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Norman et al.

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[54] TOBACCO SMOKE FILTER

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Primary Examiner—Melvin D. Rein

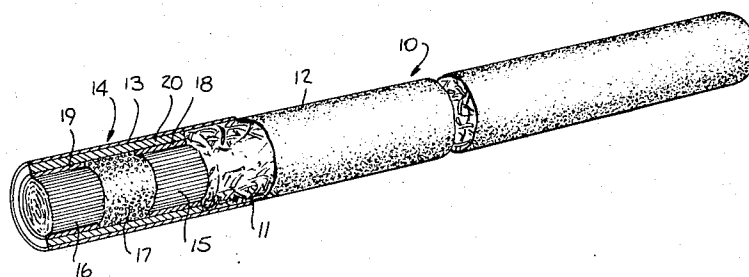
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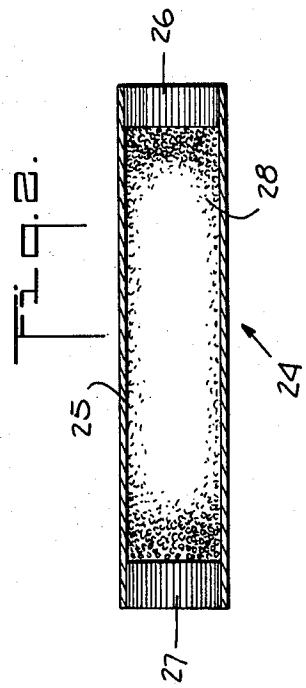
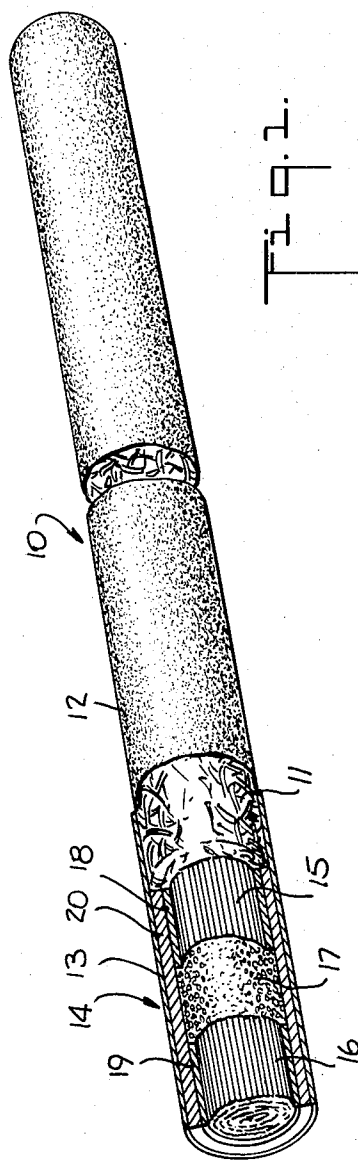
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ABSTRACT

Hydrogen cyanide is removed from tobacco smoke by passing the smoke through a filter containing a water-insoluble, mixed-metal carbonate of an alkaline earth metal selected from the group consisting of magnesium, calcium, strontium and barium and a transition metal selected from the group consisting of cobalt, nickel, copper and zinc.

16 Claims, 2 Drawing Figures





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TOBACCO SMOKE FILTER

This invention relates to a filter material for removing deleterious materials from tobacco smoke. More particularly, this invention relates to a material for removing hydrogen cyanide from tobacco smoke, especially cigarette tobacco smoke.

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. The 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 cellulose acetate, 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 hydrogen cyanide which exhibits a specific toxic action on the human tissues with which it comes into contact. This material is 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 hydrogen cyanide are found to inhibit and in higher concentrations destroy this beating action in test animals and 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 has a considerable vapor pressure at room temperature and above, and may be classified as a gas or highly volatile liquid. During the processes of imperfect combustion such as occur in cigarettes, pipes, and cigars it is liberated from the tobacco or is synthesized in a wholly vaporized state. In the brief period of time during which it is carried from the combustion zone to the smoker's mouth, there is relatively little opportunity for it to condense into the semi-liquid and solid droplets which form the visible smoke stream, and consequently it is almost entirely in a vaporized state as it leaves the smoking article and enters the smoker's mouth.

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 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, which can be removed only by the processes of physical and chemical adsorption. The smooth, non-porous and chemically relatively inert nature of the commonly used fibrous materials, while effective in capturing tobacco smoke droplets, does not effectively adsorb gaseous molecules. In some instances 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. However, cellulose acetate filters allow hydrogen cyanide 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

generally have large surface areas and extensive pore structures and function as non-selective physical adsorbents.

The principal object of this invention is to provide a material capable of selectively extracting from tobacco smoke a significantly large proportion of hydrogen cyanide.

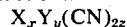
A further object of this invention is to provide a filter material adapted to reduce the hydrogen cyanide content of tobacco smoke.

In accordance with this invention it has been discovered that the hydrogen cyanide content of tobacco smoke is reduced if the smoke is contacted with certain water-insoluble, mixed-metal, carbonates, and more particularly water-insoluble, mixed-metal carbonates of certain alkaline earth metals and certain transition metals. Alkaline earth metals of interest are those having atomic numbers of from 12 to 56, inclusive, i.e., magnesium, calcium, strontium and barium. Transition metals of interest include cobalt, nickel, copper and zinc. These carbonates may be represented by the formula:

$X_xY_y(CO_3)_z$ wherein X is an alkaline earth metal; Y is a transition metal, preferably in a valence state of +2; x is an integer having a value of from 1 through 4, inclusive, and preferably from 1 through 3, inclusive; Y is an integer having a value of 1 or 2, preferably 1; and z is an integer having a value of 2 through 4, inclusive, and has a value of $x + y$ when Y has a valence of +2.

The mixed carbonates are readily prepared by dissolving water soluble salts of the alkaline earth metal and the transition metal, normally the chloride salts, in water and thereafter adding a water-soluble carbonate salt, such as sodium carbonate, to cause coprecipitation of the desired mixed-metal carbonate from the aqueous solution. The alkaline earth metal salt, the transition metal salt and the carbonate salt are usually admixed in the proportions of alkaline earth metal, transition metal and carbonate ion desired in the coprecipitated carbonate. For example, if $Ba_3Co(CO_3)_4$ is the desired coprecipitate, 3 moles of barium chloride, 1 mole of cobalt chloride and 4 moles of sodium carbonate are mixed in water. In some cases, however, one or more of the reactants may be employed in molar excess.

The mechanism by which the mixed-metal carbonates remove hydrogen cyanide from tobacco smoke has not been established. It is known that carbonates in aqueous solution will form complex cyanides of the formula:



wherein X, Y, x, y and z are as defined above. Whether a similar reaction occurs when the tobacco smoke contacts the coprecipitated carbonates is not known, particularly since it is unlikely, especially during the first few puffs on a smoking article such as a cigarette, that there is a sufficiently substantial liquid phase present to enable a direct analogy to be drawn. Moreover, the contact time of the smoke and the carbonate is very short, of the order of 0.01 seconds. As a result, and assuming that complex cyanide formation does occur, only carbonates which react extremely rapidly with hydrogen cyanide are useful. Thus, it has been found that individual carbonates, e.g., calcium carbonate and zinc carbonate, are relatively inactive, as are physical mixtures of alkaline earth metal and transition metal carbonates or coprecipitated carbonates including iron as the transition metal.

The carbonates may be employed in conjunction with any of the conventional tobacco filter media. For example, they may be distributed on cellulose or paper matrices commonly used as tobacco smoke filters, or they may be deposited on a granular support which is in turn deposited on such matrices. Alternatively, the carbonates may be employed in granular form, preferably as a deposit on a granular support such as a silica-gel or diatomite, in a chamber bounded by plugs of filter media such as is disclosed in U.S. Pat. No. 3,351,365. It is preferred to employ the carbonate in the highest surface area to weight ration possible to provide maximum efficiency.

A particularly desirable way of using the carbonates of this invention is shown in the drawing annexed to and forming a part of this specification.

FIG. 1 is a perspective view of a cut away cigarette equipped with a filter tip of the invention.

FIG. 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 this invention.

Referring to FIG. 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 the mixed-metal carbonate 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 fibers 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 millimeters 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 the carbonate. This chamber may be from 2 to 15 millimeters in length, and may contain from 40 to 400 milligrams of granular carbonate material.

Referring to FIG. 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, or 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 these 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 glued, welded or solvent sealed to the cartridge tube 25. The chamber 27 created by the cartridge tube 25 and the end plugs and/or caps 26 and 27 is loosely packed with the coprecipitated metal carbonate 28, the amount depending upon the volume of the chamber.

The amount of carbonate which is employed to reduce the hydrogen cyanide content of tobacco smoke is not highly critical and, in the case of cigarettes approximately 50–300 milligrams of carbonate per cigarette have been found useful. Optimal results have generally been obtained at levels from 100–200 milligrams of carbonate per cigarette.

The following examples are illustrative:

EXAMPLES 1–9

To a solution of 7.32 grams (0.03 mole) of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and 2.38 grams (0.01 mole) of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in 100 milliliters of water, there was added a solution of 4.24 grams (0.04 mole) of sodium carbonate in 100 milliliters of water. The resulting mixture was stirred vigorously and a coprecipitated mixed carbonate having the empirical formula $\text{Ba}_3\text{Co}(\text{CO}_3)_4$ was recovered by filtration and dried.

In a similar manner, nine additional coprecipitated mixed carbonates were obtained. Relevant data are summarized as follows:

Ex.	Coprecipitated carbonate	Alkaline earth metal carbonate	Transition metal chloride	Sodium carbonate
2	$\text{BaNi}(\text{CO}_3)_2$	4.88 g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	4.76 g. $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	4.24 g. Na_2CO_3
3	$\text{BaZn}(\text{CO}_3)_2$	4.88 g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	2.72 g. ZnCl_2	4.24 g. Na_2CO_3
4	$\text{BaCu}(\text{CO}_3)_2$	4.88 g. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	3.4 g. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	4.24 g. Na_2CO_3
5	$\text{Ca}_3\text{Co}(\text{CO}_3)_4$	33.3 g. CaCl_2	23.8 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	42.6 g. Na_2CO_3
6	$\text{CaCu}(\text{CO}_3)_2$	11.1 g. CaCl_2	17.0 g. $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	21.2 g. Na_2CO_3
7	$\text{CaZn}(\text{CO}_3)_2$	11.1 g. CaCl_2	13.6 g. ZnCl_2	21.2 g. Na_2CO_3
8	$\text{Mg}_3\text{Co}(\text{CO}_3)_4$	60.9 g. $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	23.8 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	42.6 g. Na_2CO_3
9	$\text{Ca}_2\text{Co}(\text{CO}_3)_3$	22.2 g. CaCl_2	23.8 g. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	31.8 g. Na_2CO_3

EXAMPLE 10

Each of the carbonates produced in the manner described in Examples 1–9 was compressed in a pellet press and then ground and screened to a 14×40 US mesh size. The resulting granular material was then placed in a filter cavity between two cellulose acetate plugs of a cigarette of the type disclosed in FIG. 1 of U.S. Pat. No. 3,251,365.

The filters were fitted to 65 mm long cigarette tobacco columns and smoked on a smoking machine. The smoke was analyzed for hydrogen cyanide by the method of Collins et al. disclosed in Tobacco Science, Vol. 14 (1970) on pages 12–15. In addition, the ciliary inhibition of the tobacco smoke was determined by the method of Battista ("Relationship Between Ciliary Activity and Cigarette Smoke and its Components", PhD Dissertation Boston University, 1968). The data obtained by these experiments are summarized as follows:

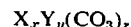
Filter medium	Amount of additive, mg.	HCN in smoke, ug./puff	Ciliary inhibition ED ₅₀ (puffs)
Control	None	30	3–4
$\text{Mg}_3\text{Co}(\text{CO}_3)_4$	100	8	8
$\text{Ca}_3\text{Co}(\text{CO}_3)_4$	200	4	8
$\text{Ca}_3\text{Co}(\text{CO}_3)_4$	100	8	8.0
$\text{Ba}_3\text{Co}(\text{CO}_3)_4$	100	17	8.0
$\text{CaZn}(\text{CO}_3)_2$	200	6	8.0
$\text{CaZn}(\text{CO}_3)_2$	100	10	5.8
$\text{BaZn}(\text{CO}_3)_2$	100	14	5.8
$\text{CaCu}(\text{CO}_3)_2$	200	3	5.8
$\text{CaCu}(\text{CO}_3)_2$	100	16	5.8
$\text{BaCu}(\text{CO}_3)_2$	100	14	5.8
$\text{BaNi}(\text{CO}_3)_2$	100	13	5.8

As is quite apparent from the above data, each of the coprecipitated mixed carbonates substantially reduced the hydrogen cyanide content of the smoke and reduced the amount of ciliary inhibition from the smoke.

What is claimed is:

1. In a filter cigarette comprising a tobacco charge, a filter portion and a wrapper, the improvement which comprises a filter for the filter portion having a coprecipitated water insoluble, carbonate of an alkali, earth metal carbonate and a transition metal carbonate, the alkali earth metal being selected from the group consisting of magnesium, calcium, strontium and barium and the transition metal being selected from the group consisting of cobalt, nickel, copper and zinc, the proportion of the alkali earth metal carbonate to transition earth metal carbonate being such as to effectively reduce the hydrogen cyanide content of the smoke in an amount greater than that possible by either carbonate taken alone or by the two carbonates physically admixed.

2. A cigarette according to claim 1 wherein said carbonate has the formula



- wherein X is said alkaline earth metal; Y is said transition metal; x is an integer having a value of from 1 through 4, inclu-

sive; y is an integer having a value of 1 or 2; and z is an integer having a value of from 2 through 4, inclusive.

3. A cigarette according to claim 2 wherein x has a value of 1 through 3, inclusive; y has a value of 1; and z has a value of x + y.

4. A cigarette according to claim 3 wherein said carbonate is $\text{BaNi}(\text{CO}_3)_2$.

5. A cigarette according to claim 3 wherein said carbonate is $\text{Ca}_3\text{Co}(\text{CO}_3)_4$.

6. A cigarette according to claim 3 wherein said carbonate is $\text{CaCu}(\text{CO}_3)_2$.

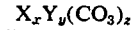
7. A cigarette according to claim 3 wherein said carbonate is $\text{CaZn}(\text{CO}_3)_2$.

8. A cigarette according to claim 3 wherein said carbonate is $\text{Mg}_3\text{Co}(\text{CO}_3)_4$.

9. The method of treating tobacco smoke to reduce the hydrogen cyanide content thereof which comprises interposing in the path of the smoke stream between a tobacco charge and the mouth of the user, a charge of a coprecipitated, water insoluble carbonate, which is of an alkali earth metal carbonate and a transition metal carbonate, the alkali earth metal being selected from the group consisting of magnesium, calcium, strontium and barium and the transition metal being selected from the group consisting of cobalt, nickel, copper and zinc, the proportion of the alkali earth metal carbonate to

transition earth metal carbonate being such as to effectively reduce the hydrogen cyanide content of the smoke in an amount greater than that possible by either carbonate taken alone or by the two carbonates physically admixed.

10. A method according to claim 9 wherein said carbonate has the formula



wherein X is said alkaline earth metal; Y is said transition metal; x is an integer having a value of from 1 through 4, inclusive; y is an integer having a value of 1 or 2; and z is an integer having a value of from 2 through 4, inclusive.

11. A method according to claim 10 wherein x has a value of 1 through 3, inclusive; y has a value of 1; and z has a value of x + y.

12. A method according to claim 11 wherein said carbonate is $\text{BaNi}(\text{CO}_3)_2$.

13. A method according to claim 11 wherein said carbonate is $\text{Ca}_3\text{Co}(\text{CO}_3)_4$.

14. A method according to claim 11 wherein said carbonate is $\text{CaCu}(\text{CO}_3)_2$.

15. A method according to claim 11 wherein said carbonate is $\text{CaZn}(\text{CO}_3)_2$.

16. A method according to claim 11 wherein said carbonate is $\text{Mg}_3\text{Co}(\text{CO}_3)_4$.

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