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**UNITED STATES NON-PROVISIONAL
UTILITY PATENT APPLICATION**

For

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**SELECTIVE FILTRATION OF CIGARETTE SMOKE
USING CHITOSAN DERIVATIVES**

by

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CROSS-REFERENCE TO RELATED APPLICATIONS

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**This international patent application is a Paris Convention filing and claims priority to
and benefit from U.S. Patent Application Serial Number 10/842,165, filed on May 10, 2004,
currently pending.**

**STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT**

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Not applicable.

FIELD OF INVENTION

**This invention concerns improvements relating to tobacco smoke filters. More
particularly, the invention relates to a cigarette filter that can selectively remove undesirable
constituents from tobacco smoke.**

BACKGROUND OF THE INVENTION

A wide variety of materials have been suggested in the prior art as filters for tobacco smoke. Examples of such filter materials include cotton, paper, cellulose acetate, and certain synthetics. Many of these filter materials, however, are only effective in the removal of
5 particulates, tars and condensable components from tobacco smoke. The art is replete with a myriad of filtration techniques and materials for removing undesirable components in smoke and for causing other reactions as the smoke passes through filtration beds or other reactive media. Among the problems encountered with prior filters has been the plugging or clogging with use and the consumption or rendering ineffective of reactive filtering surfaces and
10 materials.

Filters made from filamentary or fibrous material such as cellulose acetate tow or paper are somewhat effective in the removal of particulate phase constituents of tobacco smoke. However, they have little or no effect in removing certain gaseous components in the vapor phase of the tobacco smoke such as hydrogen cyanide, aldehydes, carbonyls, metals
15 and sulphides. These volatile constituents can be removed by adsorption and absorption on a suitable surface or by chemical reaction.

Some known substances which act as absorbents and adsorbents include activated carbon, porous minerals, and ion exchange resins. Ion-exchange resins of porous structure have been found to be somewhat effective, but their efficiency diminishes during smoking, as
20 does that of carbon and porous minerals. This may be due to the material becoming saturated and, therefore, increasingly inactive or it may be due to the release of adsorbed material by thermal desorption of retained substances.

Resins which contain major proportions of tertiary amino or quaternary ammonium groups have been found not to be suitable for removing aldehydes from tobacco smoke.

Chitosan and chitosan with a maximum number of amino groups have been found not to be effective. Among the problems encountered with these materials is that they do not provide a filtration media allowing for the continuous flow of smoke at a low pressure differential or gradient. Other problems with selective filtration medias have been found. For example, the
5 use of certain amino acids, such as glycine, have been found effective in removing aldehydes in tobacco smoke. However, it has been discovered that while glycine can reduce the level of formaldehyde in tobacco smoke, it is not stable in the cigarette filter manufacturing process. Moreover, the use of amino acids causes the release of ammonia odor during storage.

SUMMARY OF THE INVENTION

10 It has been discovered that chitosan can be chemically modified to have the physical attributes of a filter medium and have a chemical composition capable of effectively adsorbing and absorbing undesirable smoke ingredients, yielding superior performance as a cigarette filter.

Thus, it is an object of the present invention to provide cigarette filter arrangements
15 and, more particularly, cigarette filters that can selectively remove undesirable constituents in the vapor phase of tobacco smoke such as hydrogen cyanide, aldehydes, metals and sulphides without the drawbacks or disadvantages associated with the prior art as previously described.

A further object is to provide a novel cigarette and smoke filter embodying a porous resin of cross-linked chitosan.

20 An additional object is to provide cross-linked chitosan reactive materials having a high ratio of surface-to-volume and having a reduced number of reactive amino groups for selective smoke filtration in a smoking article.

According to the present invention, a tobacco-smoke filter includes an adsorbent / absorbent for removal of undesirable volatile tobacco-smoke constituents such as hydrogen

cyanide, aldehydes, carbonyls, metals and sulphides. Specifically, the instant invention is directed to particularly efficient tobacco smoke filtration compounds of chitosan cross-linked with glutaraldehyde and chitosan cross-linked with glyoxal.

5 Chitosan is cross-linked with glutaraldehyde and glyoxal to form porous resins having a high surface area to mass ratio for the selective filtration of cigarette smoke, particularly for the removal of undesirable smoke constituents such as aldehydes, hydrogen cyanide, carbonyls, sulphides and metals.

10 Chitosan is a linear polyglucosamine polymer obtained from the deacetylation of chitin, a polysaccharide found in the exoskeleton of crustaceans. Chitin also occurs in insects and in lesser quantities in many other animal and vegetable organisms. Chitin is a linear polymer of 2-deoxy, 2-acetyl-amino glucose analogous to cellulose in chemical structure. It is insoluble in almost all media except strong mineral acids and due to the acetylated amino group is relatively unreactive.

15 When chitin is deacetylated by treatment with strong alkalis, the product is chitosan which contains one free amino group for each glucose building unit in the polymer. It is still a long chain linear polymer but is now a highly reactive cationic poly-electrolyte material. It will form salts with simple organic acids, such as formic, acetic, tartaric, citric, etc. and is soluble in dilute aqueous solutions of such substances. Chitosan is nontoxic and biodegradable, and it has found utility in numerous applications, including chromatography, 20 drug delivery, and cosmetics.

A porous chitosan resin may be formed by a phase inversion technique. This is accomplished by dissolving flaked or powdered chitosan in a suitable solvent, such as aqueous acid, and then coacervating in a solution of aqueous base to form water swollen chitosan gel beads. The beads may be cross-linked using glutaraldehyde, and separately with

glyoxal, to improve the mechanical strength and reduce the solubility of the beads. The wet beads are then freeze dried to yield a porous cross-linked resin. Drying may also be accomplished by vacuum or air drying.

5 A porous resin may also be prepared using a thermally induced phase separation technique. This is accomplished by dissolving flaked or powdered chitosan in a suitable solvent, such as aqueous acetic acid, and then adding the solution to a non-solvent, such as methanol, and cooling the resulting solution below the freezing point of the chitosan solution which yields frozen beads. These beads may then be neutralized with a base and cross-linked with glutaraldehyde and separately with glyoxal to modify the final properties of the chitosan
10 resin. The resulting beads may then be freeze dried to yield a porous cross-linked chitosan resin. Drying may also be accomplished by vacuum and by air drying.

The cross-linked resins produced by both methods have a reduced number of reactive amino groups. The reduced number of reactive amino groups is a result of the cross-linking reaction with glutaraldehyde or glyoxal. It has been surprisingly discovered that the
15 described invention, having a reduced number of reactive amino groups, is selective in removing hydrogen cyanide and formaldehyde from tobacco smoke. It has also been surprisingly found that the cross-linked chitosan resin having a reduced number of reactive amino groups exhibits greater selective removal activity than that associated with the prior art where a maximum number of reactive amino groups have been employed.

20 The porous resin of the present invention may be incorporated into a cigarette in a variety of ways. The resin may be disposed between filter sections wherein these sections may be comprised of fibrous, filamentary and paper materials. The resin may also be dispersed throughout a filter tow. Alternatively, the resin may be placed within a filter bed in a filter section and the resin may be packed along the filter bed. The resin may also be

incorporated into a part of the cigarette filter such as the tipping paper, a shaped paper insert, a plug, a space, or even a free-flow sleeve. Additionally, the resin may be incorporated into cigarette filter paper, attached to the tobacco rod with tipping paper or even incorporated within a cavity in the filter.

5 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Examples of the present invention are given below by way of illustration and not by way of limitation. These examples include two distinct methods of preparing chitosan beads as well as several distinct methods of cross-linking the chitosan beads. All of the following examples yield porous cross-linked chitosan resin beads having a reduced number of reactive
10 amino groups.

EXAMPLES

EXAMPLE I:

Porous chitosan resin was synthesized according to a phase inversion technique. This was accomplished by preparing a 7% chitosan solution by dissolving approximately 20 grams
15 of chitosan flakes (practical grade) in 3.5% acetic acid. The mixture increased in viscosity and gelled upon the completion of the chitosan addition. Further dilution with acetic acid resulted in a solution having approximately 3% chitosan flake. This provided for a chitosan solution having a more manageable viscosity. The total amount of acetic acid used to dissolve the chitosan flake was approximately 665 milliliters. The solution was then filtered
20 to separate any undissolved materials. This chitosan solution was then added dropwise to a precipitation bath of 2 molar sodium hydroxide to yield water swollen gel beads. The gel beads were then filtered and washed with deionized water until neutral, pH of the wash water being approximately 7.

Heterogeneous cross-linking of the chitosan beads was then accomplished by suspending the beads for several hours in approximately 1 liter of 2.5% aqueous solution of glutaraldehyde. After cross-linking, the beads were then filtered and washed with warm deionized water to remove any excess glutaraldehyde. Subsequently, the beads were freeze
5 dried which resulted in porous glutaraldehyde cross-linked chitosan resin beads. The BET surface area of the resin was measured to be approximately $120 \text{ m}^2/\text{g}$. The beads were then milled and sieved to retain particles having approximately 16 to 70 mesh. A surface area analysis of the milled resin showed no appreciable change in surface area. The BET surface area of the sieved sample was measured to be approximately $117 \text{ m}^2/\text{g}$.

10 **EXAMPLE II:**

Porous chitosan resin was synthesized according to the phase inversion technique in Example 1. In this example the heterogeneous cross-linking of the chitosan beads was accomplished by suspending the beads for several hours in a 2.5% aqueous solution of glyoxal. After cross-linking, the beads were filtered and washed with warm deionized water
15 to remove any excess glyoxal. The beads were then freeze dried which resulted in porous glyoxal cross-linked chitosan resin beads.

EXAMPLE III:

Porous chitosan resin was prepared according to a thermally induced phase separation procedure. A 4% chitosan solution was prepared by dissolution of chitosan powder (Vansen
20 Chemical; 92% deacetylation) in 3.5% acetic acid. A precipitation bath of sodium hydroxide (2 molar) in 20:80 methanol / water solution was prepared and cooled to 0°C . The chitosan solution was then added dropwise to the precipitation bath with moderate stirring. Precipitation of chitosan occurred shortly after addition of the solution to the precipitation

bath. The precipitation bath having the chitosan precipitate was then allowed to return to room temperature. The resulting beads were filtered and washed with deionized water until the wash water became neutral, having a pH of approximately 7.

Heterogeneous cross-linking of the chitosan beads was then accomplished by
5 suspending approximately 396 grams of wet beads in approximately 1980 milliliters of 2.5% aqueous glutaraldehyde solution for several hours. After cross-linking, the beads were filtered and washed with both warm and cold deionized water to remove any excess glutaraldehyde. Subsequent freeze drying of the beads resulted in porous glutaraldehyde cross-linked chitosan resin beads. The beads were then milled and sieved to approximately
10 16 to 70 mesh. The BET surface area of the resin was measured to be approximately 210 m^2/g .

EXAMPLE IV:

Porous chitosan resin was prepared according to the thermally induced phase separation procedure in Example III. In this example, the heterogeneous cross-linking of the
15 chitosan beads was accomplished by suspending approximately 261 grams of wet beads in approximately 1300 milliliters of 2.5% aqueous glyoxal solution for several hours. After cross-linking, the beads were filtered and washed with both warm and cold deionized water to remove any excess glyoxal. Subsequent freeze drying resulted in porous glyoxal cross-linked chitosan resin beads. The beads were then milled and sieved to approximately 16 to
20 70 mesh. The BET surface area of the cross-linked resin was measured to be approximately 145 m^2/g .

EXAMPLE V:

Porous chitosan resin was prepared according to the thermally induced phase separation procedure in Example III. In this example, the heterogeneous cross-linking of the chitosan beads was accomplished by suspending the beads in a solution of glutaraldehyde and ethanol for several hours. After cross-linking, the beads were filtered and washed with
5 ethanol to remove any excess glutaraldehyde. Subsequent vacuum drying resulted in porous glutaraldehyde cross-linked chitosan resin beads.

EXAMPLE VI:

Porous chitosan resin was prepared according to the thermally induced phase separation procedure in Example III. In this example, the heterogeneous cross-linking of the
10 chitosan beads was accomplished by suspending the beads in a solution of glutaraldehyde and water for several hours. After cross-linking, the beads were filtered and washed with ethanol to remove any excess glutaraldehyde. Subsequent vacuum drying resulted in porous glutaraldehyde cross-linked chitosan resin beads.

Even though these examples specify amounts or concentrations of materials used in
15 making several embodiments of the present invention, a wide range of concentrations and amounts of materials may be used to practice the present invention. For example, the crosslinker solution may be in a range of concentration of about 0.1% to about 50%, the chitosan solution may be in a range of concentration of about 0.1% to about 20%, the acetic acid solution may be in a range of about 0.1% to about 10%, and the base solution may be in
20 a range of about 1 to about 5 molar sodium hydroxide. Additionally, the range of hours for cross-linking reaction may be from about 1 hour to up to about 24 hours.

EXAMPLES OF USE

A cigarette typically contains two sections, a tobacco-containing portion sometimes referred to as the tobacco or cigarette rod, and a filter portion which may be referred to as the filter tipping. A cigarette sample with a cavity filter was prepared by removing the existing filter on a cigarette made by standard production techniques, and replacing with a filter
5 tipping having a cellulose acetate section at the tobacco end of the filter and a cellulose acetate section at the mouth end of the filter leaving a middle cavity. Sample sets of semolina (an inert filler material), chitosan resin synthesized by phase inversion technique and cross-linked with glutaraldehyde (Ex. I), chitosan resin synthesized by the thermally induced phase separation procedure and cross-linked with glutaraldehyde (Ex. III), chitosan resin
10 synthesized by the thermally induced phase separation procedure and cross-linked with glyoxal (Ex. IV), chitosan resin synthesized by the thermally induced phase separation procedure and cross-linked with glutaraldehyde in ethanol, washed with ethanol, and vacuum dried (Ex. V), and chitosan resin synthesized by the thermally induced phase separation
15 procedure and cross-linked with glutaraldehyde in water, washed with ethanol, and vacuum dried (Ex. VI), were prepared using a 50 mg sample load in the middle cavity of the filter tipping. This loading was consistent for each sample to provide comparable results. Resin loading in a filter of the present invention may be in a range of about 10 mg to about 200 mg. Each sample was pressure drop selected to minimize smoke delivery variances.

Several tests were conducted to determine the ability of the cigarette filter of the
20 present invention to remove undesirable constituents from tobacco smoke as compared to conventional devices. The tests measured the amount of undesirable constituents removed from the mainstream smoke after the cigarette was fully smoked. The following data sets illustrate the performance achieved in the filtration of volatile constituents of tobacco smoke for each of the preferred embodiments as compared to the control material, semolina.

Analytical results are reported on the vapor phase and whole smoke analyses as indicated in the following tables. Percent reduction refers to the difference, in %, between the amount of the analyte measured in the vapor phase or whole mainstream smoke of cigarettes having filter tipping containing semolina and chitosan resin.

5 Vapor Phase Smoke Analysis for Chitosan Resin Prepared by Phase Inversion Technique
[Ex. I]

Analyte	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde Ex. I
Hydrogen Cyanide	49
Acetaldehyde	10
Acetonitrile	11
Acrolein	15
Propionaldehyde	11
Acetone	7
Methyl Ethyl Ketone + Butyraldehyde	16
Crotonaldehyde	13

10 Whole Smoke Hydrogen Cyanide Analysis for Chitosan Resin Prepared by Phase Inversion Technique [Ex. I]

Analyte	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde Ex. I
Hydrogen Cyanide	41

15 Whole Smoke Carbonyl Analysis for Chitosan Resin Prepared by Phase Inversion Technique
[Ex. I]

	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde Ex. I
Formaldehyde	36
Acetaldehyde	13
Acetone	5
Acrolein	11
Propionaldehyde	16
Crotonaldehyde	9
Butyraldehyde	17

Vapor Phase Smoke Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Exs. III-IV]

	Percent Reduction (%)	
	Chitosan cross-linked with glutaraldehyde Ex. III	Chitosan cross-linked with glyoxal Ex IV
Acetaldehyde	13	31
Acetone	21	30
Acetonitrile	18	26
Acrolein	29	36
Acrylonitrile	21	29
Crotonaldehyde	7	42
Hydrogen cyanide	60	45
Methyl ethyl ketone	21	29
Propionaldehyde	23	36
i-Butyraldehyde	27	35
n-Butyraldehyde	27	40

5 Whole Smoke Hydrogen Cyanide Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Exs. III-IV]

	Percent Reduction (%)	
	Chitosan cross-linked with glutaraldehyde Ex. III	Chitosan cross-linked with glyoxal Ex IV
Hydrogen cyanide	54	29

10 Whole Smoke Carbonyl Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Exs. III-IV]

	Percent Reduction (%)	
	Chitosan cross-linked with glutaraldehyde Ex. III	Chitosan cross-linked with glyoxal Ex IV
Acetaldehyde	1	2
Acetone	5	0
Acrolein	10	3
Butyraldehyde	14	8
Crotonaldehyde	20	9
Formaldehyde	50	46
Propionaldehyde	17	19

15 Whole Smoke Trace Metals Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Exs. III-IV]

	Percent Reduction (%)	
	Chitosan cross-linked with glutaraldehyde Ex. III	Chitosan cross-linked with glyoxal Ex IV
Cadmium	32	38

Vapor Phase Smoke Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. V]

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	Percent Reduction (%) Chitosan cross-linked with glutaraldehyde Ex. V
Acetaldehyde	9
Acetone	6
Acetonitrile	3
Acrolein	13
Crotonaldehyde	7
Hydrogen Cyanide	36
Methyl Ethyl Ketone	6
Propionaldehyde	11
i-Butyraldehyde	9
n-Butyraldehyde	10

Whole Smoke Hydrogen Cyanide Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. V]

	Percent Reduction (%) Chitosan cross-linked with glutaraldehyde Ex. V
Hydrogen Cyanide	27

10 Whole Smoke Carbonyl Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. V]

	Percent Reduction (%) Chitosan cross-linked with glutaraldehyde Ex. V
Acetonitrile	3
Acetaldehyde	27
Acetone	24
Acrolein	32
Butyraldehyde	41
Crotonaldehyde	30
Formaldehyde	58
Propionaldehyde	33

Whole Smoke Trace Metals Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. V]

	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde
	Ex. V
Cadmium	38

5 **Vapor Phase Smoke Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. VI]**

	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde
	Ex. VI
Acetaldehyde	3
Acetone	4
Acrolein	9
Crotonaldehyde	11
Hydrogen Cyanide	30
Methyl Ethyl Ketone	11
Propionaldehyde	6
i-Butyraldehyde	7
n-Butyraldehyde	11

Whole Smoke Hydrogen Cyanide Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. VI]

	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde
	Ex. VI
Hydrogen Cyanide	30

10 **Whole Smoke Carbonyl Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. VI]**

	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde
	Ex. VI
Acetaldehyde	0
Acetone	0
Acrolein	0
Butanone	1
Butyraldehyde	14
Crotonaldehyde	36
Formaldehyde	37
Propionaldehyde	0

Whole Smoke Trace Metals Analysis for Chitosan Resin Prepared by Thermally Induced Phase Separation [Ex. VI]

	Percent Reduction (%)
	Chitosan cross-linked with glutaraldehyde
	Ex. VI
Cadmium	26

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The data surprisingly showed the cross-linked chitosan resin described in this invention is selective in removing aldehydes and hydrogen cyanide in cigarette smoke compared to the inert semolina control. The glutaraldehyde cross-linked chitosan resin reduced the vapor phase delivery of hydrogen cyanide by 60% versus a control sample (Ex. 10 III). In a separate test, non-crosslinked ground chitosan particles showed no effect on the vapor phase hydrogen cyanide delivery. The glutaraldehyde cross-linked chitosan resin also decreased whole smoke hydrogen cyanide delivery by 54%, and mainstream whole smoke formaldehyde delivery was decreased by 50% compared to the control sample (Ex. III).

While the invention has been described with reference to preferred embodiments, it is 15 to be understood that variations and modifications may be resorted to as will be apparent to those skilled in the art. Such variations and modifications are to be considered within the purview and scope of the invention as defined by the claims appended hereto.

We claim:

1. A tobacco-smoke filter comprising a chitosan resin having chitosan cross-linked with a constituent selected from the group consisting of glutaraldehyde and glyoxal, said cross-linked chitosan resin having a BET surface area of at least 5 m²/g.
2. A filter according to Claim 1, wherein said resin is cross-linked with glutaraldehyde.
3. A filter according to Claim 1, wherein said resin is cross-linked with glyoxal.
4. A filter according to any one of the preceding claims, wherein said resin is in particulate form within a size range of approximately 17 mesh to approximately 70 mesh.
5. A filter according to any one of the preceding claims, wherein said resin comprises milled particles.
6. A filter according to any one of the preceding claims, wherein said tobacco smoke filter has said resin present in a range from about 10 mg to about 200 mg.
7. A filter according to any one of the preceding claims, wherein said resin is in particulate form and is disposed between filter sections, said filter sections having materials selected from the group consisting of fibrous, filamentary, paper, and combinations thereof.
8. A filter according to any one of Claims 1 to 6, wherein said resin is in particulate form and is dispersed in a filter tow.
9. A method of smoke filtration comprising the steps of providing a smoking article filter having chitosan resin cross-linked with a constituent selected from the group consisting of glutaraldehyde and glyoxal, and passing smoke through said filter, said cross-linked chitosan resin having a BET surface area of at least 5 m²/g.

10. A method of fluid-flow filtration that comprises the steps of providing a filtration bed having cross-linked chitosan resin in said bed by packing said chitosan resin within said bed, and passing fluid containing constituents through said filtration bed, said cross-linked chitosan resin having a BET surface area of at least 5 m²/g.

11. A method as claimed in Claim 10 in which said resin is in a particulate form having a size of about 16 mesh.

12. A method as claimed in Claim 10 or Claim 11 and in which said cross-linked chitosan resin is packed along said bed.

13. A method as claimed in any one of Claims 10 to 12 wherein said fluid is cigarette smoke and said constituents comprises pyrolysis products of cigarette materials.

14. A method of removing from cigarette smoke pyrolysis products of cigarette materials comprising the steps of providing a filtration region having cross-linked chitosan resin disposed throughout the region and passing said pyrolysis products through said filtration region, said cross-linked chitosan resin having a BET surface area of at least 5 m²/g.

15. A tobacco smoke filtration media obtained by the steps of:

dissolving chitosan in a first solution having acetic acid in a range of about 0.1% to about 10% forming a second solution having chitosan in a range of about 0.1% to about 20%;

filtering said second solution;

adding said second solution drop-wise to a precipitation bath, wherein said precipitation bath has sodium hydroxide in a range of about 1 molar to about 5 molar, forming gel beads;

rinsing said gel beads;

suspending said gel beads in a cross-linking solution for about 1 hour to about 24 hours forming cross-linked beads, wherein said cross-linking solution has approximately 0.1% to approximately 50% of a cross-linking compound consisting of glyoxal;

rinsing said cross-linked beads; and

drying said cross-linked beads forming a porous chitosan crossed-linked resin bead.

16. A tobacco smoke filtration media obtained by the steps of:

dissolving chitosan in an acetic acid solution having acetic acid in a range of about 0.1% to about 10% forming a chitosan solution having approximately 0.1% to approximately 20% chitosan;

cooling a precipitation bath below ambient room temperature, wherein said precipitation bath has sodium hydroxide, water, and methanol;

adding said chitosan solution drop-wise to said precipitation bath forming gel beads;

warming said precipitation bath having said gel beads to about ambient room temperature;

rinsing said gel beads;

suspending said gel beads for about 1 hour to about 24 hours in a cross-linking solution having approximately 0.1% to approximately 50% of a cross-linking compound consisting of glyoxal forming cross-linked beads;

rinsing said cross-linked beads; and

drying said cross-linked beads forming a porous chitosan crossed-linked resin bead.

17. A tobacco-smoke filter comprising in the range of about 10 mg to about 200 mg of a cross-linked chitosan resin, said resin having a size within the range of about 16 mesh to about 70 mesh, said resin having a BET surface area of at least 5 m²/g.

18. A filter according to Claim 17 for use in a cigarette, wherein said filter is attached to a tobacco rod by tipping paper.

19. A filter according to Claim 17 or Claim 18 for use in a cigarette, wherein said resin is incorporated in one or more cigarette filter parts selected from the group consisting of tipping paper, shaped paper insert, a plug, a space, and a free-flow sleeve.

20. A filter according to Claim 17 or Claim 18 for use in a cigarette, wherein said resin is incorporated in cigarette filter paper.

21. A method of manufacturing a filter which is useful for removing a gaseous component of a gas mixture, comprising steps of:

preparing a filter media having a cross-linking compound selected from the group consisting of glutaraldehyde and glyoxal, wherein said cross-linking compound is cross-linked to chitosan forming a bead having a BET surface area of at least 5 m²/g;

incorporating said filter media in a filter wherein said filter media removes said gaseous component of said gas mixture; and

attaching said filter to a tobacco rod with tipping paper.

22. A method according to Claim 21, wherein said filter media is incorporated in one or more cigarette filter parts selected from the group consisting of tipping paper, shaped paper insert, a plug, a space, and a free-flow sleeve.

23. A method according to Claim 21 or Claim 22, wherein said cross-linking compound is incorporated in a cavity of said filter.

24. A tobacco-smoke filter comprising cross-linked chitosan resin beads, said cross-linked chitosan resin beads having a reduced number of reactive amino groups than said chitosan resin beads prior to cross-linking.

25. A filter for a cigarette including the filter according to any one of claims 1 to 8.

26. A filter for a cigarette including the filter according to claim 24.

27. A tobacco-smoke filter substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

28. A method of smoke filtration substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

29. A method of fluid-flow filtration substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

30. A method of removing from cigarette smoke pyrolysis products of cigarette materials substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

31. A tobacco smoke filtration media substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

32. A method of manufacturing a filter which is useful for removing a gaseous component of a gas mixture substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.

33. A filter for a cigarette substantially as herein described with reference to any one of the embodiments of the invention illustrated in the accompanying drawings and/or examples.