. The preferred adsorbent is highly activated charcoal. Such material of gas adsorbent grade has a specific surface area in excess of 5 million square centimeters per gram. Suitable charcoals for this purpose are obtained from nut shells or can be manufactured from bituminous coal, petroleum residues, and other carbonaceous materials.

According to one embodiment of the invention, the adsorbents are in the form of granules or particles of a size less than 8 mesh, that is, of such size that they will pass through a U.S. Series No. 8 sieve. Particles larger than 8 mesh are difficult to handle and to incorporate in the filtering material. There is no limit to the fineness of particles which will accomplish the desired action, but in order to eliminate the problems associated with the handling of very fine adsorbent materials and to provide cigarettes which contain sufficient adsorbent for effective HCN and H_2S removal without excessive draw resistance, it is frequently preferable for the adsorbent particles to be predominantly in the range of 8 to 50 mesh.

The first step in impregnating an adsorbent for use according to this invention consists in immersing the adsorbent in an aqueous ammoniacal impregnating solution containing compounds of the metals to be impregnated. The impregnating solution contains a compound of cobalt, copper, or zinc which is soluble in the aqueous ammoniacal solution plus at least one other compound of cobalt, copper, zinc, silver, or molybdenum, which is also soluble in the aqueous ammoniacal solution. All of the impregnating metals form complex ions with ammonia, which greatly enhance their solubility in aqueous solutions. The impregnating procedure will be described with particular reference to carbon, but it will be understood that any of the aforementioned solid adsorbents can be impregnated in the same manner.

The impregnating solution contains at least 20% by weight of NH_3 (some of which is present in the form of NH_4OH). For best results the solution should be saturated or substantially saturated with respect to ammonia; that is, it will contain about 28 or 29% by weight of ammonia. It has been found that impregnating solutions which are substantially saturated with respect to ammonia or at least contain more than 20% by weight of ammonia are far superior to solutions having lower concentrations of ammonia. This is particularly true when the carbon or charcoal to be impregnated has a very high surface area, for example in excess of about 1 million square centi-

meters per gram. The reason for this improved efficiency of impregnation is believed to be that the substantially saturated ammoniacal solutions of this invention yield a much greater gas volume than conventional impregnating solutions during the subsequent heating step in which the metal compound is converted into a metal oxide. The rapid liberation of large quantities of ammonia during heating prevents the plugging of the pores by the impregnant.

The impregnating solution also contains one or more metal compounds which are soluble in the aqueous ammoniacal solution and decomposable into a metal oxide impregnant. The metal compound is generally a salt of an organic acid such as carbonic acid or oxalic acid. Carbonates are preferred salts because they result in the liberation of carbon dioxide as well as ammonia during the subsequent heating step, furnishing additional quantities of gas to prevent plugging of the pores of the carbon. Other organic salts such as oxalates, citrates and tartrates are similarly preferred since they liberate copious quantities of CO_2 and other gaseous products upon thermal decomposition. Salts such as chlorides which leave a residue on heating in the carbon are preferably avoided, since it is desirable to convert all of the soluble metal impregnating compound into the metal oxide.

A concentration of metal salts in the impregnating solution is such as to give an adsorbent containing 1 to 13% by weight, preferably 4 to 6% by weight, of an oxide of cobalt, copper, or zinc, plus 1 to 13% by weight, preferably 4 to 6% by weight, of a second metal oxide selected from the oxides of cobalt, copper, zinc, silver and molybdenum, following roasting of the adsorbent as will be hereinafter described. All weights herein are based on the weight of dry unimpregnated adsorbent. The combined weight of metal oxide impregnants is not greater than 14% of the weight of dry unimpregnated adsorbent.

After immersion of the carbon for a sufficient length of time to yield a product of the desired composition, the wet carbon is removed from the excess impregnating solution, as for example by vacuum evaporation. The wet carbon is then roasted at a temperature in the range of 175° C. to 500° C. in order to convert the metal compound in the impregnating solution into a corresponding metal oxide and to evaporate the water of the impregnated solution. The furnace in which roasting is carried out is preferably preheated to a temperatnre of about 160° to 180° C., or higher if desired, in order to heat the carbon rapidly as it is introduced into the furnace. The rapid heating of carbon in the drying operation causes rapid liberation of gaseous ammonia. This is beneficial in preventing the pores of the carbon from becoming clogged with the metal oxide impregnant. Where the metal compound in the impregnating solution is a carbonate, carbon dioxide is also liberated during the heating step, and this further aids in the impregnation of the pores of the carbon and in the prevention of plugging of the pores.

Heating may be carried out in either an inert atmosphere or in an oxygen-containing atmosphere. For example, the carbon may be roasted in an air current at temperatures in the range of about 175° to about 350° C. A preferred mode of heating, however, is to pass a current of inert gas such as nitrogen through the carbon while tumbling in a suitable apparatus such as a rotary dryer at a temperature in the range of about 300° to about 500° C. and preferably about 400° to about 500° C. Tumbling time is that which is sufficient to convert the metal compound into the corresponding metal oxide. Good results have been obtained with 30 to 60 minutes of tumbling at 400° to 500° C.

As an alternative to the use of a single impregnating solution, a pair of aqueous ammoniacal impregnating solutions, each containing a salt of the metal to be impregnated, may be used. This technique is especially advantageous when one of the metals to be impregnated is silver. It is not critical which metal is impregnated first. According to this technique dry carbon is immersed in the first impregnating solution, and is then removed therefrom and excess solution removed by suitable means such as vacuum filtration. The carbon is then dried at normal drying temperatures, i.e. 110° to 120° C. Excessive temperatures sufficient for roasting are avoided at this stage. The carbon is then placed in the second impregnating solution, and after soaking, is removed, and the excess solution removed by suitable means such as vacuum filtration. The carbon is then rotated as aforedescribed in order to convert both metal compounds to the corresponding oxides.

The impregnated adsorbents prepared as described above can be incorporated in filter cigarettes of various types. These adsorbents are particularly advantageously incorporated into the center chamber of a three-chamber filter such as that shown and described in our copending application Serial No. 262,653, filed Mar. 4, 1963. The filter according to the aforesaid application comprises a pair of plugs in coxial alignment, which are spaced apart to form an empty chamber therebetween which is filled with impregnated adsorbent granules. The two filter plugs preferably consist of plasticized cellulose acetate tow having a large number of substantially longitudinally extending crimped filaments with a denier per filament of 1.5 to 25 and a total denier of 30,000 to 90,000. However, the impregnated adsorbents of this invention can also be incorporated in other known types of filter cigarettes, such as those described in the aforementioned U.S. Patents 2,881,770 and 2,915,069.

The impregnated adsorbens of this invention have been found to decrease markedly the amounts of hydrogen cyanide and hydrogen sulfide reaching a smoker's mouth when these impregnated adsorbents are incorporated into cigarette filters in conjunction with fibrous filtering agents. Where such incorporation would formerly reduce the capacity of the adsorbent to remove hydrogen cyanide and hydrogen sulfide from the flowing smoke screen due to a deactivation of the absorbent during the manufacturing process, the advantage of these metal oxides in the absorbent is found to maintain the filter capacity both during the manufacturing and cigarette aging processes. It is found for example that filters containing a treated adsorbent of this invention when attached to a cigarette for periods of six months or more continue to remove from the smoke screen essentially the same amount of hydrogen cyanide as they did when new. It is also found that such impregnated adsorbents are unimpaired in their initial capacity for adsorbing hydrogen cyanide when moistening and flavoring agents are added to the adsorbent in appreciable quantities. For example, addition of water in amounts of up to 35% of the weight of the adsorbent, addition of water and propylene glycol in amounts of 1 to 10% of each material, and addition of menthol, a known strongly adsorbed flavoring agent, in amounts up to 5% of the weight of the adsorbent, are found not to materially reduce the capacity of an impregnated charcoal for removing hydrogen cyanide from tobacco smoke.

According to a second embodiment of this invention, a finely divided adsorbent and particularly charcoal having a particle size of predominantly 50 mesh and smaller is used as the solid adsorbent. The adsorbent according to this invention may have some particles of slightly larger size, generally not any larger than 40 mesh. Most of the particles of adsorbent according to this embodiment are in the range of about 50 to 100 mesh as a rule.

The adsorbent is impregnated according to this embodiment of the invention with at least one oxide of cobalt, copper or zinc. In addition, the adsorbent may also be impregnated with at least one other metal oxide selected from the oxides of cobalt, copper, zinc, iron, silver and molybdenum. Each of the metal oxides is present in an amount of 1 to 13% by weight, and preferably 4 to 6% by weight, of the unimpregnated adsorbent granules. The combined weight of all metal oxides

present as impregnants is not in excess of 14% of the weight of unimpregnated adsorbent granules.

The charcoal or other adsorbent is impregnated according to this embodiment of the invention is substantially the same manner as in the first embodiment, except that a somewhat wider variety of impregnating solutions may be employed in view of the greater number of metal oxides which may be impregnated according to this embodiment of the invention. The impregnating solution in general is an ammoniacal solution containing about 20 to 29% by weight of ammonium hydroxide plus solutions of salts of the impregnating metals which are soluble in the ammoniacal solution. The metal compounds are generally salts and preferably carbonates, although other organic salts are also advantageously used. The concentration of metal salts is chosen so as to give the desired metal oxide amounts after roasting of the impregnated adsorbent. According to this embodiment of the invention, the adsorbent may be impregnated with a single metal oxide, i.e. an oxide of cobalt, copper, or zinc, rather than with a pair of oxides. In that instance, of course, the impregnating solution contains a compound of only the one material. Where a pair of metal oxides are to be impregnated, the impregnating solution contains salts corresponding to each of the oxides. Alternatively, a pair of aqueous ammoniacal solutions, each containing a salt of one of the metals to be impregnated, may be used in lieu of a single solution containing salts of both metals.

A roasting procedure is carried out in the same manner as in the first embodiment. This results in the decomposition of the metal salts into corresponding oxides. Where iron is one of the impregnant metals and charcoal is the adsorbent, some reduction of iron from the ferric to the ferrous state takes place.

The finely divided impregnated adsorbent of this invention may be incorporated into cigarette filters such as those described in U.S. Patents Nos. 2,881,770 and 2,915,069. The charcoal may be incorporated on the surface of cellulose acetate filaments as described in the Patent No. 2,881,770. This may be done for example by passing a continuous filament tow of cellulose acetate yarn through a slurry of impregnated charcoal in water. The cellulose acetate yarn may contain about 2.0 denier per filament and a total denier of about 25.0, although these values are merely representative and in no sense limiting. The ratio of impregnated carbon to cellulose acetate is in the range of about 0.1 to 1. Impregnated charcoal or other adsorbents of this invention may also be incorporated in a paper filter such as that described in the aforementioned Patent No. 2,915,069. In that case the charcoal is preferably included in the paper sheet by adding the impregnated charcoal along with the paper stock to the beater, forming paper sheet, and then preparing the filter. In either case, the filter comprises a fibrous cellulosic material with individual granules or particles of adsorbent adhering to the surfaces of the fibers. The finely divided adsorbents of this second embodiment of the invention are not suitable for incorporation into three-chamber filters such as those described in our aforesaid application Ser. No. 262,653, because the draw resistance of cigarettes having such filters becomes excessive when substantially all of the adsorbent particles are finer than about 40 mesh. Instead it is necessary that the fine particles of this embodiment be in adhering relationship with a cellulosic filter material as has been described earlier in this paragraph.

Filters containing a finely divided adsorbent according to this second embodiment of the invention, i.e. predominantly 50 mesh and finer, remove hydrogen cyanide and hydrogen sulfide more efficiently from cigarette smoke than do otherwise identical filters employing a coarser adsorbent. Thus for example, a filter containing carbon impregnated with iron and zinc oxides incorporated into a cellulose acetate filament matrix are found to be more efficient in the removal of hydrogen cyanide and hydrogen sulfide thaan are filters containing charcoal having a particle size range of predominantly 14 to 40 mesh or even 30 to 40 mesh, also impregnated with iron and zinc oxides and incorporated into the identical cellulose acetate matrix. The differences in the amount of hydrogen cyanide removed is quite surprising and striking. For example, the content of hydrogen cyanide in cigarette smoke has been found to be approximately 60% less when finely divided (less than 50 mesh) charcoal impregnated with iron and zinc oxides was used than when charcoal having a particle size range of about 14 to 40 mesh and also impregnated with iron and zinc oxides was used, the oxide amounts and all other characteristics of the cigarettes including tobacco, type of filter, and length of both filter and cigarette, were otherwise identical. The impregnated adsorbents according to this second embodiment of the invention also give significantly greater hydrogen cyanide removal than do filters containing unimpregnated charcoal of the same particle size.

This invention will now be described further with reference to specific embodiments thereof.

A series of stock solutions for use in impregnating carbon were prepared as follows:

Stock Solution 1.—21.0 grams of cobaltous carbonate (reagent grade) was dissolved in an aqueous solution containing about 15 ml. of concentrated ammonium hydroxide (NH_3 approximately 28% by weight) and about 50 ml. of aqueous citric acid (citric acid 40% by weight). The cobaltous ion was allowed to oxidize to the cobaltic ion by allowing the solution to stand in air with stirring for 1 hour, and the solution was diluted to 200 ml. with concentrated ammonium hydroxide and then saturated with gaseous NH_3. This gave a solution containing 52 grams per liter of cobalt (as Co), 93 grams per liter of citric acid, and 28% by weight of ammonia.

Stock Solution 2.—70.0 grams of cupric acetate monohydrate (reagent grade) was dissolved in sufficient concentrated ammonium hydroxide (NH_3 approximately 28% by weight) to form a solution having a volume of 200 ml. and containing 113 grams per liter of copper.

Stock Solution 3.—25.0 grams of zinc carbonate (reagent grade) was dissolved in sufficient concentrated ammonium hydroxide (NH_3 approximately 28% by weight) to form a solution having a volume of 200 ml. and containing 65 grams per liter of zinc.

Stock Solution 4.—120 grams of ferric citrate trihydrate (USP VIII grade) was dissolved in sufficient ammonium hydroxide (NH_3 approximately 28% by weight) to form a solution having a volume of 200 ml. and containing 112 grams per liter of iron.

Stock Solution 5.—28.0 grams of molybdenum trioxide (reagent grade, 85% MoO_3 by weight) was dissolved in sufficient concentrated ammonium hydroxide (NH_3 approximately 28% by weight) to form a solution having a volume of 200 ml. and containing 79 grams per liter of molybdenum.

Stock Solution 6.—11.0 grams of silver carbonate (reagent grade) was slurried witht about 5 cc. of aqueous citric acid (citric acid 40% by weight). This slurry was mixed with sufficient concentrated ammonium hydroxide (NH_3 approximately 28% by weight) to form a solution having a volume of 200 ml. and containing 43 grams per liter of silver.

The above stock solutions were used in making up the impregnating solutions described in the examples which follow.

Example 1

Samples of 14 to 40 mesh (US Standard Sieve Series) adsorbent carbon (Pittsburgh Activated Carbon Company, Grade BPL), each weighing 20 grams, were soaked for 10 minutes with stirring in 30 ml. of impregnating solution. The impregnating solutions were prepared by taking either 30 ml. of a single stock solution or 15 ml. each of two stock solutions as described above. Each of

the impregnating solutions contained a compound of at least one metal selected from the group consisting of cobalt, copper and zinc (stock solutions 1, 2 and 3 respectively). The excess solution was removed by vacuum filtration. The wetted carbon was roasted in a rotary tumbler for 30 to 60 minutes in a slow stream of nitrogen at temperatures between 400° and 500° C. The tumbler was preheated to about 165° C. before introduction of the carbon and thereafter heated to the operating temperature in the range of 400° to 500° C. Table I below indicates, for each sample, the stock solutions used to make up the impregnating solution, the metals present in solution, and the concentration of the metal (on the metal basis) in grams per liter. Table I also indicates the metal oxide or oxides present in the impregnated carbon and the weight percentage of each metal oxide, based on the weight of dry unimpregnated carbon.

TABLE I

	Impregnating solution			Impregnated carbon	
	No.	Metal	Conc., g./l.	Metal oxide	Wt. percent
Sample No.:					
1	1	Co	26	CoO	2.4
	4	Fe	56	Fe_2O_3	5.4
2	2	Cu	57	CuO	5.5
	4	Fe	56	Fe_2O_3	5.1
3	1	Co	26	CoO	2.0
	2	Cu	57	CuO	5.8
4	1	Co	26	CoO	1.8
	3	Zn	33	ZnO	3.4
5	1	Co	26	CoO	2.2
	5	Mo	40	MoO_3	3.6
6	2	Cu	57	CuO	5.5
	3	Zn	33	ZnO	3.4
7	2	Cu	57	CuO	5.9
	5	Mo	40	MoO_3	5.6
8	3	Zn	33	ZnO	2.8
	5	Mo	40	MoO_3	4.1
9	1	Co	52	CoO	4.6
10	2	Cu	113	CuO	9.6
11	3	Zn	65	ZnO	6.2

Example 2

Samples of 14 to 40 mesh (U.S. series) adsorbent carbon (Pittsburgh Activated Carbon Company, Grade BPL), each weighing 20 grams, were soaked for 10 minutes with stirring in 20 ml. of a first impregnating solution. Excess solution was removed by vacuum filtration and the carbon was dried at 110° C. The carbon was then soaked in 20 ml. of a second impregnating solution. Excess solution was removed by vacuum filtration. The wetted carbon was roasted in a rotary tumbler from 30 to 60 minutes in a slow stream of nitrogen between 400° and 500° C. The tumbler was preheated to about 165° C. before introduction of the carbon and thereafter heated to the operating temperature in the range of 400° to 500° C. Each of the impregnating solutions consisted of a 20 ml. portion of a single stock solution as aforedescribed. Table II below indicates, for each sample, the metal present in the impregnating solution and the concentration of the metal in grams per liter. Table II also indicates the metal oxides present in the impregnated carbon and the weight percentage of each metal oxide, based on the weight by dry unimpregnated carbon.

TABLE II

	First impregnating solution		Second impregnating solution		Impregnated carbon	
	Metal	Conc.	Metal	Conc.	Metal oxide	Wt. percent
Sample No.:						
12	Ag	43	Co	52	CoO	4.1
					Ag_2O	3.8
13	Ag	43	Cu	113	CuO	10.3
					Ag_2O	3.7
14	Ag	43	Zn	65	ZnO	6.2
					Ag_2O	3.7

Carbon impregnated according to any of the procedures in the foregoing examples may be used in any tobacco smoke filter and particularly in cigarette filters such as those described above. The use of carbon thus impregnated greatly increases the removal of hydrogen cyanide and hydrogen sulfide, and improves the taste of the cigarette when compared with an otherwise identical cigarette having an unimpregnated carbon filter.

Example 3

Sample cigarettes were prepared with filters having the impregnated charcoal adsorbents prepared as described in Examples 1 and 2. Level scoopfuls of adsorbent, each having a volume of 0.28 ml. and containing 100 to 120 mg. of impregnated carbon, were hand packed into a chamber of about 6 mm. in length between two 7 mm. plasticized cellulose acetate filter plugs having 2.8 denier per filament and a total denier of 50,000. A wrapper maintained the filter plugs in spaced coaxial alignment and formed the side wall of the chamber. The resulting filter plugs, 20 mm. in length, were attached to cigarettes 65 mm. in length containing a standard commercial tobacco blend to make a finished cigarette having a length of 85 mm. and a circumference of 24.75 mm. For comparison purposes a cigarette having unimpregnated charcoal in the filter plug chamber, but identical to the test cigarettes with respect to dimensions, tobacco blend and cellulose acetate filter plugs was prepared.

The sample cigarettes were tested for the content of hydrogen cyanide in the effluent smoke stream. Five cigarettes of each impregnant composition were smoked on an automatic smoking machine to a 30 mm. butt by taking 40 ml. puffs of 2 seconds duration once every minute. In general, the cigarettes were consumed in 8 puffs. The particulate matter in the smoke stream was removed by a Cambridge CM–113 filter pad, and the filtered gas stream was passed through a fritted bubble trap containing 100 ml. of 0.1 N aqueous sodium hydroxide, which scrubbed out the HCN gas.

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 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 average values and standard deviations for each sample cigarette are listed in Table III.

The hydrogen sulfide content of the smoke obtained from the sample cigarettes was estimated by a color reaction involving the formation of methylene blue dye. The method described by M. B. Jacobs in the "Analytical Chemistry of Industrial Poisons, Hazards, and Solvents," 2nd edition, page 326, was utilized. A trapping solution consisting of 62.5 ml. of 1% of aqueous zinc acetate and 2.5 ml. of 10% of aqueous sodium hydroxide was placed in the fritted bubble trap previously described in the hydrogen cyanide determination. Four cigarettes of each sample were smoked with 8 puffs in the automatic smoking machine used in the hydrogen cyanide determination, and the hydrogen sulfide in the gaseous smoke stream was collected in the sodium hydroxide trapping solution. After the smoking operation was completed, 12.5 ml. of a solution containing 0.1 gram of N,N-dimethyl-p-phenylenediamine sulfate in 100 ml. of 1:1 HCl in water was added to the solution in the bubble trap. 2.5 ml. of a 0.02 molar

solution of ferric chloride in a 1:9 hydrogen chloride-water mixture was also added. The combined solution was transferred to a volumetric flask for washing and dilution with water to bring the volume up to 100 ml. The smoke gas solution with these additions was shaken well and allowed to stand for at least 2 hours for complete color development, at which time the optical density was measured at a wave length of 665 millimicrons. By comparison of this optical density with that of dye solutions containing known amounts of hydrogen sulfide, the concentration of hydrogen sulfide in the smoke gases can be estimated. Such measurements were made on the 4 cigarettes of each of the 14 samples. The average and standard deviation of the average of these measurements are given in Table III.

The 14 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 CORESTA, No. 1961–1, page 120 (1961). The cigarettes were coded and unidentified during this evaluation. Each panelist rated each cigarette on a scale 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 III.

Each of the 14 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 are the same as those evaulated 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. The individual evaluations of each panelist was averaged for each taste element and an overall evaluation was computed by adding the average ratings of the desirable qualities and subtracting from this the average rating of the undesirable qualities, thus providing a scale of taste evaluations ranging from a highly undesirable rating of −15 to a highly desirable rating of +10. These ratings and the ratings for each individual desirable and undesirable taste factor are listed in Table III.

Example 4

An impregnating solution containing 300 grams per liter of ferric citrate trihydrate, 62.5 grams per liter of zinc carbonate, in concentrated aqueous ammonium hydroxide (NH_3 approximately 28% by weight) was prepared. 20 grams of finely divided charcoal, finer than 40 mesh and predominantly 40 to 100 mesh, was introduced into 30 ml. of the impregnating solution with stirring. The resulting slurry was stirred for 10 minutes, and then the excess solution was removed by vacuum filtration. The wet carbon was roasted for 1 hour at 400° to 500° C. in a slow stream of steam in a furnace which had been preheate dto 200° C. The resultant charcoal contained between 4 and 5% each of iron oxide (computed as Fe_2O_3) and zinc oxide.

60 grams of the impregnated charcoal was placed on the surfaces of plasticized cellulose acetate filaments having a total weight of 101 grams. The cellulose acetate consisted of a crimped continuous filament tow of yarn-type cellulose acetate of 2.1 denier per filament with a total denier of 52,000. The impregnated charcoal was applied by passing the cellulose acetate filaments through an aqueous slurry of the charcoal. The filamentous tow was cut into lengths of 2.0 centimeters. Each of these lengths was incorporated in a sample cigarette, all of the sample cigarettes being identical with respect to tobacco blend, length (8.5 cm.) and paper wrapper.

The cigarettes were smoked on a smoking machine similar to that described in Example 3. Hydrogen sulfide and hydrogen cyanide were collected in the smoking machine as described in Example 3. The contents of hydrogen cyanide and hydrogen sulfide in micrograms per puff are given in Table IV below. For comparison purposes, samples if cigarettes using coarser carbon, 14 to 40 mesh and 30 to 40 mesh, but otherwise identical to the test cigarettes, were also smoked. Both impregnated and unimpregnated charcoal filter cigarettes for each particle size were smoked. Results are given in Table IV below.

For comparison 4 additional cigarettes of the same length as the above described sample cigarettes but having an empty filter chamber in place of the above described filter were also smoked according to the same procedure. The smoke emanating therefrom had an average HCN content of 35 μg./puff and an H_2S content of 4.0 μg./puff.

A further measure of the ability of the test filter and the five comparison filters to remove HCN from a gaseous stream was made in a hydrogen cyanide removal test. This test consisted of preparing a dilute mixture of HCN and air containing approximately 40 μg. of HCN per

TABLE III

Sample number	Oxide impregnant	Desired taste elements: Sweet fragrance	Desired taste elements: Smoothness rating	Undesired taste elements: Bitter taste	Undesired taste elements: Drying sensation	Undesired taste elements: Throat irritation	Total taste rating	HCN, μgm./puff	H_2S, μgm./puff
1	Co-Fe	3.2	3.4	2.0	2.2	1.1	+1.3	8.0	1.0
2	Cu-Fe	2.8	3.4	2.0	2.3	1.2	+0.7	10.5	0.5
3	Co-Cu	3.2	3.2	2.2	2.0	1.7	+0.5	5.0	0.9
4	Co-Zn	2.7	3.5	1.5	3.0	1.3	+0.4	9.3	0.7
5	Co-Mo	3.1	2.9	1.6	2.4	1.1	+0.9	9.7	0.7
6	Cu-Zn	2.8	3.3	1.2	2.3	1.0	+1.6	6.2	0.6
7	Cu-Mo	3.2	3.0	2.0	1.7	2.2	+0.3	8.7	0.7
8	Zn-Mo	2.7	3.2	2.0	2.3	1.0	+0.6	9.2	0.8
9	Co	3.3	3.5	1.8	2.1	1.3	+1.6	6.5	1.0
10	Cu	3.0	3.8	1.6	2.0	1.2	+2.0	9.2	1.2
11	Zn	3.4	3.5	1.8	2.5	1.6	+1.0	8.3	0.7
12	Co-Ag	3.0	3.2	1.9	2.3	1.4	+0.6	6.3	1.1
13	Cu-Ag	3.2	3.7	1.7	2.0	1.2	+2.0	7.5	0.7
14	Zn-Ag	2.8	3.2	1.9	2.5	1.0	+0.6	7.9	0.6
Control	None	2.6	2.8	1.9	2.6	1.4	−0.5	12.0	1.3

40 ml., passing ten 40 ml. puffs of this mixture through a 20 mm. length of the filter rod and measuring the percent HCN removed from the gas stream by the filter.

TABLE IV

	HCN, μg./puff	H_2S, μg./puff	Percent HCN removal
14–40 mesh:			
Impregnated	11	1.3	72.4
Unimpregnated	20	1.6	59.1
30–40 mesh:			
Impregnated	6.7	0.73	84.2
Unimpregnated	11	1.1	34.0
-40 mesh:			
Impregnated	3.8	0.56	91.0
Unimpregnated	8	1.34	48.0

What is claimed is:

1. A smoking article having a burnable tobacco charge, a mouth end and a filter interposed between said tobacco charge and said mouth end, said filter containing non-toxic adsorbent granules of charcoal, alumina, natural or synthetic clay, or silica gel having a specific surface area of at least one million square centimeters per gram and a particle size not greater than 8 mesh, and impregnated with about 1 to 13% by weight, based on the weight of unimpregnated absorbent granules, of an oxide selected from the group consisting of cobalt, copper, or zinc oxides, plus about 1 to 13% by weight, based on the weight of unimpregnated adsorbent granules, of at least one other oxide selected from the group consisting of cobalt, copper, zinc, silver, or molybdenum oxides, the combined weight of metal oxides not exceeding 14% of the weight of unimpregnated adsorbent granules.

2. A cigarette having a burnable tobacco charge, a mouth end and a filter interposed between said tobacco charge and said mouth end, said filter containing non-toxic adsorbent granules of charcoal, alumina, natural or synthetic clay, or silica gel having a specific surface area of at least one million square centimeters per gram and a particle size not greater than 8 mesh, and impregnated with about 1 to 13% by weight, based on the weight of unimpregnated adsorbent granules, of an oxide selected from the group consisting of cobalt, copper, or zinc oxides, plus about 1 to 13% by weight, based on the weight of unimpregnated adsorbent granules, of at least one other oxide selected from the group consisting of cobalt, copper, zinc, silver, or molybdenum oxides, the combined weight of metal oxides not exceeding 14% of the weight of unimpregnated adsorbent granules.

3. A cigarette according to claim 2 in which said adsorbent granules consist essentially of charcoal.

4. A cigarette according to claim 2 in which said filter comprises a pair of filter plugs, 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 chamber, said chamber containing said adsorbent granules, said adsorbent granules having a particle size in the range of 8 to 50 mesh.

5. A cigarette according to claim 2 in which said filter comprises fibers of a cellulosic material, said adsorbent granules adhering to the surfaces of said fibers.

6. A cigarette according to claim 5 in which said cellulosic material is paper and said adsorbent material is uniformly distributed throughout said paper.

7. A cigarette according to claim 5 in which said cellulosic material is cellulose acetate in filament form and said adsorbent adheres to the surfaces of the filaments.

8. The smoking article of claim 1 in which the particle size is not greater than 50 mesh.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,460,543 August 12, 1969

Charles H. Keith II, et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 70, "This" should read -- They --. Column 2 lines 1 and 2, "state. In the brief period of time during whic they are from the tobacco or are synthesized in a wholly vaporized" should read -- from the tobacco or are synthesized i a wholly vaporized state. In the brief period of time during which they are --. Column 6, line 19, "coxial" should read -- coaxial --. Column 7, line 15, "are also" should read -- als are --. Column 8, line 2, "thaan" should read -- than --. Colum 12, line 35, "if" should read -- of --.

Signed and sealed this 23rd day of June 1970.

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents