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TREATMENT OF TOBACCO SMOKE

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This invention relates to the treatment of tobacco smoke for the purpose of reducing the proportion of components therein which are harmful to health, and it is concerned more particularly with the removal from tobacco smoke of not only nicotine but also the tarry substances containing ingredients which in recent years have come under suspicion as being carcinogenic.

The harmful physiological effects of nicotine found in tobacco smoke have long been recognized, and although evidence of possible carcinogenic behavior of some of the tar components has only recently been found, activity in the art directed toward the development of techniques and devices for substantially reducing nicotine and tars in tobacco smoke has been earnestly pursued for at least seventy-five years. However, the various processes and devices of the prior art failed to satisfy completely the requirements of the industry and, so far as we are aware, most of such prior art developments have never been adopted to any considerable extent. For example, some of the techniques and devices of the prior art were rejected because of their low efficiency in the removal of toxic substances from the tobacco smoke, or because the treating agents employed were themselves toxic to an objectionable degree, or were of a physical form which rendered them inconvenient to use. In other instances of the prior art, especially in those cases in which the treating agents were incorporated directly with the tobacco, rejection by the industry was based on the fact that such agents adversely affected the burning characteristics of the tobacco or the taste of the smoke.

We have found that the foregoing shortcomings of the prior art may be obviated, and the harmful physiological effects of tobacco smoke eliminated, or substantially reduced, by contacting the smoke with an oxidative resin, to be more fully described hereinafter, thereby effecting oxidation of the nicotine and of at least some of the tar in which, according to a considerable body of medical opinion, any carcinogenic substances in tobacco smoke will be found. It is known that the chemical carcinogens are very active from a chemical standpoint and that, upon oxidation, their carcinogenic potential either disappears entirely or is substantially reduced.

In practicing the present invention the oxidative resin is incorporated in a suitable smoke filtering device which may be physically attached to the end of a cigar or cigarette, or may take the form of a disposable cartridge insertable in pipes or in cigar or cigarette holders, in a manner well known in the art. Preferably, the resin is finely divided to provide the maximum surface per unit weight thereof for contact by the smoke. Preferably also, the resin has a highly porous structure which not only further increases its available oxidizing surface but greatly improves its adsorptive quality, thereby providing a filter for tobacco smoke which advantageously combines high oxidizing power with the property of physical adsorption.

In general, the oxidative resins which we have found to be useful for practicing the present invention are ion-exchange resins having adsorbed thereon an oxidizing ion,

and resins of this class which have proved eminently satisfactory are anion-exchange resins on which has been adsorbed an anionic ceric complex of an acid, preferably of a strong acid, such as sulfuric or nitric acid. These oxidative resins are made by bringing an acidic solution of the anionic ceric complex, e. g., anionic ceric sulfate or nitrate complex, in contact with particles of an anion-exchange resin in any suitable manner, as by soaking or agitating the particles of the resin in a solution of the ceric complex, and thereafter separating the treated resin from the solution of the complex. Alternatively, an acidic solution of the ceric complex may be passed through a column of particles of the resin in the same way that aqueous solutions are treated by the conventional columnar technique. It will be understood that although the oxidative resins are defined herein for the sake of simplicity as having adsorbed thereon "an oxidizing ion," or "an anionic ceric complex," or the like, actually a great number of such ions or complexes is normally adsorbed by the functional ion-adsorbing groups of the polymeric resin matrix formed during manufacture of the resin.

The anion-exchange resins which may thus be converted to the oxidative resins useful in the present invention may be of the weakly basic or strongly basic types. Many of these resins are available commercially and representative examples thereof are described in U. S. Patents 2,106,486; 2,151,883; 2,223,930; 2,251,234; 2,259,169; 2,285,750; 2,341,907; 2,354,671; 2,354,672; 2,356,151; 2,366,008; 2,388,235; 2,402,384; 2,540,985; 2,591,573; 2,591,574; and 2,614,099.

We have found to be particularly satisfactory strongly basic anion-exchange resins which contain, as their functional anion-adsorbing groups, quaternary ammonium groups, such as the resins described in U. S. Patents 2,540,985; 2,591,573; and 2,614,099. Of this class of resins, the type preferred is that which contains only hydrocarbon substituents on the nitrogen atoms in the quaternary ammonium groups, this preference being based on the fact that the ceric complex naturally tends to oxidize the resin itself, and those resins which are free of readily oxidizable substituents are the most stable. This last type is exemplified by a resin which is produced by the reaction of a tertiary amine, such as trimethylamine, with a haloalkylated cross-linked copolymer of a monovinyl hydrocarbon, such as styrene, and a polyvinyl hydrocarbon, such as divinylbenzene, the haloalkyl groups on the copolymer prior to reaction with the amine having the general formula $-C_nH_{2n}X$ in which X is a member of the group consisting of chlorine and bromine and n is an integer of value 1 to 4. A description of this group of resins, together with methods of preparing them as the finely divided or highly porous products which we prefer, is given in U. S. Patent 2,591,573.

Prior to treatment with the ceric complex solution, the ion-exchange resin is advantageously converted to the salt form, preferably to the sulfate or nitrate, and this conversion may be effected by treating the resin with either sulfuric acid or nitric acid. The solution of ceric sulfate or nitrate complex with which the resin is treated is acidic, as stated above, having pH below 5.0 and preferably from about 0.5 to 2. Sulfuric or nitric acid is used to impart acidity, sulfuric acid in conjunction with ceric sulfate and nitric acid in conjunction with ceric nitrate. In the presence of the acid, an anionic ceric sulfate or nitrate complex is formed which is strongly adsorbed by the anion-exchange resin. Although the exact composition of the complex of ceric sulfate or nitrate is not established, it is known to be anionic. For the purpose of illustration and not as a limitation, the formation of the sulfate complex can be represented as follows:

$$n.SO_4^{--} + Ce^{++++} \rightleftarrows \left[Ce(SO_4)_n\right]^{4-2n}$$

Since the oxidation potential of the finished product, and therefore its activity and efficiency as an oxidizing agent, depends on the number of available oxidizing groups per unit weight of the resin, and since the number of such oxidizing groups which may be adsorbed by a given weight of resin varies inversely with the particle size of the resin, we prefer to use resins in a finely divided state, e. g., of a size to pass through a U. S. standard sieve No. 50, or smaller. Also, in order to provide the greatest oxidation potential the resin is saturated with a solution of the anionic ceric sulfate or ceric nitrate complex; that is, the ceric complex is adsorbed to the full extent of the capacity of the resin. It will be understood, however, that resins having adsorbed thereon less than the maximum amount of the ceric complex that they are capable of adsorbing may nevertheless be used to advantage in our invention.

The following examples illustrate the preparation of several oxidative ion-exchange resins having utility in the present invention:

Example I

The ion-exchange resin employed was a commercially available strongly basic, quaternary ammonium anion-exchange resin supplied by Rohm & Haas Company under its designation Amberlite IRA–400, and described in U. S. Patent 2,591,573. This resin was known to have been made by the reaction of trimethylamine with a chloromethylated, cross-linked copolymer of 92% styrene and 8% of a commercial grade of divinylbenzene. The resin was sieved and only that portion passing through a U. S. standard sieve No. 50 was employed. This resin, which was in the chloride form, and wet with water, was converted to the sulfate by treatment with 5% sulfuric acid. The resin was then formed into a bed or column in a glass tube through which was slowly passed an aqueous solution containing 26.4 grams of the ceric salt, tetrasulfato-ceric acid of the composition $Ce(HSO_4)_4$, and 50 ml. of 96% sulfuric acid per liter of solution. After the anionic ceric sulfate complex was adsorbed on the resin to the fullest extent of the capacity of the resin the product was rinsed with deionized water.

Example II

In a similar manner, an oxidative resin having anionic ceric nitrate complex as the oxidizing group was prepared by treating the same quaternary ammonium anion-exchange resin described in Example I with an 8-molar solution of nitric acid containing 27.4 grams of ammonium hexanitro cerate $(NH_4)_2Ce(NO_3)_6$, per liter.

Example III

An oxidative resin was prepared by treating, with the same solution of the ceric nitrate complex described in Example II, a commercially available weakly basic anion-exchange resin supplied by Rohm & Haas Company under its designation Amberlite IR–45 and described in U. S. Patent 2,591,574. This resin was known to have been made by reacting triethylenetetramine with particles of a chloromethylated cross-linked copolymer of 92% styrene and 8% divinylbenzene of the commercial grade.

Another group of oxidative resins which we have found useful for the purpose of the invention are the cation-exchange resins of the class defined generally as the sulfonated copolymer of a monovinyl hydrocarbon and a polyvinyl compound, and on which is adsorbed the ceric ion (Ce^{++++}). The resins, of this group which we have found to be particularly satisfactory are those in which the polyvinyl compound which copolymerizes with the monovinyl hydrocarbon contains at least two vinylidene groups ($CH_2=C=$), as described in U. S. Patent 2,366,-007, a specific example being commercially available under the designation Amberlite IR–120, manufactured by the Rohm & Haas Company, and comprising the sulfonated copolymer of styrene and divinylbenzene. Other

cation-exchange resins which may be converted to oxidative types by adsorption of the ceric ion are the sulfonated phenol formaldehyde resins, such as those disclosed in U. S. Patents 2,228,159, 2,228,160, 2,259,455 and 2,333,-754. Adsorption of the ceric ion on these cation-exchange resins may be effected simply by soaking the finely divided resin in an acidic aqueous solution of a ceric salt, such as ceric sulfate.

When tobacco smoke is brought into contact with oxidative resins of the character disclosed herein, as by conducting the smoke through a filter device containing such a resin, it is observed that the proportion of nicotine and tar in the filtered smoke is materially reduced. The extent to which such resins are effective to reduce the proportions of these injurious substances in tobacco smoke will of course depend on the character of the resin (e. g., the number of available oxidizing groups adsorbed thereon) and the volume of smoke treated thereby. We have found, for instance, that a filter containing about one gram of the oxidative resin of Example I, which represents a volume of resin well within the size limitations established by conventional filters, will oxidize or mechanically remove not only substantially all of the nicotine from the smoke produced by a standard commercial cigarette, but a large proportion of the tarry substances as well.

Suitable smoke filtering devices incorporating oxidative resins for reaction with the oxidizable smoke components may be made in a number of ways. For example, an effective filter may be made simply by loosely packing a quantity of the oxidative resin in a small container having perforated ends to permit passage of the smoke therethrough. Such a filter is especially adapted for use in cigarette holders or in pipes, since it affords the advantage of ready replacement when its oxidizing and adsorbing powers have been exhausted.

For filtering devices adapted to be physically attached to the end of a cigarette, the oxidative resin is preferably incorporated in a suitable fibrous material, such as paper, which is thereafter formed into a porous plug through which the smoke may pass. In such case, the oxidative resin, finely divided, may be conveniently mixed with the fibrous material in a beater, after which a sheet may be formed from the beaten pulp slurry by conventional paper making methods. Alternatively, the finely divided untreated ion-exchange resin (i. e., prior to the addition thereto of the oxidizing groups) may be incorporated in a fibrous sheet by conventional paper making techniques, and the sheet thereafter treated with a suitable solution containing ceric ions or the ceric acid complex, whereby the resin in the sheet is converted in situ to the oxidative type having utility in the present invention.

We claim:

1. The method of treating tobacco smoke to reduce the proportion of harmful components therein which comprises contacting the smoke with an ion-exchange resin on which is adsorbed cerium in the ceric state.

2. The method of treating tobacco smoke to reduce the proportion of harmful components therein which comprises contacting the smoke with an anion-exchange resin on which is adsorbed an anionic ceric complex of an acid.

3. The method of treating tobacco smoke to reduce the proportion of harmful components therein which comprises contacting the smoke with an anion-exchange resin on which is adsorbed a ceric acid complex selected from the group consisting of anionic ceric sulfate complex and anionic ceric nitrate complex.

4. The method of treating tobacco smoke to reduce the proportion of harmful components therein which comprises contacting the smoke with a strongly basic quaternary ammonium anion-exchange resin on which is adsorbed a ceric acid complex selected from the group consisting of anionic ceric sulfate complex and anionic ceric nitrate complex.

5. The method of treating tobacco smoke to reduce the proportion of harmful components therein which comprises contacting the smoke with a cation-exchange resin on which is adsorbed ceric ions.

6. The method according to claim 3 wherein said resin comprises the reaction product of a tertiary amine with a haloalkylated cross-linked copolymer of a monovinyl hydrocarbon and a polyvinyl hydrocarbon, the haloalkyl groups on said copolymer prior to reaction with said amine having the general formula —$OnH_{2n}X$ in which X is a member of the group consisting of chlorine and bromine and n is an integer of value 1 to 4.

7. The method according to claim 3 wherein the resin comprises the reaction product of an amine selected from the group consisting of trimethylamine and triethylenetetramine with a chloromethylated cross-linked copolymer of styrene and divinylbenzene.

8. The method according to claim 5 wherein said resin comprises a sulfonated copolymer of a monovinyl hydrocarbon and a polyvinyl compound, the latter containing at least two vinylidene groups.

9. The method according to claim 5 wherein said resin comprises a sulfonated copolymer of styrene and divinylbenzene.

10. A filter for tobacco smoke, said filter containing an effective amount of an ion-exchange resin on which is adsorbed cerium in the ceric state.

11. A filter for tobacco smoke, said filter containing an effective amount of an anion-exchange resin on which is adsorbed an anionic ceric complex of an acid.

12. A filter for tobacco smoke, said filter containing an effective amount of an anion-exchange resin on which is adsorbed a ceric acid complex selected from the group consisting of anionic ceric sulfate complex and anionic ceric nitrate complex.

13. A filter for tobacco smoke, said filter containing an effective amount of a strongly basic quaternary ammonium anion-exchange resin on which is adsorbed a ceric acid complex selected from the group consisting of

anionic ceric sulfate complex and anionic ceric nitrate complex.

14. A filter for tobacco smoke, said filter containing an effective amount of a cation-exchange resin on which is adsorbed ceric ions.

15. A filter according to claim 12 wherein said resin comprises the reaction product of a tertiary amine with a haloalkylated cross-linked copolymer of a monovinyl hydrocarbon and a polyvinyl hydrocarbon, the haloalkyl groups on said copolymer prior to reaction with said amine having the general formula —$CnH_{2n}X$ in which X is a member of the group consisting of chlorine and bromine and n is an integer of value 1 to 4.

16. A filter according to claim 12 wherein said resin comprises the reaction product of an amine selected from the group consisting of trimethylamine and triethylenetetramine with a chloromethylated cross-linked copolymer of styrene and divinylbenzene.

17. The filter in accordance with claim 14 wherein said resin comprises a sulfonated copolymer of a monovinyl hydrocarbon and a polyvinyl compound, the latter containing at least two vinylidene groups.

18. The filter in accordance with claim 14 wherein said resin comprises a sulfonated copolymer of styrene and divinylbenzene.

19. The method for treating tobacco smoke comprising passing tobacco smoke into intimate contact with an active oxidant, including cerium in the ceric state, adsorbed on finely divided resinous material.

20. A filter for tobacco smoke, comprising an active oxidant, including cerium in the ceric state, adsorbed on finely divided resinous material.

References Cited in the file of this patent

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